Advanced materials for lithium batteries and electrochemical capacitors

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Advanced Materials for Lithium Batteries and Electrochemical Capacitors

by

Nooshin L Haj Hassan

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the award of

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Abstract

This thesis describes research carried out in the area of materials electrochemistry. The general goal was to develop and test advanced materials that might improve the performance of real-world electrochemical systems. Particular systems of interest were lithium thionyl chloride batteries, lithium sulphur batteries, and carbon-based electrochemical capacitors. Developments are reported in all three cases.

Materials electrochemistry is an interdisciplinary field that investigates the relationship between the structure, properties, processing and electrochemical performance of novel materials. These may be electrodes, solutions, or combinations of both. Besides conventional electrochemical measurements, materials electrochemistry also includes elements of process development and engineering.

In the present work, much effort was expended on the formulation, mixing, extrusion and curing of particulate carbon electrodes. In particular, numerous large-scale screening programs were carried out to examine the effects of multiple independent variables on battery performance. Although this required much effort to set up, the pay-off was that it allowed improved processing parameters, and materials of advanced performance to be determined with a high level of confidence. Considerable effort was also expended on the development of apparatus for handling air-sensitive battery solvents, such as thionyl chloride.

Amongst the achievements of the present work are: (i) the successful reformulation of the manufacturing solvent for commercial lithium battery electrodes, to halve the quantity of isopropyl alcohol used. In the future this will allow the manufacturing process to continue within UK/EU regulations. (ii) The improvement of the mechanical strength and electrochemical capacity of thick-film carbon electrodes by adding conducting carbon fibre. (iii) The development of an easy-to-implement test that accurately predicts the performance of lithium thionyl chloride battery electrodes. (iv) The development of a novel electrolyte solution for lithium sulphur batteries (using a sulfolane/ethylene carbonate mixture). (v) The discovery that this solution can be gelled
with PVDF, and finally (vi) the discovery that some carbon blacks out-perform activated carbon in thick-film electrodes for electrochemical capacitors.
Acknowledgments

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1 Introduction

There is a need for high-capacity high-power energy storage in many areas of modern technological society. Examples include computing and communications, remote sensing, electric vehicles and energy management. As technologies evolve, the demand for higher capacity and power is set to increase rather than decrease. At the same time there is a need for efficient methods of conserving energy and minimising environmental damage. Clearly, these issues are important to both the UK and the international community.

In 2007 the UK Energy Research Centre sponsored the “Accelerated Materials Discovery for Energy Storage and Conversion Devices” meeting. The International Energy Agency’s Office of Energy Technology and Research and Development were also involved in this meeting. Topics such as electrochemical devices and methods of rapid screening for new improved materials were discussed. It was clear there was a need to improve electrochemical energy storage devices.

Murray has also discussed the need for improving electrochemical energy storage devices in an editorial for the Analytical Chemistry journal in May 2007 [1]. The increased use of mobile phones and laptops in recent years, (and therefore the batteries needed to power them), was highlighted. Expectations that technologies will keep up with demands for faster rates of energy release must be met. In order to meet these expectations, more research is needed in the expanding areas of battery technology and electrochemical capacitors.

A capacitor stores electrical energy by the separation of negative and positive charges on two metal plates. An electrochemical capacitor is based on the same principle of charge separation, but utilises the electrochemical double layer that exists between an electrode surface and the surrounding electrolyte solution. An electrochemical capacitor is capable of releasing energy over a short time period, and is therefore known as a high power device. A large area of research revolves around the materials used in electrochemical devices, and so an understanding of their chemical properties is essential for improving existing technologies. Arico et al. in a recent review article said
"new materials hold the key to fundamental advances in energy conversion and storage" [2].

1.1 Scope of the Thesis

In batteries, energy is stored in chemical bonds. When a battery is connected to an external circuit, chemical energy is converted to electrical energy. This is in contrast with a capacitor, which is purely an electrical device where opposite charges build up on two metal plates separated by a dielectric material. In this case, energy is stored in the electrical field. In an electrochemical capacitor the two layers of opposite charge consist of electron density in a carbon electrode and ions in the surrounding electrolyte solution. An electrochemical capacitor is really a hybrid device, as its total capacitance is the sum of energy stored in an electrical field and in chemical bonds. The latter is referred to as pseudocapacitance, which is the capacitance arising from redox active species, and not from the electrical field. The present study reports work carried out for both batteries and electrochemical capacitors.

Lithium is a light-weight metal that has one of the most negative standard reduction potentials known (−3.04 V vs. SHE) [3]. This makes it an ideal material for high voltage batteries. Amongst the commercially available lithium batteries, lithium-thionyl chloride has one of the highest practical energy densities, ranging from 243 Wh kg\(^{-1}\) for an AA cell (1.2 Ah capacity) to 661 Wh kg\(^{-1}\) for a D cell (18.5 Ah capacity) [4]. Some other lithium batteries are predicted to have higher theoretical energies, but these have not yet been commercialised [5]. Lithium-thionyl batteries also have an excellent shelf-life (approximately 10 years).

Initial development of the lithium-thionyl chloride battery took place during the nineteen seventies and nineteen eighties. Today the lithium-thionyl chloride battery is sold by companies such as Saft and Tadiran, and is used in applications such as security alarm systems, computer memory back-up, and automotive electronics. In the UK, Schlumberger WCP Ltd manufacture lithium-thionyl chloride batteries for use in oilfield down-hole drilling applications.
The battery consists of high porosity carbon black electrodes wrapped around a core of lithium metal, with a glass wool separator, and fitted into a stainless steel cylinder. The cylinder is then hermetically sealed and injected with 1.4 M LiAlCl₄ thionyl chloride electrolyte solution. Unfortunately, a problem with the carbon black electrodes is that they have a tendency to crack during cell assembly. In addition, the concentration of isopropyl alcohol that is used in the manufacture of the electrodes presents a health hazard. It was therefore of interest to explore the possibility of reducing the required volume of this solvent.

Whilst it is true that the lithium-thionyl chloride battery has one of the highest energy densities known, it is a primary battery and therefore can be used only once. It would be of great interest to have a comparable rechargeable system, which would save a great deal of money in the long-term. The lithium-sulphur battery is one such system, but is hampered by sulphur solubility. Accordingly, the present study also investigated new electrolyte/solvent systems for lithium-sulphur batteries.

Electrochemical capacitors are high power devices that are used in applications such as memory back-up. However, it has recently been suggested that they might also be used to store energy from the utility grid during off-peak times [6]. Unfortunately, the present study has revealed that current electrode materials (particularly activated carbon) are not appropriate for this application, due to electrolyte starvation. It was therefore of great interest to investigate novel materials such as high porosity carbon blacks.

An additional interesting application for electrochemical capacitors could also be in supporting lithium batteries. A well-known drawback with many lithium systems is the fact that a passivation layer builds up on the lithium metal surface during storage. Whilst this passivation layer is advantageous in protecting the battery from self-discharge, it can also prevent immediate use of the battery. This is due to a phenomenon known as 'voltage delay'. Depending on battery storage conditions and time stored, the passivation layer can become substantial in thickness. The usual working potential of the battery cannot be realised until the passivation layer has been removed (by passing current). After this time, the working potential increases to the expected voltage [7]. If electrochemical capacitors could work in parallel with batteries (which give a long-term
response, allowing the electrochemical capacitor to be re-charged), the combination could deliver power over all timescales.

Finally, gelled electrolyte solutions were investigated due to their health and safety benefits. Should electrochemical devices be accidentally pierced, highly corrosive and harmful solutions would escape into the surrounding area. To minimise this hazard, it was realised that a gelling agent could be added, such that the solution would not leak so readily. Large volumes of gel would also be easier to manipulate during battery manufacture, and might reduce the exposure of personnel to noxious fumes. For all these reasons, polymer-gelled solutions were investigated.

1.2 An Introduction to Carbon Electrode Materials and Electrolyte Solutions

The aim of this thesis is to identify improved materials (or combinations of materials) for use in lithium batteries and in electrochemical capacitors, and to test their performance under realistic conditions. Before describing the basic science of each storage device, this section briefly introduces (1) the carbon materials used in electrodes, and (2) the theoretical and practical considerations behind the choice of electrolyte solutions.

1.2.1 Carbon Materials Used in Electrodes

The two regularly ordered allotropes of carbon are graphite and diamond. At room temperature and pressure, graphite is the more thermodynamically stable form:

\[ C(\text{diamond}) \rightleftharpoons C(\text{graphite}) \quad \Delta G = -2.9 \text{kJ mol}^{-1} \]

If the pressure exceeds 60 GPa, then diamond becomes the more stable form [8]. This is because diamond is denser than graphite (\( \rho = 3.51 \text{ g/cm}^3 \) versus \( 2.26 \text{ g/cm}^3 \)).

Diamond is sp\(^3\) bonded and therefore lacks \( \pi \)-orbitals. By contrast, graphite is sp\(^2\) bonded and hence contains extended planes of \( \pi \)-orbitals. For this reason, diamond is
an electrical insulator and graphite is an electrical conductor. Combined with its low electrochemical reactivity and low cost, this makes graphite (and related graphitic carbons) a popular choice for the manufacture of electrodes.

In defect-free graphite the carbon atoms are arranged in hexagonal, two-dimensional layers, known as graphene sheets (Figure 1.01). These are held together by both $\sigma$- and $\pi$-bonds. Weak van der Waals forces also exist between the layers. Conductivity is greater in the plane of the graphene sheets, and lesser perpendicular to the graphene sheets.

\[ \text{Figure 1.01. The structure of a single graphene sheet.} \]

It should be noted that to obtain a single crystal of graphite is very rare, as most specimens have defects in their structures. For this reason, a special vocabulary is used to describe carbons. \textit{Graphitic carbon} refers to any carbon that has local regions of graphitic structure. \textit{Amorphous carbon}, on the other hand, refers to any carbon lacking long-range crystalline order [9]. Amorphous carbons retain some short-range order, however.

Carbons lacking long-range crystalline order also contain strained carbon-carbon bonds that react readily with oxygen in air, even at room temperature. This leads to the appearance of “oxygen functionalities” on their surface [10]. Figure 1.02 illustrates the wide variety of oxygen functionalities that can appear on carbon surfaces. These functionalities may be acidic or basic, depending on the history of the specimen, but generally carbon surfaces have both types of functionality [11].
1.2.1.1 Carbon Blacks

Carbon black is the name given to a large group of carbon products formed by incomplete combustion of organic substances [12]. Due to its highly fragmented structure, carbon black tends to have more edge sites than graphite, and hence forms more oxygen surface functionalities.

All carbon blacks are made up of small (nanometre scale) solid carbon particles that can form aggregates. The structure of carbon black, on a micro-scale, is very similar to that of graphite. In an IUPAC publication, carbon black was defined as “an industrially manufactured colloidal carbon material in the form of spheres and of their fused aggregates with sizes below 1000 nm” [13].

An SEM image of a carbon black material is shown in Figure 1.03.
Some of the different types of carbon black include lampblack, furnace black, channel black and thermal black. These different types will now be discussed in a little more detail.

Lampblack is the product obtained from burning naphthalene, creosote or other aromatic oils. The burning of the oil takes place with a limited supply of air and the carbon black itself is collected from the resulting smoke.

Channel black is made from natural gas. It contains smaller particles than other carbon blacks, which gives it a ‘blacker’ appearance. The carbon formed by this process may become exceedingly oxidised on exposure to air. The yield from the channel process is also very low, and so can prove to be more costly.

Furnace black can be made by a gas or oil furnace process. In the former, natural gas is thermally decomposed in a flame. In the latter, carbon black is produced by injection of liquid fuel into a flame. Yields of carbon black from these processes range from 20%-50%. The more aromatics that are contained within the feedstock, the higher the resulting “structure” of the carbon black. Low structure carbon blacks tend to have a
low degree of aggregation, whereas *high structure* carbon blacks have a high degree of aggregation.

Thermal black is created by a cyclic process of decomposition at about 1300°C, followed by cooling, followed by re-heating. The feedstock is composed mostly of methane. The most important type of thermal black is acetylene black, which is made by decomposition of acetylene, firstly in air. The air supply is later closed off, and the decomposition allowed to continue. Temperatures used are between 800-1000°C, and the yield is near quantitative.

### 1.2.1.2 Carbon Fibre

Although carbon fibres can be prepared from a variety of precursor materials, including natural materials such as wool, two man-made materials are of most interest industrially; polyacrylonitrile (PAN) and mesophase pitch (MP) [14]. Production of PAN-based carbon fibres starts with oxidation of PAN for several hours at temperatures around 220°C, followed by graphitisation at >2000°C. Production of pitch-based fibres starts with polymerisation of a commercial pitch to form a ‘mesophase’ (liquid-crystal phase) at temperatures around 450°C. Graphitisation then takes place at temperatures >2000°C. The process of graphitisation involves orientating the fibres under tension at high temperatures to create parallel layer planes. Well-aligned layer planes give rise to good electrical and thermal conductivity.

Structural characterisation of carbon fibres is normally achieved by using X-ray diffraction techniques, or SEM/TEM. Mechanical characterisation typically involves the measurement of tensile strength and modulus (flexibility). Carbon nanofibres have also been manufactured for use in electrochemistry, and may be useful electrode materials, although they are of primary interest for electroanalytical experiments [15].
1.2.1.3 Activated Carbon

Activated carbon is a granular or powdered form of carbon which has powerful adsorptive properties. Precursor materials for the production of activated carbon include coconut shells, bituminous coals and some types of wood [16]. “Activation” is a generic term used to describe a variety of processes such as the increase of surface area, the removal of impurities, and the chemical formation of surface functionalities. The most common method of activation is thermal activation. This process generally requires heating to temperatures around 850-950°C in steam and/or CO₂. Another method of activation is chemical activation. This process is carried out at lower temperatures, generally 400-500°C, and uses reagents such as zinc chloride or phosphoric acid. One result of activation is that solid surfaces are often both physically and chemically inhomogeneous. This can give rise to many different electrochemical properties, for example, a solid surface may have a number of different crystal faces or a diverse range of adsorbed ions on its surface. An SEM image of an activated carbon material is shown in Figure 1.04.

Figure 1.04. An SEM image of an activated carbon material. Note that the pores are too small to be observed in this image.
1.2.1.4 Porosity of Carbon Materials

High porosity carbon materials are often used to speed up electrochemical reactions, since they present a high surface area to interfacial reactions. However, the access of the reactant to the pore walls frequently becomes a limiting factor in practical devices. For this reason, high pore volume is also desirable because it acts as a reservoir for the reactant.

To understand the behaviour of carbon electrodes it is necessary to understand that porosity arises in two different ways (Figure 1.05).

![Figure 1.05. Carbons may contain dead volume and/or pore volume. Dead volume consists of space between particles (inside an aggregate). Pore volume consists of space inside single particles.](image)

Terminology for the characterisation of porous solids is recommended by IUPAC [17]. **Pore volume** (cm$^3$) is the volume of pores inside individual particles. **Dead volume** (cm$^3$) is the void space between particles. (An assembly of randomly close-packed spheres has a dead volume of ~33%.) **Pore area** (cm$^2$) is the area of pore walls excluding any external surface area of the particle.

Pores are also classified into three types:

- *Micropores* having diameters $d < 2$ nm.
- *Mesopores* having diameters $2$ nm $< d < 50$ nm.
- *Macropores* having diameters $d > 50$ nm.

Surprisingly, carbon black does not have any pore volume, but has a very high dead volume. Individual particles approach the density of graphite. By contrast, activated
carbon has a very high pore volume. For this reason these two materials have very different electrochemical performances.

1.2.1.5 Measurement of Porosity

Porosity (dimensionless) is defined as the ratio of the pore volume (cm$^3$) to the apparent volume (cm$^3$) of a particle. Porosity may also be expressed in terms of the real density (g/cm$^3$) and the apparent density (g/cm$^3$) of a particle [18]:

$$
\varepsilon = 1 - \left( \frac{\rho_{\text{app}}}{\rho_{\text{real}}} \right),
$$

where $\varepsilon$ = porosity, $\rho_{\text{app}}$ = the apparent density and $\rho_{\text{real}}$ = the real density of the particle. For graphite the real density is 2.26 g cm$^{-3}$.

The main method for determining pore volume is *Mercury Porosimetry*. Mercury porosimetry uses liquid mercury to fill the pores inside porous materials. It is based on the principle that a non-wetting liquid will not enter a rigid pore unless a critical intrusion pressure is exceeded. Pore diameters may then be evaluated from critical intrusion pressures by means of the Kelvin Equation,

$$
d = \frac{-4\gamma \cos \theta}{P}.
$$

Here $d$ is the pore diameter (m), $P$ is the critical intrusion pressure (Pa), $\gamma$ is the surface tension of the non-wetting liquid (N/m), and $\theta$ is the contact angle between the liquid and the pore wall. For mercury $\gamma \approx 484$ mN m$^{-1}$ and $\theta \approx 140^\circ$. (Note: a rigid pore is one that will not deform when it experiences a force.)

In the case of carbon, high pressures (up to 100 MPa) are required as mercury does not wet the carbon surface easily. Due to the high pressure, mercury porosimetry is not a suitable technique to use for friable carbons, or for the estimation of the volume of micropores. Instead, it is reserved for meso- and macroporous carbons, and can be
useful in estimating both pore volume and pore size distributions. Mercury porosimetry also assumes that pores are cylindrical, so derived pore volumes must be treated with caution.

The main method for determining dead volume is *Oil Absorption*. The standard method for carbons is ASTM D 2414-01, which was originally developed for measuring the dead volume of carbon blacks. This test measures the amount of Dibutyl Phthalate (DBP) or paraffin oil that is absorbed by a carbon sample until it reaches a predetermined viscosity. The results are usually expressed in units of cm³/100 g of carbon.

The main method for determining the internal surface area of a porous solid is the *Brunauer-Emmett-Teller method (B.E.T. method)*. This involves the measurement of nitrogen adsorption isotherms at 77 K. At these low temperatures multilayer adsorption is possible and the theory is correspondingly complex. However, the B.E.T. adsorption isotherm takes the form:

\[
\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}, \quad \text{where } z = \frac{p}{p^*}, \quad \text{Eqn. 1.03}
\]

where \(V\) is the volume of adsorbed material, \(V_{\text{mon}}\) = the volume corresponding to monolayer coverage, \(p\) is the partial pressure of adsorbing gas, \(p^*\) is the limiting pressure at which the adsorbing gas liquifies on the surface, and \(c\) is a constant.

Although widely used, the B.E.T. method does have some limitations. It is inaccurate for small specific surface areas (<10 m²/g), and it cannot determine the area of closed pores. In addition, N₂ gas may have limited accessibility to some micropores and may completely fill others, which can lead to false values of specific surface area. The maximum specific surface area of exfoliated graphite is 1800 m²/g [19].

Other techniques may be employed to obtain specific information about pore size distributions and pore shape. Some of these are imaging techniques, such as Scanning Electron Microscopy (SEM). However, only two-dimensional images may be obtained using SEM, so sectioning of samples is required for three-dimensional information. The
use of High Resolution Transmission Electron Microscopy can also provide structural
details. Finally, structural information can be obtained by using Small-Angle Scattering.
The latter directs a fine beam of X-rays or neutrons onto the sample, and detects part of
the resulting scattered beam. The scattering is caused by variations in electron density
throughout the sample.

1.3 Electrolyte Solutions

Coulombic, or ‘primary’ solvation exists in all electrolyte solutions to some degree
because the electric field of ions polarises the nearby solvent molecules, causing them
to lose some of their translational and/or rotational degrees of freedom. In the case of
small or multi-valent ions the electric field is very high.

1.3.1 Theoretical Considerations

Solvents having a low relative static permittivity, such as benzene ($\varepsilon_r = 2.2$) and
hexane ($\varepsilon_r = 1.8$), are not suitable as solvents in electrochemistry, as they do not
dissolve electrolytes to any significant extent. By contrast, solvents such as ethylene
carbonate ($\varepsilon_r = 89.8$) and water ($\varepsilon_r = 78.3$) are of more interest, because they have
high values of relative static permittivity. The relative static permittivity measures the
solvent’s ability to screen electrostatic charges. Screening electrostatic charges involves
solvent molecules surrounding individual ions, hence achieving solvation. Thus, the
solubility of salts correlates with the relative static permittivity of solvents [20]. In the
absence of full solvation, ion pairing may take place according to the equilibrium:

$$ M^+ + X^- \leftrightarrow K_a M^+ X^- $$

where $K_a$ is the ion pair association constant. For high relative static permittivity
solvents, the above equilibrium lies to the left. For low relative static permittivity
solvents the equilibrium lies to the right.
The solubilities of salts also depend on the lattice energies of their crystalline forms, because energy is required to separate the ions in the crystal lattice. Lattice energies can be estimated experimentally using the Born-Haber method, or theoretically using the Born-Mayer equation:

\[
U = \frac{N_A z_A z_B e^2}{4\pi \varepsilon_0 d} \left(1 - \frac{d^*}{d}\right) A, \tag{Eqn. 1.04}
\]

where \(U\) = lattice energy (J), \(N_A\) = the Avogadro number, \(z\) = charge number of ions, \(e\) = the charge of the electron (C), \(\varepsilon_0\) = the permittivity of a vacuum \((8.85 \times 10^{-12} \text{ F/m})\), \(d\) = is the distance between the cations and anions (in Å), \(d^*\) is a scaling factor \((0.345 \text{ Å})\), and \(A\) = the Madelung constant. The Madelung constant is dependent on the geometric arrangement of the constituent ions in a crystal structure.

An alternative to the Born-Mayer equation is the Kapustinskii approximation. Kapustinskii suggested a formula that grouped all the constant terms together, thus calculating the lattice energy \(U\) as:

\[
U = 287.2 \Sigma n \frac{z_A z_B}{\tau_C + \tau_A} \left(1 - \frac{d^*}{\tau_C + \tau_A}\right), \tag{Eqn. 1.05}
\]

where \(\tau_C + \tau_A\) = sum of ionic radii (pm), \(z\) = charge number, and \(d^*\) is an exponential scaling factor \((0.345 \text{ Å})\) and \(\Sigma n\) = the number of ions in the chemical formula \([21]\).

For \(\text{Li}^+\) and \(\text{Na}^+\) lattice energies are higher (more stable) for similarly-sized ions, and lower (less stable) for differently-sized ions (see Table 1.01).
Table 1.01. Lattice energies of alkali metal halides (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>I⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>1036</td>
<td>853</td>
<td>807</td>
<td>757</td>
</tr>
<tr>
<td>Na⁺</td>
<td>923</td>
<td>787</td>
<td>747</td>
<td>704</td>
</tr>
<tr>
<td>K⁺</td>
<td>821</td>
<td>715</td>
<td>682</td>
<td>649</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>785</td>
<td>689</td>
<td>660</td>
<td>630</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>740</td>
<td>659</td>
<td>631</td>
<td>604</td>
</tr>
</tbody>
</table>

From the lattice energy data it is apparent that LiI is less stable in the crystalline state, and is therefore a more soluble salt. In contrast LiF is more stable in the crystalline state and therefore tends to be insoluble. This general trend explains why salts of differently-sized ions (e.g. lithium triflate) are preferred for making concentrated electrolyte solutions.

Theoretically, there are a number of different factors that influence the ability of solvents to solvate ions. These all fall under the general category of “ion-dipole interactions”. Cations, which are good electron pair acceptors, are readily solvated by solvent molecules having lone pairs of electrons. Anions may be solvated in two different ways [22]. Anion solvation by protic solvents is dominated by hydrogen bond formation. In contrast, anion solvation by aprotic solvents is dominated by dispersion forces or van der Waals interactions. In all cases the number of solvent molecules attached to an ion increases with the charge density on the ion. Thus, all things being equal, 3+ ions are more solvated than 1+ ions, and 3– ions are more solvated than 1– ions.

Experimentally, it is found that small anions are much better solvated by protic solvents than by aprotic solvents, because hydrogen-bonding interactions with anions do not take place in aprotic solvents [22]. On the other hand, large anions are often better solvated by aprotic solvents than by protic solvents because of structural and polarizability effects. For this reason, KCl is much more soluble in methanol than DMF, but KI is more soluble in DMF than methanol. This is interesting to note, especially since
methanol and DMF have comparable values of relative static permittivity (33 and 37 respectively).

1.3.1.1 Structure Making and Structure Breaking of Water

The theory of ion solvation in water is dominated by two ideas. Firstly, that the charge density of the ion determines the local water structure in the first hydration shell. Secondly, that Coulombic forces from the central ion compete with hydrogen bonding forces from the solvent. As a crude generalisation, small, high valency ions tend to be structure-making and large, low valency ions tend to be structure-breaking. For example, solutions of KI are less viscous than pure water, being influenced by the structure-breaking effect of the large iodide ion. By contrast, solutions of KOH are more viscous than pure water, being influenced by the structure making effect of the hydroxide ion. Evidence of this is given in Table 1.02.

<table>
<thead>
<tr>
<th>Concentration of KI in H₂O (mol/L)</th>
<th>Absolute viscosity (mPa s)</th>
<th>Concentration of KOH in H₂O (mol/L)</th>
<th>Absolute viscosity (mPa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.312</td>
<td>0.976</td>
<td>0.362</td>
<td>1.038</td>
</tr>
<tr>
<td>0.648</td>
<td>0.946</td>
<td>0.736</td>
<td>1.079</td>
</tr>
<tr>
<td>1.088</td>
<td>0.921</td>
<td>1.124</td>
<td>1.126</td>
</tr>
<tr>
<td>2.106</td>
<td>0.895</td>
<td>1.938</td>
<td>1.233</td>
</tr>
<tr>
<td>2.913</td>
<td>0.890</td>
<td>3.261</td>
<td>1.436</td>
</tr>
</tbody>
</table>

Table 1.02. Data showing the change in viscosity with change in concentration of KI and KOH in water [23].

Salts that exert an overall structure-breaking effect tend to be those that bind to water, preventing the formation of many hydrogen bonds. Salts that exert a structure-making effect tend to be those that enhance hydrogen-bonding in water, thereby increasing the proportion of tetra-bonded water molecules [24].

Y. Marcus discussed hydrogen bonding in water in terms of $G_{HB}$ values, defined as the average number of hydrogen bonds in which a water molecule participates [25]. Assuming a linear relationship with structural entropy, data describing the change in the average number of hydrogen bonds a water molecule may participate in upon the addition of a solute to pure water ($\Delta G_{HB}$ values) were estimated. Some of these values
are listed here in Table 1.03. As a guideline, ions with $\Delta G_{\text{HB}} < -0.1$ are considered structure breakers, and those with $\Delta G_{\text{HB}} > 0.1$ are considered structure makers, although Y. Marcus admitted an overall uncertainty level of ± 0.2.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta G_{\text{HB}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>-1.09</td>
</tr>
<tr>
<td>$\text{Br}^-$</td>
<td>-0.80</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>-0.61</td>
</tr>
<tr>
<td>$\text{K}^+$</td>
<td>-0.52</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>-0.03</td>
</tr>
<tr>
<td>$\text{F}^-$</td>
<td>0.08</td>
</tr>
<tr>
<td>$\text{Li}^+$</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 1.03. $\Delta G_{\text{HB}}$ values for a number of ions [25].

It is now useful to note some lower and upper limits of concentration, and their effect on conductivity. Nazri discussed this topic in detail, and suggested that concentrations of <0.4 M were generally of no practical use for electrochemical devices. It was also stated that conductivity is often optimised at approximately 1 M [26]. At higher concentrations ion pairing is increased, hence there is a fall in the number of charge carriers available, which limits conductivity. At low operating temperatures the electrolyte can precipitate from extremely concentrated solutions. Multi-solvent systems are often employed to reduce the effect of these problems.

It is clear that solubilities of salts in solvents is a complex phenomenon, and can be dependent on many factors. Izutsu has provided a good summary of the different factors contributing to solvation, which includes electrostatic interactions, anion interactions with hydrogen-bonding solvents, and electron pair acceptor/donator interactions [27].

### 1.3.2 Practical Considerations

There are a number of practical considerations that must be taken into account when selecting a lithium battery electrolyte solution. These are summarised in Table 1.04.
High conductivity helps to minimise cell resistance, and therefore also reduces power lost as heat \( (P = I^2R) \).

Low viscosity maximises transport rate of ions.

High boiling point prevents gassing at high temperature, and low melting point prevents phase separation at low temperature.

Must be compatible with lithium metal, and not decompose.

Ability to tolerate a wide voltage window without oxidation or reduction of solution.

Low toxicity solvents are safer to handle, especially on an industrial scale and in enclosed spaces.

Must be affordable.

Non-polluting and easy to dispose of.

Table 1.04. A list of practical considerations for electrolyte solutions for lithium batteries.
1.4 Research Hypothesis

The research presented in this thesis is based on the hypothesis that the use of new carbon electrode materials and novel electrolyte/solvent combinations can result in superior performance, superior ease of manufacture, and/or enhanced safety in lithium batteries and electrochemical capacitors. A materials electrochemistry approach has been taken in proving this hypothesis.

1.4.1 Research Questions

The number of different electrode materials combined with novel electrolyte/solvent permutations, whilst not infinite is potentially large, such that exhaustive research in this area is beyond the scope of a single thesis. The research presented here makes a substantial contribution to knowledge in this field by addressing the following research questions:

1. Can carbon fibres be added to carbon black electrodes, with the intention to enhance strength and flexibility without diminishing electrochemical performance in lithium-thionyl chloride cells?
2. Can the volume of isopropyl alcohol used in the manufacturing process be decreased without compromising the electrode microstructure and electrochemical performance of the finished product?
3. Can better electrolyte/solvent combinations be found for use in lithium-sulphur cells by combining some of the best performing materials reported in the scientific literature?
4. Can carbon black materials give superior performances to activated carbon electrodes when used in thick film electrodes for electrochemical capacitors?
1.5 Chapters of the Thesis

Chapter 2 is a review of the relevant background electrochemistry theory.

Chapter 3 is a review of the relevant literature covering three main areas: the lithium thionyl chloride cell (Li-SOCl₂), the lithium sulphur cell (Li-S) and electrochemical capacitors (EC's). Finally, there is a small section about gelled electrolyte solutions.

Chapter 4 covers all the experimental procedures carried out during research for this thesis. Test methods and equipment used are discussed initially, before more detail is given for individual experiments.

Chapter 5 presents the results from experiments carried out on carbon electrodes for use in lithium thionyl chloride batteries. A full discussion of these results is also in this chapter.

Chapter 6 presents the results from experiments carried out on carbon electrodes and electrolyte solutions for use in lithium sulphur batteries. A full discussion of these results is also in this chapter.

Chapter 7 presents the results from experiments carried out on carbon electrodes for use in electrochemical capacitors. A full discussion of these results is also in this chapter.

Chapter 8 concludes the reported research and summarises the main achievements of this thesis. Further work is also suggested here.

Chapter 9 is the bibliography. Finally, lists of figure numbers, table numbers, and appendices can be found after Chapter 9.
2 Background Electrochemistry Theory

Electrochemistry is the study of the interconversion of electrical and chemical energy. Electrochemical processes involve the transfer of electrons, and typically occur across an electrode-solution interface. Electrodes are normally metals or degenerate semiconductors such as carbon. (Semiconductors are said to be degenerate if they exhibit high conductivity due to dopants or structural disorder.) Solutions are normally polar solvents containing high concentrations of dissolved electrolyte [28].

Interfacial electron transfer consists of an electron tunnelling from a delocalised energy level within a metal to a localised empty orbital on an ion or molecule in the solution, or the reverse process. The common property of metals that permits rapid electron transport through them is high conductivity (low resistivity). In a metal, electrons are delocalised in \textit{d}-orbitals which provide the conductivity. In carbon, electrons are delocalised in \textit{\pi}-orbitals arranged in graphene sheets. In both cases the energy levels are numerous and are very closely spaced; in fact, they are so close together that they may be regarded as existing in a continuous band. By the \textit{aufbau} principle electrons fill the energy levels up to a limiting energy known as the Fermi energy. Thus, the Fermi energy is the highest occupied energy level. The Fermi energy also corresponds to the electrode potential.

The solutions used in electrochemical experiments typically consist of an electroactive species, a high concentration of current-carrying electrolyte, and a solvent.

2.1 Types of Mass Transport

Three main processes control the mass transport of ions in electrolyte solutions. They are diffusion, convection and migration [29].

Diffusion is an entropy-maximising process which tends to create uniform concentration, or activity, of all species in solution. The net result is that species diffuse from areas of high concentration to areas of low concentration, i.e., down the
concentration gradient. Fick’s first law of diffusion assumes that the flux of material is proportional to the concentration gradient [30]:

\[ J = -D \frac{\partial C}{\partial x} \]  

*Eqn. 2.01*

where \( J \) = flux (mol m\(^{-2}\) s\(^{-1}\)), \( D \) = diffusion coefficient (m\(^2\) s\(^{-1}\)), and \( \frac{\partial C}{\partial x} \) = concentration gradient (mol m\(^{-4}\)). The characteristic scale of length of a diffusion process is given by:

\[ \langle x^2 \rangle^{\frac{1}{2}} = (2Dt)^{\frac{1}{2}}. \]  

*Eqn. 2.02*

Fick’s second law of diffusion describes the rate of change of concentration with time:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

*Eqn. 2.03*

where \( C \) = concentration (mol m\(^{-3}\)), \( t \) = time (s), \( D \) = diffusion coefficient (m\(^2\) s\(^{-1}\)), and \( x \) = distance (m).

Convection is movement of solution by mechanical means. Convection can be forced or natural. Forced convection may be accomplished through stirring, or by bubbling gas through a cell. Natural convection occurs as a result of density gradients in solution. Density gradients may be due to thermal gradients or reaction products accumulating near an electrode. Thermal gradients may be present due to an endothermic or exothermic electrochemical reaction. In general, natural convection is difficult to predict or control, and so is highly undesirable. In simple geometries, the hydrodynamic behaviour of convecting systems can sometimes be described by mathematical models, but more often computer simulations are needed.

Migration is the motion of ions caused by an electric field. At the electrode/solution interface there is a drop in the electric potential, and so an electric field exists. This field exerts an electrostatic force on any ions within the interface, hence inducing movement.
to or from the electrode. The resulting ion flux is determined by a number of variables, including the electric field, the concentration of ions, and the ionic mobility, the latter of which is dependent upon ionic size and charge.

All types of mass transport may affect measurements in electrochemical cells. Migration can be suppressed by using a concentrated “supporting” electrolyte, which is inert both chemically and electrochemically. This also has the added benefit of compressing the diffuse part of the double layer. Convection can be suppressed by the avoidance of stirring and by maintaining a uniform temperature inside the cell. This leaves diffusion as the principal type of mass transport in electrochemical experiments. Since it is driven by concentration gradients, it does not interfere with electrochemical measurements at low rates of reaction.

The overall reaction rate in an electrochemical cell is influenced by the electron transfer kinetics and by diffusion. The former is controlled experimentally via electrode potential, whereas the latter is dependent upon the concentration gradient of electroactive species. Pure electron transfer kinetics (free of diffusion) are described for one electron processes by the Butler-Volmer equation:

$$I_{\text{total}} = -FAk_f^0C_G \exp\left(-\frac{\beta_f FE}{RT}\right) + FAk_b^0C_R \exp\left(\frac{\beta_b FE}{RT}\right), \text{ Eqn. 2.04}$$

where $I$ = net rate of electric flux, or current (A), $F$ = the Faraday constant (96485 C mol$^{-1}$), $A$ = electrode surface area (m$^2$), $k$ = rate constant (m s$^{-1}$), $C$ = concentration (mol L$^{-1}$), $\beta$ = symmetry factor, $E$ = electrode potential (V), $R$ = the gas constant (8.315 J K$^{-1}$ mol$^{-1}$), and $T$ = absolute temperature (K).

In more complex (multi-electron) reactions the symmetry factor $\beta_f$ must be replaced by the transfer coefficient $\alpha_f$ [31]. Here

$$\alpha_f = n_p + n_q\beta_f, \quad \text{Eqn. 2.05}$$
where \( n_p \) = the number of electrons transferred in the step prior to the rate determining step (RDS), and \( n_q \) = the number of electrons transferred in one act of the rate determining step.

### 2.2 Electrode Potentials

Single potentials of electrodes cannot be measured directly. Their relative values can, however, be measured by comparing them to a reference half-cell. Most potentials are measured using the standard hydrogen electrode (SHE), defined by the half cell:

\[
\text{Pt(s), } H_2(g; \, p = 1 \, \text{atm}) \, | \, H^+(aq; \, a = 1) \, ||
\]

Although individual standard potentials are generally listed in the “electrochemical series” with respect to the SHE, in practice it is very difficult to prepare a solution having precisely unitary single ion activity of the hydrogen ion \( H^+ \). For this reason, a saturated calomel electrode (SCE) is widely used in its place:

\[
\text{Pt(s), } Hg(l), Hg_2Cl_2(s) \, | \, Cl^-(aq; \, \text{satd. KCl}) \, ||
\]

The single potentials obtained with respect to the SCE are then converted to the SHE scale by adding 0.241 V [3]. Another advantage of the SCE is that the KCl is an equitransferent electrolyte, which minimises the size of liquid junction potentials. The latter typically occur inside the glass frit of the reference half-cell.

All chemical reactions require a driving force. At constant temperature and pressure, this is the Gibbs energy \( G \). The Gibbs energy is related to the equilibrium potential via the equation

\[ \Delta G = -nFE, \quad \text{Eqn. 2.06} \]

where \( n \) = number of electrons, \( F \) = the Faraday constant \((96485 \, \text{C mol}^{-1})\) and \( E \) = voltage (V)
2.3 The Nernst Diffusion layer

In electrochemistry it is useful to think in terms of a finite layer near the electrode surface in which the diffusive flux is most concentrated. This layer is known as the “Nernst diffusion layer” and is denoted by the symbol $\delta$. Within this layer, the concentration gradient may be assumed to be linear, whilst outside this layer the concentration gradient may be assumed to be zero. This greatly simplifies the mathematical analysis. A representation of the Nernst diffusion layer is shown in Figure 2.01.

For a fully diffusion controlled reaction occurring at a planar electrode, the Nernst diffusion layer thickness is given by:

$$\delta = \sqrt{\pi D t} , \quad Eqn. \ 2.07$$

so that the thickness of the diffusion layer increases as $t^{1/2}$. The corresponding flux (and therefore the electric current) diminishes as $t^{-1/2}$. This equation is clearly analogous to the Einstein diffusion equation, of which there are many forms [30] [32] [33]:

$$\langle x^2 \rangle^{1/2} = \sqrt{2Dt} , \quad Eqn. \ 2.08$$
where $\langle x^2 \rangle$ is the mean-square displacement in the $x$-direction in time $t$, with diffusion coefficient $D$.

When diffusion is complicated by convection, the Nernst diffusion layer thickness also becomes dependent on flow from stirring and/or convection in the bulk solution [32].

### 2.4 Theory of Electrochemical Techniques

Many different electrochemical techniques may be employed to facilitate different types of electrochemical research. For the purpose of this thesis three techniques are discussed here.

#### 2.4.1 Cyclic Voltammetry

Cyclic voltammetry is the technique of choice for many electrochemical studies. The process measures current as a function of applied potential, under well-defined boundary conditions. The applied potential is varied linearly with time and the total current is measured. A summary of cyclic voltammetry theory has recently been published by Bond, and this forms the basis of the following discussion [34]. The fundamental reaction taking place at an electrode surface involves the transfer of an electron to an oxidised species (O) to create a reduced species (R):

$$ \text{O} + e^- \rightleftharpoons \text{R} $$

The oxidised species diffuses towards the electrode surface and the reduced species diffuses away, as depicted in Figure 2.02.
A typical cyclic voltammogram is shown in Figure 2.03.

Scanning the potential window in a negative direction, from $E_1$ towards $E_2$ (see Figure 2.03), the oxidised species O is converted into the reduced species R. The concentration of O at the electrode surface $[O]_{x=0}$ therefore decreases. This generates a concentration gradient between the bulk of solution and the electrode surface, which stimulates a diffusional flux of O to the electrode surface. The current and diffusional flux are related by the following equation:

$$I = nFAD\left(\frac{\partial[O]}{\partial x}\right)_{x=0},$$

*Eqn. 2.09*

where $I$ = current (A), $n$ = number of electrons, $F$ = Faraday constant (96485 C
mol$^{-1}$), $A$ = electrode surface area (m$^2$), $D_x$ = diffusion coefficient of $x$ (m$^2$ s$^{-1}$), and $D(\partial [O]/\partial x)$ = diffusional flux of O.

At the reduction peak the concentration of O becomes zero, and the diffusional flux is a maximum. At yet more negative potentials the current falls because O now has to diffuse from further and further away from the electrode surface. On reversing the direction of the scan from $E_2$ towards $E_1$ (now scanning in a positive direction) the reduction rate of O starts to fall, and the oxidation rate of R starts to rise. At the oxidation peak the concentration of R becomes zero, and the diffusional flux of R is a maximum. At yet more positive potentials the current falls because R now has to diffuse from further and further away from the electrode surface. This completes the characteristic shape of the voltammogram.

Experimental analysis of a faradaic process (as shown in Figure 2.03) may include the measurement of peak height or the charge associated with the oxidation process. In non-faradaic processes peaks are not observed, and the resulting voltammogram appears as a rounded rectangle. This represents double layer capacitance, which may be measured by calculating the height of the “steady state” current from the forward scan and dividing by the scan rate. When the cyclic voltammogram is not perfectly symmetrical, it is preferable to take an average of the steady state currents from the forward and backward scans.

2.4.2 Potential Step Technique

The potential step technique is an alternative to cyclic voltammetry. It measures current as a function of time, at a constant applied potential. It is particularly effective in separating double layer charging from faradaic (charge transfer) reactions (Figure 2.04).
If the faradaic reaction is under diffusion control, then the current-time response is described by the Cottrell equation:

$$I(t) = \frac{nFAD_0^{1/2}[O]}{(\pi t)^{1/2}}.$$  \hspace{1cm} Eqn. 2.10

where $D_0$ is the diffusion coefficient of the species O. The diffusion coefficients of common ions range in value from approximately $0.5 \times 10^{-5}$ cm$^2$ s$^{-1}$ to $2.0 \times 10^{-5}$ cm$^2$ s$^{-1}$ in water at room temperature.

It is evident from this equation that the current is determined by the area of the working electrode ($A$), the diffusion coefficient ($D_0$), and the concentration of species O.

### 2.4.3 Galvanostatic Technique

The galvanostatic technique is yet another alternative to cyclic voltammetry. It measures voltage as a function of time, at a constant applied current. It is particularly suitable for large electrodes because the applied current is more readily controllable than the voltage. Typical graphical outputs for this technique are depicted in Figure 2.05.
O molecules at the electrode surface are reduced, and diffusion processes supply more O. The diffusion layer increases until O can no longer be supplied fast enough to sustain the required current. At this point the potential decreases rapidly. The time taken for this to occur is referred to as the transition time $\tau$. Sand derived an expression for $\tau$:

$$\sqrt{\tau} = nFAC_0 \frac{\sqrt{\pi D_0}}{2l},$$  

*Eqn. 2.11*

where $n = \text{number of electrons}$, $F = \text{the Faraday constant (96484.6 C/mol)}$, $C_0 = \text{initial concentration of O (M)}$, $D_0 = \text{diffusion coefficient of O (m}^2/\text{s})$ and $I = \text{net current (A)}$.

## 2.5 Porous Carbon Electrodes

Porous carbon electrodes have substantial benefits over non-porous carbon electrodes. For example, porous carbon electrodes have a large surface area, which allows high specific capacitance and high current density. The pores can also accommodate large volumes of electrolyte solution, which eliminates the need for long range diffusion. However, there are some drawbacks to using porous carbon electrodes; they can be highly resistive and have a tendency to crumble. In addition, it is sometimes difficult for the electrolyte solution to wet the pores.
A generic equivalent circuit of a porous carbon electrode is shown in Figure 2.06. The macroequivalent circuit is seen to consist of three microequivalent circuits labelled $x$, $y$ and $z$. The circuit $x$ corresponds to the impedance of the solution inside the pores, whilst the circuit $z$ corresponds to the impedance inside the carbon. Typically, both of these may be assumed to be resistors. The circuit $y$ is the interfacial impedance and may have a variety of complex forms depending on the type of carbon and its surface pre-treatment. It is immediately clear that resistive losses can be minimised if the impedances $x$ and $z$ can be minimised. This implies the use of a highly conducting carbon and a highly conducting electrolyte solution.

![Figure 2.06. The generic equivalent circuit of a porous carbon electrode](image)

A good model for the impedance $y$ is a Debye network (Figure 2.07). This consists of a capacitor $C_1$ representing the double layer, and a resistor-capacitor combination $R_2C_2$ representing slow faradaic reactions on the carbon surface (pseudocapacitance). This model is particularly apt because it mimics the time-dependence of the observed capacitance, which shows a lower value at a higher rate of charge and discharge (“capacitance dispersion”).

![Figure 2.07. The Debye equivalent circuit.](image)
The flux of reactant to the internal surface of the carbon is a separate issue. Activated carbons have a high surface area (typically > 1000 m$^2$/g) but their pores are narrow, which forces any electrochemical reactions onto the diffusional time-scale. By contrast, carbon blacks have extremely wide voids which act as a reservoir for reactant, and thereby obviate the need for long range diffusion. As a result, electrodes based on carbon blacks can sustain very high rates of electrochemical reaction, which makes them ideal candidates for high power battery electrodes.
3 Literature Review

3.1 The Lithium-Thionyl Chloride Cell

This chapter shows the industrial importance of lithium-thionyl chloride cells, and details their use in oilfield applications. A good summary of lithium-thionyl chloride cell technology and their manufacture was published in 1998 Hensley et al. [7]. The lithium thionyl chloride cell (Li-SOCl₂) has a negative electrode made of lithium metal. Carbon electrodes are wrapped around the lithium core, with the electrodes separated by a glass wool paper. The positive electrode is a combination of a solution of lithium tetrachloroaluminate (LiAlCl₄) in thionyl chloride (SOCl₂) and a carbon electrode (SOCl₂ reduction takes place at the carbon surface).

Lithium has one of the most negative standard potentials of any metal; −3.04 V [3]. A freshly manufactured lithium thionyl chloride (SOCl₂) cell has an open circuit voltage of ~3.6 V, although the working voltage is slightly less than this (~3.3 V), as can be seen in Figure 3.01:

![Figure 3.01. A typical discharge curve for a lithium thionyl chloride cell.](image)

It is generally agreed that the overall lithium thionyl chloride cell reaction proceeds according to the following two half-cell reactions [36] [37]:

\[
\text{Li + SOCl}_2 \rightarrow \text{LiSOCl}_2 + \text{Cl}_2
\]
and

\[ 2\text{SOCl}_2 \ + \ 4e^- \rightarrow S \ + \ \text{SO}_2 \ + \ 4\text{Cl}^- \] (2)

yielding the overall cell reaction:

\[ 4\text{Li} \ + \ 2\text{SOCl}_2 \rightarrow S \ + \ \text{SO}_2 \ + \ 4\text{LiCl} \] (3)

It is evident that the reaction produces a gaseous product (SO\(_2\)) and a solid product (LiCl). The SO\(_2\) typically dissolves in the SOCl\(_2\), but the LiCl accumulates inside the dead volume of the carbon electrode. A key design requirement is therefore that the carbon electrode must be porous enough to accommodate the LiCl formed during discharge.

Historically, there was considerable disagreement concerning the details of the cell chemistry. Apparently Gabano (in 1971) was the first to suggest that the overall cell reaction took place via Eq. (3) [38] [39]. However, other researchers did not agree with Gabano's scheme, and suggested alternative reactions. For example, Auborn \textit{et al.} suggested the following overall cell reaction [40]:

\[ 8 \text{Li} \ + \ 3 \text{SOCl}_2 \rightarrow 6 \text{LiCl} \ + \ \text{Li}_2\text{SO}_3 \ + \ 2 \text{S} \] (4)

However this scheme was rejected because SO\(_2\) is widely observed as a reaction product [38].

In 1976, Dey proposed a more detailed reaction scheme involving an intermediate species, sulphur monoxide [41]:

\[ \begin{align*}
4\text{Li} &\rightarrow 4\text{Li}^+ \ + \ 4e^- \\
2\text{SOCl}_2 \ + \ 4\text{Li}^+ \ + \ 4e^- &\rightarrow 2\text{SO} \ + \ 4\text{LiCl} \\
2\text{SO} &\rightarrow S \ + \ \text{SO}_2 \\
2\text{SOCl}_2 \ + \ 4\text{Li} &\rightarrow 4\text{LiCl} \ + \ S \ + \ \text{SO}_2 
\end{align*} \] (5-8)
SO is an unstable molecule normally found only in the gas phase, where it is in equilibrium with a dimeric form, $\text{S}_2\text{O}_2$. It therefore seems unlikely this species would be observed in the cell discharge. Further explanation as to the existence of SO was provided by Bowden et al. in 1980 [42]. Analysis of 1.8 mM SOCl$_2$ in acetonitrile with supporting electrolyte (tetrabutylammonium hexafluorophosphate) was carried out using UV-Visible spectroscopy during an electrolysis experiment. These authors observed peaks corresponding to S and SO$_2$, and an additional peak which they assigned to an intermediate species. The third peak was found to increase initially in magnitude, then decrease towards the end of the experiment. It was proposed that this intermediate species was SO, and that the SO reacted as shown in reaction 7 previously.

3.1.1 The “Solid-Electrolyte Interphase” (SEI)

Despite its extremely electropositive character, lithium metal is surprisingly stable against bulk dissolution in many electrolyte solutions, including thionyl chloride solutions. This stability arises from a passivating film on its surface, formed rapidly upon being submerged in the solution. It is not clear whether the film forms due to reaction with the thionyl chloride itself, or by forming a salt with chloride ions in solution. Since the LiAlCl$_4$ salt dissolves in thionyl chloride (providing chloride ions) it seems energetically unfavourable for a lithium salt to form upon the lithium surface in the same solution. The more likely theory is the formation of a passivating film due to reaction between the lithium and thionyl chloride.

Peled discussed the properties of this passivating film, which is widely referred to as the “Solid-Electrolyte Interphase” (SEI) [43]. The SEI inhibits further reaction between metallic lithium and SOCl$_2$, which accounts for the excellent shelf-life of Li-SOCl$_2$ batteries (approximately ten years). The reaction is inhibited because the passivating film prevents further direct contact between the lithium metal and the thionyl chloride electrolyte solution. However, since the passivating film selectively conducts lithium ions, the thickness of the film does grow very slowly over time. This is the cause of a phenomenon known as ‘voltage delay’. Many Li-SOCl$_2$ cells that have been in storage for a long period of time initially have a lower discharge potential than normal. The
potential then rises after a short period of time, after which it behaves normally. This suggests that the SEI breaks down to some extent during use.

There has been some disagreement over the chemical origin of the passivating film. Bro et al. state that the passivating film is Li$_2$S$_2$O$_4$, and that SO$_2$ may be added to form this [44]. By contrast, Hensley et al. state that the film is LiCl [7]. These authors do not advocate the addition of SO$_2$; they say the film is formed instantaneously when thionyl chloride electrolyte solution is added to the cell during manufacture.

### 3.1.2 The Carbon Electrode

Carbon electrodes in lithium-thionyl chloride cells are commonly made from carbon blacks, which are particulate forms of carbon. Carbon blacks can be made from many types of material, such as hydrocarbon gases, aromatic-rich fuels and oil. Acetylene black is a special type of carbon black, produced by the decomposition of acetylene. Compared to other carbon blacks, it has an elevated level of aggregation and a more graphitic structure. For this reason acetylene black is the most popular carbon black used in lithium-thionyl chloride cells.

As shown earlier (Figure 1.03), carbon blacks contain large numbers of aggregates, which can provide significant dead volume. This latter parameter is a measure of the ability of an electrode to absorb electrolyte solution, although this is complicated by other parameters, such as the solution surface tension and the electrode ‘wettability’.

Electrodes made solely from acetylene black are prone to tearing, and are more resistive than other carbon blacks. Therefore, other carbon blacks are added. One such carbon black is Ketjenblack EC-300J. Although this carbon black has a similar dead volume to acetylene black, its aggregates are much smaller. This imparts resistance to tearing, and improved conductivity to the mixture.
3.1.3 Conductivity and other Properties of Carbon Black Electrodes

Carbon black behaves as a degenerate semi-conductor, and has a band gap of around 0.5 eV. (This may be compared with diamond, which has a band gap of around 6 eV). Short-range order still exists in carbon black, but the inter-atomic distances and bond angles are somewhat different from those in graphite. Due to structural disorder a large number of states exist inside the band gap. As a result, large numbers of electrons are thermally excited into the conduction band at room temperature. This ensures there is never a large potential drop inside the surface of carbon black electrodes.

Previous work at Loughborough University identified some of the most important properties of carbon black materials used in battery electrodes [45]. These included high electrical conductivity, and high dead volume. Fletcher et al. found that carbon black electrodes, upon extrusion, fall into one of two categories; “open structured” having high dead volume, or “closed structured” having low dead volume. Although some dead volume is necessary to accommodate the electrolyte solution, an electrode with excessive dead volume is undesirable, as the more open structure imparts low tensile strength (tendency to tear). This is illustrated in Figure 3.02.

To inhibit tearing, a 1:4 ratio of Ketjenblack to Shawinigan Acetylene Black may be used (a secret commercial formulation). This provides a composite electrode with both
high dead volume and low tendency to tear. Figure 3.03 depicts the ideal mechanical properties of a carbon electrode, in the form of a Venn diagram.

![Figure 3.03. Ideal mechanical properties of a carbon electrode](image)

In the open literature, Auborn et al. have experimented with a number of alternative, non-metallic positive electrode materials, but found carbon to perform better [40]. Generally, positive carbon electrodes are fabricated by mixing carbon black with a solvent and binder, and pasting this mixture onto a screen (often nickel mesh) before allowing to dry.

SOCl$_2$ is reduced during discharge inside the carbon positive electrode, and the solid discharge products accumulate inside the dead volume. LiCl is one of the main discharge products, and the increasing deposition of this material eventually fills the dead volume of the carbon electrode, and terminates the reaction [46] [47].

In 1983 Szpak noted the need to allow for some electrode expansion during discharge, because analysis of carbon electrodes showed that carbon grains were separated at locations where SOCl$_2$ reduction had taken place [48]. Szpak also suggested that the LiCl precipitate restricted the area available for access to electrode dead volume. In 1985, Klinedinst related the capacity of different carbon blacks to their total porosity, as determined by the Dibutyl Phthalate (DBP) measurement [49]. It was discovered that higher porosity carbons gave higher capacities than lower porosity carbons (Figure 3.04). Shawinigan appeared to be an anomaly here, for unknown reasons.
Despite the relatively poor performance of Shawinigan acetylene black shown above, this material is an industry standard for carbon black electrodes. Shawinigan was also used in work by Dey, and the porosity was estimated at 70-80% (the method of estimation was not stated) [41].

More recently, a study of carbon electrodes was carried out by Carmier et al. who used mercury porosimetry to assess pore volumes before and after discharge [46]. These researchers reported that pore volumes became re-distributed during discharge; the volume of smaller pores increased during the discharge, and the volume of larger pores decreased. The effect was attributed to the gradual deposition of discharge products that caused the electrodes to swell. Apparently, the combination of pore volume re-distribution and electrode swelling resulted in little overall change in total porous volume. Carmier et al. suggested that to optimise the carbon electrode for use would require both a high pore volume (attributed to meso- and macroporosity), and a high surface area (attributed to microporosity).

The identification of carbon materials for electrodes is an important area of research, and continues to be of interest in recent work [50].
3.1.4 The Electrolyte Solution

In order to improve the ionic conductivity of SOCl₂ solution, lithium tetrachloroaluminiminate (LiAlCl₄) is added as ‘supporting electrolyte’. This dissociates as:

\[
\text{LiAlCl}_4 \rightarrow \text{Li}^+ + \text{AlCl}_4^{-}
\]

This electrolyte is soluble in SOCl₂, and is relatively inexpensive. Auborn et al. experimented with different concentrations of LiAlCl₄, formed in situ by AlCl₃ and LiCl in SOCl₂ [40]. The optimum concentration was found to be approximately 1.5 M, as shown in Figure 3.05.

*Figure 3.05. Conductivities measured with different equimolar concentrations of LiCl and AlCl₃ in SOCl₂ [40].*
3.1.5 Safety

The three major safety concerns with lithium thionyl chloride batteries are (1) leakage of electrolyte solution, (2) short circuiting of cells and (3) forced over-discharge [7]. High pressure may build-up due to excessive SO₂ production. The pressure causes damage to the welds at the top and bottom of the cells and ultimately allows leakage to occur. If thionyl chloride leaks from the cell it reacts with moisture in the air and forms hydrochloric acid and sulphur dioxide. On a cell assembly line steps are taken to reduce the possibility of thionyl chloride leaking from cells, by not over-filling cells and by ensuring good welds. Once the cells are in use, pressure build-up is avoided by using cells only within their specified temperature range. Heat generation in cells can lead to melting of S or Li in extreme cases. Short circuiting of cells may be avoided by careful design; for example ensuring that the lithium and carbon electrodes do not come into contact inside the cell. This is normally achieved by using an appropriate separator such as fibreglass paper. Forced over-discharge (to 0 V) compromises safety as it can lead to formation of lithium dendrites, which are unstable in thionyl chloride. Therefore, equipment using lithium thionyl chloride cells is designed to stop high load on a cell after the voltage has decreased to 2 V. Lithium dendrites can also form if the thionyl chloride becomes depleted in a cell whilst there is still lithium available. Cell constituents must therefore be optimised, and most cells are designed to be limited by the carbon electrode.
3.2 The Lithium-Sulphur Cell

Much work is being carried out on the development of the lithium sulphur system because it has the potential to be a rechargeable, high energy power source. It has a theoretical specific capacity of 1672-1675 mAh/g [5] [51] [52]. This value is much higher than for other systems, as seen in Table 3.01, and arises from two high energy density reactions. On discharge lithium is oxidised to lithium ions, and on charge the lithium ions are reduced to lithium metal:

$$\text{Li} \leftrightarrow \text{Li}^+ + e^-$$

At the other electrode sulphur is reduced to sulfide ions on discharge, and sulfide ions are oxidised to sulphur on charge.

$$S + 2e^- \leftrightarrow S^{2-}$$

The high theoretical specific capacity is attributable to the combination of the two-electron process and low molecular weight active materials.

When comparing different lithium battery systems, an important point to note is how the specific capacity is calculated. Some researchers calculate the capacity per gram of ‘active material’ whilst others calculate the capacity per gram of cell weight (Table 3.01). Frustratingly, some researchers do not indicate how they have calculated their specific capacities, which makes it impossible to assess their results.
<table>
<thead>
<tr>
<th>Li battery couple</th>
<th>Theoretical Specific Energy (Wh/kg total cell)</th>
<th>Practical Specific Energy (Wh/kg total cell)</th>
<th>Theoretical Specific Capacity (mAh/g active material)</th>
<th>Practical Specific Capacity (mAh/g total cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/Li₈Mn₂O₄</td>
<td>428</td>
<td>120</td>
<td>285 (x = 2)</td>
<td>100-120</td>
</tr>
<tr>
<td>LiCu/Li₈Co₃O₄</td>
<td>570</td>
<td>180</td>
<td>273 (x = 1)</td>
<td>136</td>
</tr>
<tr>
<td>Li/Li₈V₂O₈</td>
<td>890</td>
<td>150</td>
<td>412 (x = 8)</td>
<td>309</td>
</tr>
<tr>
<td>Li/Li₈TiS₂</td>
<td>480</td>
<td>125</td>
<td>225 (x = 1)</td>
<td>58</td>
</tr>
<tr>
<td>LiS</td>
<td>2600</td>
<td>-</td>
<td>1672</td>
<td>&gt; 200⁰</td>
</tr>
</tbody>
</table>


Table 3.01. Comparison of some rechargeable lithium cells.

3.2.1 Information About Sulphur

Sulphur is known to exist in several allotropic forms but the most abundant is known as ‘rhombic sulphur’. This is a yellow solid substance which crystallises with orthorhombic symmetry [53]. Rhombic sulphur melts at 112.8°C to form a straw-coloured liquid, which can then crystallise into monoclinic sulphur. Monoclinic sulphur melts at 119.2°C and is the stable form of sulphur above the transition temperature of 95.5°C (also known as the equilibrium temperature). Sulphur molecules exist as S₈ staggered-ring configurations in both the orthorhombic and monoclinic forms, as well as the straw coloured liquid. These large ring molecules arise due to the preference of sulphur to form two single bonds as opposed to one double bond. The viscosity of liquid sulphur drastically increases when it is heated between 160°C and 180°C due to the polymerisation of sulphur [54]. Many of the rings break open and join together forming molecules with an average chain length of 10⁵ – 10⁶ atoms. At temperatures higher than 180°C the viscosity drops again as the chains are disrupted by heat.

3.2.2 Electrochemistry of the Lithium-Sulphur Cell

Some of the main problems faced by lithium sulphur cells are the inability to fully recharge the cell, the inability to maintain a useful discharge potential, and the inability to be cycled many times. These problems, and some attempts at solving them, will now be discussed.
The lithium-sulphur cell is commonly made up of a porous carbon/sulphur electrode and a lithium counter electrode submerged in a non-aqueous electrolyte solution. Sulphur is an insulator and so must be mixed with an electronically conducting material to form a composite. Sulphur is most often mixed with carbon.

The formal cell reaction is:

$$2\text{Li}^+ + S^{2-} \leftrightarrow \text{Li}_2S$$

However, many side reactions also occur, yielding complex polysulfides and many other unwanted products. $\text{Li}_2S$, the main discharge product, can build up on the porous electrode and eventually blocks it; a process known as electrode passivation. The exact details of the lithium/sulphur/polysulfide electrochemistry remain unclear, but there is no shortage of theories. For example, Kolosnitsyn et al. suggested that the sulphur reduction reaction occurs via a number of steps [55]. These researchers carried out experiments in 1M LiClO$_4$ in sulfolane, using chronopotentiometry, and suggested the following scheme:

$$\begin{align*}
\text{step 1} & \quad S_8 + 2e^- \rightarrow S_8^{2-}, \\
& \quad S_8^{2-} \rightarrow S_6^{2-} + 1/4S_8, \\
\text{step 2} & \quad S_6^{2-} + 2e^- \rightarrow 2S_3^{2-}, \\
& \quad S_6^{2-} + 2S_3^{2-} \rightarrow 3S_4^{2-} \\
\text{step 3} & \quad S_4^{2-} + 2e^- \rightarrow 2S_2^{2-}.
\end{align*}$$

The same authors also suggested that $\text{Li}_2S_8$ produced in the first step might be poorly soluble, so that steps one and two would be dependent on a solid phase sulphur reduction mechanism. $\text{Li}_2S_4$ produced in the second step was thought to be much more soluble, and so step 3 was assumed to occur via a solution mechanism.
A number of other polysulfide products have been suggested; Mikhaylik et al. reported that polysulfides Li$_2$S$_x$ with $x \sim 6$–8 are formed during the first plateau region (2.3 – 2.4 V) and that further reduction takes place at the lower plateau region [56].

A typical discharge curve is shown in Figure 3.06, from the work of Ryu et al. [57]. The electrode contained 60 wt. % sulphur. It is generally agreed that the first plateau region (a) represents the electrochemical reduction of sulphur, and the subsequent plateau represents the reduction of polysulfide products.

![Figure 3.06. Typical discharge curves; (a) represents 100 mAh/g, (b) represents 600 mAh/g and (c) represents 1268 mAh/g [57].](image)

Cheon et al. investigated the structural changes in carbon-sulphur electrodes as discharge and charge proceeded, and also discussed sulphur utilisation, capacity fade rate and surface passivation [58] [59]. These researchers found that the first plateau region observed in the discharge of lithium sulphur cells (2.4 – 2.1 V) was due to the reduction of elemental sulphur to soluble polysulfides. The second region (2.1 – 1.5 V) was found to arise from the reduction of soluble polysulfides to solid Li$_2$S$_2$ and/or Li$_2$S. Using SEM imaging, they showed how a film of Li$_2$S was observed on discharged electrode surfaces, but gradually disappeared upon charging of the cell, indicating its conversion back to soluble polysulfides. Between the cycles of electrode surface passivation by Li$_2$S and the dissolution of soluble polysulfides some important changes were said to occur. It was suggested by Cheon et al. that the soluble polysulfides inside the carbon matrix increased the viscosity of the solution, thereby impeding the diffusion of lithium ions. This in turn impeded the electrochemical reactions, and so reduction tended to take place on the outer surface only. Thicker electrodes presented a greater diffusion length. The second important point noted by these authors was the effect that
re-distribution of soluble polysulfides, (and therefore the solid products of polysulfide reduction), had on electrode structure. Initial deposition of Li$_2$S was found to cause stress within the electrode, leading to destruction of the carbon matrix and thus a breakdown in electrical contact. Irreversible deposition of Li$_2$S therefore caused loss of active material and the carbon matrix itself. Higher discharge rates were found to enhance this problem.

Ryu et al. made carbon/sulphur composite electrodes by forming a slurry of 60 wt.% sulphur, 25 wt.% acetylene black and 15 wt.% PEO binder in acetonitrile [57]. The slurry was cast onto a glass plate and dried, leaving a film of ~ 50 μm thick. These authors obtained discharge profiles of the electrodes in a PVDF-gelled solution of 0.5 M LiCF$_3$SO$_3$ in tetruglyme. The discharge curves were composed of an upper plateau region of 2.45 V, and a lower plateau region of 2.05 V, which is very close to other reported plateau voltages [60]. Ryu et al. assigned the following reactions to these plateau regions:

\[
\begin{align*}
2 \text{Li} + n \text{S} &\rightleftharpoons \text{Li}_2\text{S}_n \quad \text{(Upper plateau region)} \\
\text{Li}_2\text{S}_n + (2n - 2) \text{Li} &\rightleftharpoons n\text{Li}_2\text{S} \quad \text{(Lower plateau region)}
\end{align*}
\]

SEM imaging was used to show the carbon/sulphur composite electrode surface at various points during discharge. This is shown in Figure 3.07.
These images show some agglomeration as discharge proceeds, and are similar in appearance to those reported by Cheon et al. [58] [59]. Ryu et al. also used DSC analysis to show that endothermic peaks attributed to sulphur disappeared as discharge progressed. The upper plateau region of the discharge curve also disappeared as discharge progressed, which illustrated that elemental sulphur was not being formed on re-charging of the cell.

### 3.2.3 The Polysulfide Shuttle Effect

The ‘polysulfide shuttle effect’ is a term given to describe a mechanism whereby polysulfides travel to the lithium electrode during charging and react with the passivation layer. This passivation layer is made up of lithium sulfides. Once reacted, the reduced polysulfide products may travel back to the carbon/sulphur electrode, where they will be re-oxidised. Thus, more energy may be required to charge the battery than
Mikhaylik et al. defined a charge-shuttle factor $f_c$, which defines the rechargeability of the cell [56]:

$$f_c = \frac{k_s q_H [S_{total}]}{I_c},$$

where $q_H$ = high plateau sulphur specific capacity (mAh / g), $[S_{total}]$ = total S concentration, $I_c$ = charge current, and $k_s$ = shuttle constant. This last parameter is generally a function of other cell components, and the concentration of electrolyte.

When $f_c < 1$, the cell can be completely charged. When $f_c > 1$ the cell never completely re-charges. The voltage levels off and the higher polysulfides cannot be re-oxidised to elemental sulphur. The shuttle constant also dictates the reduction of polysulfides on lithium according to:

$$\frac{d[S_H]}{dt} = \frac{I}{q_H} - k_s [S_H],$$

where $[S_H]$ = concentration of higher polysulfides.

### 3.2.4 Materials Used in Lithium Sulphur Cells

Many different electrolyte solutions have been tested by research groups developing the lithium sulphur system. A small collection is shown in Table 3.02. The work of the authors listed is discussed in more detail throughout this review.
The varieties of chemistries that have been experimented with indicate that the lithium sulphur battery is still in a development stage.

Choi et al. stated that cell performance was improved in lithium sulphur cells when using mixed solvents (tetraglyme/1,3-dioxolane, 1:1 v/v) compared to single solvents [61]. They attributed this to a less viscous solution allowing better transport of the lithium ion. These experiments were carried out using 1M LiCF$_3$SO$_3$, and electrodes were made by ball-milling sulphur (60 wt. %), carbon (20 wt. %) and PVDF (20 wt. %). These authors reported a number of other findings, including the importance of cell solution volume; 30 μl cells had a faster rate of capacity fade than 12 μl cells. The latter cells were found to give a better performance. The steady state capacity for such cells was reported as 503 mAh/g. The two plateau regions were ~2.4 V and ~2.0 V. As the number of cycles increased the higher voltage region almost disappeared. Work was
also carried out using polymer gelled solutions, which did not perform as well as liquid electrolyte solutions. In experimenting with the addition of organic additives, they reported that the addition of 5% (by volume) toluene increased the specific capacity. This was attributed to film formation on the electrode surface, improving electrode/electrolyte solution interface.

Other researchers have experimented with different solvent systems, and agree that multi-solvent systems often give better cell performances [62]. Many researchers have used a high boiling point glyme in combination with another non-aqueous solvent. Glymes (ethylene glycol dimethyl ethers) are good lithium coordinating solvents, which helps the solvation of lithium-based electrolytes. An example of a glyme molecular structure is shown in Table 4.03. Glymes are commercially available, miscible with many other solvents, and are stable due to the terminal methyl groups in the molecule [63].

Lithium triflate (LiCF$_3$SO$_3$) is one of many salts used in the scientific literature in non-aqueous media. Others include lithium hexafluorophosphate (LiPF$_6$) and lithium perchlorate (LiClO$_4$). LiCF$_3$SO$_3$ is highly conducting in organic solutions and unlike LiClO$_4$ it is compatible with a wide range of organic solvents and strong reducing agents [62]. The lithium cation has a very small ionic radius, and hence a high charge density. When combined with a large anion in a salt, the attractive forces are not very strong, and the Gibbs lattice energy of the crystal is small in magnitude. Therefore the lattice energy is easily overcome by the energy of solvation. In addition, the combination of the small lithium cation (with high charge density) and the large triflate anion (with low charge density) favours the dissociation of the electrolyte in solution. It is therefore reasonable to expect a salt such as LiCF$_3$SO$_3$ to be dissolved in large quantities in organic solvents.

Matsuda et al. investigated a number of sulfolane based solutions and three different electrolytes [64]. These researchers found that 1M LiPF$_6$ in sulfolane/1,2-dimethoxyethane (1:9 v/v) was highly conducting, and that this solution gave better cycling efficiency than LiBF$_6$ or LiClO$_4$ solutions.
Wang et al. reported a very interesting idea for improving the utilisation of sulphur [65]. A mix of 30 wt. % sulphur in activated carbon was heated to 200°C for six hours, with the aim of allowing melted sulphur to enter the pores of the activated carbon. This composite was then mixed with acetylene black and a PTFE binder to form the electrode (7:2:1 w/w). Gelled membranes were made, and then both the electrode and membrane were soaked in electrolyte solution before being incorporated into a coin cell. Discharge of the cell was carried out using a current density of 0.3 mA/cm², and a voltage cut-off point of 1 V. The authors reported sulphur utilisation of almost 90%, and a stable capacity of around 440 mAh/g. A limitation of these cells was the relatively low discharge voltage of approximately 1.75 V. It should also be pointed out that 0.3 mA/cm² is a very low current density for discharging cells, and this is probably part of the reason sulphur utilisation was so high. Both sulphur utilisation and the average discharge voltage have been found to decrease when current density is increased [66].

A clever alternative idea was put forward by Rauh et al., who experimented with polysulfide electrolyte solutions, in an attempt to create a system like the Li-SOCl₂ system, where the redox-active species was completely soluble [67]. These researchers used tetrahydrofuran (THF) as a solvent, as it was found to be capable of dissolving large amounts of lithium polysulfides. Whilst dissolution of polysulfides may allow higher utilisation of active material, there is also the risk of losing active material by diffusion away from the carbon/sulphur electrode. This can slow the re-charge reaction.

It was reported by Marmorstein et al. that when lithium sulphur cells were discharged to almost their full theoretical capacity the rate of capacity fade was extremely high [5]. The rate of capacity fade was decreased by limiting the cell depth of discharge to approximately 30%. Suggestions given for high rates of capacity fade were that polysulfides may have diffused away into the electrolyte solution, the redox reactions were not reversible, and that electrical contact may have been lost during cycling. Marmorstein et al. used polymer-gelled electrolyte solutions in their study, and found that although solutions gelled with poly (ethylene glycol) dimethyl ether had the highest conductivity, cell with solutions gelled using poly (ethylene oxide) gave the best initial discharge capacity. It was also reported that specific capacity was higher for cells with 75 wt. % S electrodes than 50 wt. % S electrodes, but sulphur utilisation was higher for the latter. Contrary to these authors suggesting polysulfide dissolution away from the
electrode, Wang et al. suggested that interactions between sulphur particles and a polymer matrix might prevent polysulfide dissolution [66].

Experimentation with different solvents was also carried out by Kim et al., who claimed that changing the amount of 1, 2-dimethoxyethane (DME) and diglyme (DG) altered both polysulfide stability and the electrochemical reactions of the polysulfides [68]. 1,3-dioxolane (DOX) was claimed to stabilise the lithium surface, as it was thought the cyclic structure broke down (via a ring-opening reaction) to form a layer on the lithium surface. The discharge curves reported by these researchers did not show two defined plateau regions (Figure 3.08), as other groups have previously reported. The reason for this is not clear.

These authors also used a statistics software package to calculate an optimum solvent composition. This was found to consist of DME/DG/DOX 4:4:2 (v/v). Kim et al. had previously found that a ratio of 12:3:5 had resulted in a good cell performance; approximately 26 mAh for forty cycles, discharging at an average voltage of approximately 2.01 V. The calculated solvent composition was then tried experimentally, and found to give a cell capacity of 26 mAh, running at an average voltage of 1.96 V.
Choi et al. claimed to improve sulphur utilisation by using carbon materials of high DBP values for electrode fabrication [69]. This was explained by the presence of larger void volumes within the carbon electrodes, which accommodated larger volumes of \( \text{Li}_2\text{S} \) on discharge. These authors also claimed that smaller sulphur particle sizes allowed for better utilisation of sulphur. A rather complicated explanation was provided, which suggested the dissolution of solid sulphur in the electrolyte solution left small pores behind, which could then accommodate \( \text{Li}_2\text{S} \). This implied that solid sulphur dissolved in solution rather than being electrochemically reduced on the carbon surface. If this were true, it would make the earlier assumption that \( \text{Li}_2\text{S} \) would deposit inside the carbon void volume unlikely, as the products of sulphur reduction might already have diffused away.

To overcome the dual problems of diffusion of active material away from the electrode surface, and poor structural stability, some researchers have added substances to the electrode that might adsorb polysulfides and/or increase mechanical strength. This approach to improving electrodes for lithium sulphur cells was investigated by Han et al. who added multi-walled carbon nanotubes (MWNTs) to sulphur/carbon electrodes [60]. The aim was to hold the polysulfide groups inside the electrode, and additionally impart good structural stability to the electrodes. These authors claimed that MWNTs improved electrical conductivity, and provided good structural stability, which helped to improve sulphur utilisation. They explained that the addition of MWNTs had helped in retaining soluble polysulfide products in the carbon electrode, and this led to these electrodes maintaining a higher specific capacity for a longer period of time than electrodes without MWNTs. The specific capacity obtained was approximately 300 mAh/g after 50 cycles.

The charge/discharge characteristics of lithium sulphur cells were investigated by He et al., who made coin type cells with carbon sulphur electrodes consisting of S/acetylene black/PTFE binder in the ratio of ratio of 80/15/5 by weight [70]. The electrolyte solution was 1 M LiPF\(_6\) in ethylene carbonate/diethyl carbonate (1:1 v/v). The first discharge was approximately 967 mAh/g, and ran at 1.5 V. Subsequent discharges ran at higher voltages; around 1.95 V, and the capacity stabilised at around 800 mAh/g. After 30 cycles the capacity dropped to around 758 mAh/g. The current density was
0.25 mA/cm². The published discharge curves did not show two clear plateau regions, as seen in work by other researchers.

Jung et al. attempted to improve the cycle life of lithium sulphur cells by two approaches [52]. The first involved trying to maintain the morphology of the carbon/sulphur electrode during cycling. To do this, Jung et al. used a mixed binder system (polyvinyl pyrrolidone and polyethylene-imine) and lowered the overall binder content. The second approach focused on the replacement for expensive imidazolium salts that had previously been identified as beneficial to cycle performance [51].

Jung et al. used different composite electrodes for these two approaches; the first used S/Super-P carbon black/PVP binder in a ratio of 16:2:1, the second used S/Ketjenblack carbon black/PEO binder. The first approach dispersed the materials in isopropyl alcohol; the second dispersed the materials in acetonitrile. Both mixtures were ball-milled and the resulting slurries coated onto current collectors. More useful conclusions may have been drawn from this work had the same experimental procedure been maintained throughout. Nevertheless, these authors claimed that a mixed binder system allowed a higher discharge voltage to be maintained, and that the replacement of imidazolium salts with a mixed salt system of 0.5 M LiCF₃SO₃ and 0.5 M TBAPF₆ (TBA = tetrabutylammonium) gave a comparable performance. The authors provided no detailed explanation as to why these salts improved performance, suggesting only that it may be related to enhancement of polysulfide reactivity and improved lithium stability. A further explanation might be that the improvement is related to solvation of discharge products.
3.2.5 A Summary of Problems with the Lithium Sulphur Battery

In summary, for lithium/sulphur cells to be of practical use there is a need to improve the cycling efficiency and maintain high capacities at practical discharge voltages. This has not yet been achieved. Despite the vast amount of research carried out on the lithium-sulphur cell, the following problems remain:

1. Sulphur is an insulator, and therefore must be efficiently blended with a chemically inert conducting material, such as carbon. Optimisation of the ratio of sulphur to carbon has not yet been achieved.

2. Due to diffusion of soluble polysulfides away from the carbon positive electrode, the lithium-sulphur cell is not currently fully reversible, i.e., the first discharge capacity is often much larger than the subsequent ones.

3. Polysulfide ions can travel through the cell solution by diffusion, allowing Li$_2$S to precipitate on the lithium surface (the 'polysulfide shuttle').

4. The 'polysulfide shuttle' has one advantage, however. It prevents overcharge, and so operates as a safety device in lithium/sulphur batteries. However, this mechanism is not ideal for a high rate battery.

From a materials science point of view, the future development of lithium/sulphur cells depends upon the optimisation of the active materials, so that sulphur utilisation and cycling efficiency can be enhanced. It seems that both the solubility of lithium sulfide and the effective discharging of the cell depend strongly upon the identity of the electrolyte solution. Another materials-related issue is whether the system performs better when elemental sulphur is embedded in a carbon matrix, or when polysulfides are dissolved in the electrolyte solution.

From an electrochemical point of view, it is generally agreed that the first plateau region observed in the lithium sulphur cell discharge is due to the reduction of elemental sulphur, and the second plateau region arises from the reduction of polysulfide products. The exact mechanism details are not known. It is also unclear as to whether elemental sulphur can be re-formed on charging of the cell. Both polysulfide
dissolution and blockage of electrodes have been cited as reasons for battery failure/capacity fade. Despite these problems, there is still a great interest in these batteries; not only from an academic viewpoint but also within industrial organisations. The United States Patent and Trademark Office have almost forty patents relating to lithium sulphur batteries stored on their database since 1976. Five of these have been added during 2008, which clearly shows this work is of current interest.
3.3 Electrochemical Capacitors

A conventional capacitor is a device capable of storing potential energy at a given voltage, by the separation of charge. An electrochemical capacitor is a device capable of storing potential energy by two different processes:

1. By the separation of charge across the electrochemical double layer.
2. By surface redox reactions.

The first process is a type of normal capacitance. The second process is rather different, and is called “pseudocapacitance”. In pseudocapacitance, the potential energy is not stored in delocalised electric fields, but in localised chemical bonds.

Large surface area materials enhance both processes. The combination of such factors results in very large capacitances being measured, and for this reason, electrochemical capacitors are also known as supercapacitors or ultracapacitors. These devices exhibit several Farads per gram. Other devices, such as electrolytic capacitors ('medium capacitance devices'), provide only tens of milli-Farads per gram. The crucial requirement for obtaining high capacitance in a small volume (approximately 1 cm$^3$), according to Conway, is the use of high surface area materials such as activated carbon with a surface area of around 1000 m$^2$ g$^{-1}$ [71]. Conway also states electrochemical double layers typically have capacitances of 16 – 50 μF/cm$^2$.

The first patent granted for this principle of energy storage was in 1957 to Becker et al [72]. The patent was based on porous carbon electrodes and an aqueous electrolyte solution. Since then, both aqueous and non-aqueous solutions have been used for supercapacitors.

At constant temperature and pressure, energy storage is described by,

\[ G = \frac{1}{2} CV^2, \]

where $G$ = Gibbs energy (J), $C$ = capacitance (F), and $V$ = voltage (V).
Note that the Gibbs energy increases as the square of the voltage. It is therefore advantageous to increase the voltage at which energy that can be stored. Unfortunately, the voltage is limited in aqueous solutions, as water begins to decompose above 1.2 V. Larger voltages can be reached only in non-aqueous solvents.

Ways of storing electrical energy can be grouped into two main categories of direct, or indirect, as seen in Table 3.03. This distinction in energy storage is crucial to understanding a fundamental difference between electrochemical capacitors and batteries.

<table>
<thead>
<tr>
<th>Directly; as electrostatic energy</th>
<th>Indirectly; as Gibbs energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>This requires coupled build-ups of negative and positive charges, e.g., on the plates of a capacitor.</td>
<td>This requires coupled electrochemical reactions of redox active species on electrode surfaces.</td>
</tr>
<tr>
<td>This is a <em>non-faradaic</em> process because there is no change in the chemical composition of the system during charge and discharge.</td>
<td>This is a <em>faradaic</em> process because there is a change in the chemical composition of the system during charge and discharge.</td>
</tr>
</tbody>
</table>

Table 3.03. Two types of electrical energy storage.

An important difference between the faradaic and non-faradaic processes is their long-term reversibility. In electrochemical capacitors, the faradaic reactions that take place due to pseudocapacitance can result in chemical inter-conversions at the electrode surfaces. This may lead to gradual deterioration of electrodes. In conventional capacitors no chemical changes are involved and the electrodes have a long life. Since the system depends on movement of electrons only, it is highly reversible.

### 3.3.1 Pseudocapacitance

Pseudocapacitance arises from electrochemical reactions of surface functional groups such as ketones, carboxylates, and phenols. Pseudocapacitance exhibits a potential dependence that regular capacitance doesn’t. The surface functional groups also confer ‘wettability’ on the carbon surface, which improves their performance. The requirement for protons to take part in many redox reactions also means that pseudocapacitance is
generally lower in organic solvents, such as sulfolane. If protons are not available in solution, the redox chemistry cannot take place.

3.3.2 The Electrochemical Double Layer

The most basic representation of a double layer is a model showing two parallel layers of opposite charge separated by a very thin layer of solution (atomic dimensions). There have been many discussions of the electrochemical double layer, and the original model by Helmholtz has been modified many times. A good review of the development of the electrochemical double layer was written by Conway [71]. Conway’s summary opens with a discussion of the Helmholtz model (created in 1853) which was developed for colloid surfaces. In this model, the build-up of surface charges is attributed to acid-base ionisation or adsorption of ions. Conway’s review then progresses to Gouy and Chapman’s adaptation of this basic idea to allow for the fact that ions in solution are affected by thermal fluctuations, and hence do not behave as static charges. Finally, Stern is credited with the discovery that the ions are distributed in two different regions; an inner region of ions trapped at the electrode surface, and an outer region (“the diffuse layer”) of the Gouy-Chapman type. The historical development of these ideas is illustrated in Figure 3.09.

![Figure 3.09. The development of the double layer model, where (a) is the Helmholtz model, (b) is Gouy’s point-charge model (where $\sigma = \text{specific charges per unit area}$), and (c) is Stern’s adaptation, combining the two previous models and showing the two distinct regions [71].](image-url)
This final model implies there is a series relation between the capacitance arising from the compact layer \( C_H \), and the capacitance arising from the diffuse layer \( C_{\text{diff}} \). The total double layer capacitance is therefore given by the series combination of the two capacitances,

\[
\frac{1}{C_{\text{dl}}} = \frac{1}{C_H} + \frac{1}{C_{\text{diff}}}.
\]

A typical modern representation of the double layer used today is shown in Figure 3.10. Note that cations, being small often carry a higher charge density than anions. This often results in cations becoming highly solvated, whilst anions are thermodynamically stable in solution without attracting many solvent molecules.

![Diagram of the electrochemical double layer](image.png)

*Figure 3.10. A general representation of the electrochemical double layer, showing solvent molecules, solvated ions and non-solvated ions [71].*

Kötz *et al.* state the thickness of double layer as 0.1–0.5 nm for concentrated electrolyte solutions [73]. Extremely concentrated electrolyte solutions may compress the double layer further, but this is dependent upon the size of the ions. The electric field in the double layer can be very high; around \( 10^6 \text{ V/cm} \).
3.3.3 Uses of Electrochemical Capacitors

Kötz et al. list a number of uses of electrochemical capacitors, including many back-up applications in clocks and electrical device programmed functions [73]. Two important uses are for boosting batteries and fuel cells in hybrid electric vehicles and for recovering braking energy so that it can used again later for acceleration. A number of companies were reported to be manufacturing electrochemical capacitor devices at this time, including Maxwell and Panasonic. A further important use of electrochemical capacitors is for memory back-up in laptops. They can also be used to provide regenerative energy on sites where a great deal of mechanical energy is wasted, for example on gantry cranes. The potential use of electrochemical capacitors to store power from the grid during off-peak times has also recently been discussed [6]. The topic of electrochemical capacitors, and in particular the carbon materials used as electrodes, has been an active area of research for some time, and continues to be of great interest today [2] [74] [75].

3.3.4 Electrochemical Capacitor Materials and Design

Some electrodes may incorporate metal oxides such as ruthenium. These materials are expensive. Other electrodes may incorporate polymers, which may suffer from swelling and shrinking behaviour, and so are unstable in practical devices. The most popularly used material for electrochemical capacitors is carbon. This material is inexpensive, stable over an acceptable range of potentials and temperatures, and is readily available in a variety of different types.

In order to maximise the energy density of electrochemical capacitors it is necessary to maximise their electrode internal surface area. Carbon materials often have naturally high surface areas, which can be further enhanced by activation techniques. Some carbon powders are ideal electrode materials as they naturally have a large surface area, and therefore provide a large double layer capacitance. Other carbon powders, such as graphite powder, have a much lower surface area and are comparatively ineffective. Amorphous carbons such as carbon blacks have a high specific area but can be difficult to handle due to their low bulk density.
In early work carried out by Koresh et al. it was suggested that optimisation of the electrode design merely required increasing the ratio of internal surface area to geometrical surface area [76]. This can readily be achieved by making thicker electrodes, although this may also increase the resistivity of the pores. These researchers used two different types of carbon fibre electrodes to investigate pore structure, ion transport through a pore, and the double layer capacitance that could be measured. They found that ‘ultramicroporous’ carbon fibre electrodes charged more slowly than graphitised carbon fibre electrodes, and they also found that resistivity in the pores was several orders of magnitude higher than in the bulk solution. These researchers reported that surface oxides play a greater role in determining capacitance in ultramicroporous electrodes, as the surface dipoles had a stronger effect on adsorption and ion mobility in these pores. Depletion of hydration spheres was needed before ions could penetrate these very small pores (< 5.6 Å diameter), and it was noted that charging rate was slower when using lithium salt solutions compared to sodium salt solutions. Evidently, the lithium ions retained their hydration shells more strongly.

In an extensive review by Sarangapani et al. a large number of materials for use in electrochemical capacitors were reported [77]. Porous RuO₂ matrices for electrochemical capacitors were said to give superior performance only when very thin films were used. A number of technologies were reported using carbon electrodes in sulphuric acid solution, and thirty-four US patents were listed, many of which advocated the use of carbon materials. These authors believed there was a lack of chemical information regarding electrochemical capacitors, and suggested future work should focus on the use of electrolyte solutions that were stable over large operating potentials, thus allowing maximum energy storage. They also suggested designing capacitor systems with an inner Helmholtz plane of high dielectric constant and small value of ‘d’. Presumably this was suggested to increase capacitance, according to:

\[ C = \frac{\varepsilon A}{d}, \]

where \( C \) = capacitance (F), \( \varepsilon \) = dielectric constant, \( A \) = electrode area (m²) and \( d \) = distance between layers (m).
Morimoto et al. advocated the use of a high surface area activated carbon electrode for high performance electrochemical capacitors [78]. They also suggested the activated carbon electrode should have suitable surface chemistry and pore geometry. Three different types of activated carbon were used; one derived from coconut shells, one from petroleum coke, and one from phenol resin. It was reported that specific capacitances correlated with pore volume and B.E.T surface area. The highest values of surface area and pore volume were measured in activated carbons derived from petroleum coke. Cells with electrodes made from coconut-derived or phenol-derived activated carbons were found to be more stable in tests of capacitance change over time. The differences in capacitance were attributed to differences in percentage of oxygen functionalities on the carbon surface; more oxygen functionalities gave larger changes in capacitance.

Activated carbon electrodes were also used in work by Zheng et al., in which thin film electrodes were tested electrochemically in a solution of tetraethylammonium tetrafluoroborate in propylene carbonate [79]. Capacitance values for a single electrode were measured and capacitor energies calculated. These authors found that performance depended strongly upon electrolyte concentration. At higher concentrations (0.2–0.6 M) energies of ~ 70 J were reported. At lower concentrations (0.05–0.16 M) energies varying from 16–67 J were reported. The decrease in stored energy was attributed to lower operating voltages recorded when using lower electrolyte concentrations. High rates of energy decay when using high discharge currents were also noted for low concentration solutions. This was explained by the fact that electrochemical capacitor performance relies on the ability to remove ions from the bulk solution to form the electrical double layer. At low electrolyte concentrations this is clearly limited.

An alternative material was used by Toyoda et al., who exfoliated carbon fibre. This was obtained by rapidly heating pitch-based fibres to 2800°C [80]. The resulting B.E.T surface areas seemed to be dependent upon the method of fibre preparation and activation. Table 3.04 summarises the results from this paper:
Toyoda et al. claimed that the capacitance of exfoliated fibres was strongly dependent upon B.E.T surface area; however the results above do not support this statement. Carbon fibres have also been investigated by Xu et al., who activated polyacrylonitrile fibres and mixed them with acetylene black and a binder to form electrodes [81]. The aim of this work was to determine the role of mesopores in carbon electrodes. If the measured capacitances are plotted against increasing mesoporosity, it can be seen that there is no correlation after approximately 15% for both aqueous and propylene carbonate (PC) solutions. Only the ionic liquid showed a significant effect, as seen in Figure 3.11.

Salitra et al. also used activated carbon fibres in their work and showed that capacitance was dependent on ion adsorption interactions in pores, which indicates that pore size is important [82]. Heavily solvated ions (having a large effective ion size) could not enter all the pores, and so could not contribute to double layer capacitance measured. They

<table>
<thead>
<tr>
<th>Method of Fibre Preparation/Activation</th>
<th>B. E. T Surface Area (m²/g)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared in nitric acid</td>
<td>150</td>
<td>60</td>
</tr>
<tr>
<td>Prepared in sulphuric acid</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>Activated in air at 600°C</td>
<td>420</td>
<td>160</td>
</tr>
</tbody>
</table>

*Table 3.04. Summary of some results from work by Toyoda et al.*[80].

*Figure 3.11. Dependence of measured double layer capacitance upon percentage mesoporosity in carbon electrodes.*
found smaller capacitances were measured using lithium electrolyte solutions compared to potassium electrolyte solutions, as lithium ions tend to become more highly solvated than potassium ions.

An alternative material for electrochemical capacitor electrodes was made by Tabata et al., who synthesised poly(furfuryl alcohol) around a silica template [83]. This composite was carbonised before the silica template was etched away, leaving a mesoporous “inverse opal” carbon material. B.E.T surface area decreased as the diameter of the silica template spheres increased, and the highest capacitance (∼ 100 F/g) was obtained when using silica opals of 50 nm diameter.

Beck et al. reported the activation of industrially available carbon black materials. This was carried out by ‘etching’ the carbon blacks at 750 – 1100°C, via the Boudouard reaction [84]:

\[
C + CO_2 \rightleftharpoons 2 CO
\]

These authors found that higher B.E.T values were measured after activation, and single electrode capacitances of over 200 F/g were reported for carbon blacks such as Ensaco 114MM and Black Pearls 2000.

Activated carbons are the most common materials to use for electrodes in electrochemical capacitors, as they are relatively inexpensive raw materials and can have large surface areas. It should be noted the activation process itself may increase the cost of these materials substantially, as it often involves heating at high temperatures for extensive periods of time. Some activation methods also include a chemical activation step. Many research groups continue to report very high values of capacitance using activated carbon; some in the region of 100 – 200 F g⁻¹, and this is generally attributed to their large surface areas [85] [86] [87].

Claims of extremely high surface area should be treated with caution. Byrne et al. calculated the maximum theoretical surface area obtainable (for an extended layer of graphite) as approximately 1800 m²/g [19]. Higher values should be treated with scepticism.
3.3.5 Electrochemical Capacitor Electrodes Made From Carbon Black

To date, activated carbons have been the material of choice for electrochemical capacitor electrodes. The use of carbon blacks is a comparatively neglected field, and only a small number of research groups have experimented with them.

Wu et al. made carbon black composite electrodes for a study of conductivity percolation in electrochemical capacitor electrodes [88]. The electrodes were made from a conducting carbon black (Vulcan XC72) mixed with a high surface area activated carbon. The authors reported that a volume fraction of 25% carbon black was close to the conductivity percolation threshold. It was also suggested that higher ratios of carbon black to activated carbon diminished the overall surface area, and thus lowered the capacitance.

Generally, small specific capacitances have been measured when using carbon black electrodes. For example, Leitner et al. reported a specific capacitance of 23 F/g [89]. Furtado et al. reported a specific capacitance of 30 F/g, and commented that the cell was stable over hundreds of cycles [90].

More recently, Panić et al. also used Black Pearls 2000 in work that aimed to investigate accessibility of carbon black internal surface area [91]. These authors reported a specific capacitance of 43 F/g from accessing the outer surface of carbon agglomerates in the electrode. They claimed that much higher capacitances could be measured if the internal surface area of carbon agglomerates could be accessed.
3.4 Gelled Electrolyte Solutions

The gelling of electrolyte solutions is of interest for practical reasons as it inhibits solvent flow after accidental cell piercing and/or damage.

A gel can be defined as a colloidal system, in which solid particles are distributed throughout a liquid. There may be varying degrees of aggregation of the solid particles but ideally crystallisation does not occur. A gel may also be described as a "semi-solid" because it is solid-like in its rheological performance. The term 'sol-gel conversion' is sometimes used to describe the conversion of a solution to a gel. The process of 'gelation' may involve the formation of covalent bonds, or other types of interaction that result in the aggregation of molecules.

Gels can be made by use of polymer gelling agents or small organic molecules. The former can involve covalent interaction of polymer chains (cross-linking), which then swell in electrolyte solution. Such solutions are often thermally irreversible [92]. Small organic molecules usually cause gelation through non-covalent interactions, using self-assembly as the gelling mechanism. These solutions are often thermally reversible. Gels are usually formed by the addition of 0.1–10% gelling agent to hot solvent. Upon dissolving, the solution can then be cooled to a temperature below that of the gelation temperature ($T_{gel}$).

Research carried out to investigate the phenomenon of gelation includes the work of Wang et al. [93] [94]. These authors describe gels as large volumes of solvent trapped in a three-dimensional network. The mechanism of organogel formation was stated as "ambiguous", however their work indicated that strong interactions form between gelators and solvents. Wang et al. used atomic force microscopy to monitor sol-gel conversion during cooling. The images they recorded are shown in Figure 3.12. ‘De-wetting’ of the solution from the surface was observed as the gel formed.
Figure 3.12. Sol-gel phase transition. Time transient AFM images (in amplitude mode). The heated sol-gel was cooled to room temperature. Phases are shown after (a) 0 min, (b) 10 min, (c) 15 min, (d) 18 min, (e) 21 min, (f) 31 min. The scale is $12 \times 12 \, \mu m$ [93].

As the temperature of the heated mixture gradually falls, fibres ‘crystallise out’, and trap solvent, and thus the gel is formed. The gelation process therefore involves a balance between crystallisation and solubilisation; a portion of the solution crystallises out to form fibre-type structures, and a portion of the solution remains as a liquid, trapped by these fibres. The gelator molecule must be chosen carefully in order that this balance is satisfied. If too much crystallisation occurs the gel will be brittle and if too much solubilisation is allowed the gel will flow.

In order to understand gels in more depth, the structure has been broken down into primary, secondary and tertiary structures, much like the break-down of protein structures [92].
The primary structure is concerned with forces that promote molecular aggregation. The balance between aggregated and dissolved molecules must be maintained in order that a gel consistency is achieved. This appears to be the foundation of the gelation process.

The secondary structure is concerned with the morphology of the aggregates. Fuhrhop et al. depicted how the aggregation of amphiphilic organic molecules leads to the formation of multiple morphologies, as shown in Figure 3.13 [95]. An amphiphilic molecule is one that has both hydrophilic and hydrophobic properties. Vesicles, micelles and bilayer sheets are all examples of aggregation in different morphologies. Evidence for formation of multiple morphologies was also reported by Meng et al.[96].

Figure 3.13. Repulsive head-group interactions create spherical micelles (A) and vesicles (B). Crystallisation of micelle head-groups creates new structures; possibly the first to form are disk micelles (C). Disk micelle aggregation results in bilayer rods (D). Micelles and vesicles can also form bilayer sheets (E). Bending of these sheets can form helical ribbons (F), and mono- or multi-layer tubules (G, H) [95].

The tertiary structure is concerned with the interactions between individual aggregates. This part of the structure determines whether or not aggregates such as fibres will precipitate completely out of the solution, or have the ability to trap large amounts of solution. This ultimately determines whether or not a gel is formed.
Hydrogels are gels formed from aqueous solution. These typically contain amphiphilic molecules that have a hydrophobic part which promotes aggregation, and a hydrophilic part which promotes dissolution. Small molecule gelators can be characterised by their type and the placement of their polar groups. Conventional amphiphiles take on the following structure:

![Figure 3.14. A representation of a conventional amphiphile that can be used as a gelling agent.](image)

The polar head can be a carboxylic acid, sugar or amine. Kunitake et al. found that the final structure of the aggregate could be changed by altering the length of the flexible linker, and/or the flexible tail [97]. Other amphiphiles include bolaamphiphiles, which have two hydrophilic head groups, gemini surfactants, which are slightly more complex, and sugar-based systems. Also important are the use of aromatic groups to promote π–π stacking and the use of side chains to promote aggregation, which then promote fibre formation and hydrogelation [92]. Short chains with hydrophobic anionic cross-linkers create fibres that result in gel formation, but longer chains prevent gel formation due to electrostatic repulsions. Fluorination of alkanes leads to molecules with a low critical micelle constant, and hence a tendency to self-assemble in water. It has been demonstrated by Liu et al. that branched or entangled fibres form gels, and physically flexible fibres are better at trapping solvents [98].

The alternative to using organic molecule gelators is to use polymers. Polymer electrolyte solutions have been investigated by Avery et al., who experimented with a vinylidene difluoride/hexafluoropropene copolymer called Kynar 2800 [99]. This polymer was used to gel a solution of 1 M LiClO₄ in an ethylene carbonate and propylene carbonate mix (1:1). Organic carbonates were reported by these authors to
show the best performance for electrolyte solutions. The resulting mixture was blended
with THF to form a viscous solution, which was then cast to form a film. The THF
evaporated, and the remaining film was found to have a conductivity of $10^{-3}$ S/cm at
20°C. The authors discovered that the gelled lithium carbonate mix was electronically
insulating, but did conduct Li$^+$, which was ideal. Anions such as CF$_3$SO$_3^-$ and PF$_6^-$ were
found to be stable and non-coordinating.

Polymer electrolyte solutions prepared with ethylene carbonate have been discussed by
other researchers, who added this solvent to improve ionic conductivity in the polymer
gel [100]. A loss in mechanical strength was noted in this case, and so there was a
requirement for curing the gel. An alternative method is to soak a polymer membrane in
an electrolyte solution. A two-phase system results, with an amorphous region able to
trap liquid electrolyte solution, and a crystalline region providing mechanical strength.
Curing in this instance is not needed [101].

Prosiniet al. investigated the possibility of making a gelled polymer electrolyte (GPE)
that also had properties of a ‘true solid polymer electrolyte’ (TSPE) [102]. The aim was
to combine the mechanical integrity of a TSPE with the high conductivity of a GPE.
These authors first fabricated a TSPE, using polyethylene oxide (PEO) and LiCF$_3$SO$_3$
as the electrolyte. The TSPE was then dipped in a solution of LiCF$_3$SO$_3$ in propylene
carbonate to allow the electrolyte solution to enter the TSPE, ultimately forming a
structure resembling a GPE. The conductivity reached $10^{-3}$ S/cm if the TSPE was
soaked in a 0.1 M solution of LiCF$_3$SO$_3$. However, dipping of TSPE’s in solutions of
higher concentration did not yield higher conductivity values. This was thought to be
due to ion-pair formation reducing the number of free ions available to carry charge.
The GPE’s were then used in lithium batteries, and were reported to have a cycling
efficiency of 83.5%.

In addition to lithium batteries, polymer gels have also been used in electrochemical
capacitors. One example of work in this is area is a paper by Osaka et al., in which a
number of polymers were suggested for use in gelled systems, due to their high
conductivites and good structural properties [103]. Some of the suggested polymers
were PEO, PMMA (poly(methylmethacrylate)) and PVDF-HFP
(poly(vinylidenefluoride-co-hexafluoro-propylene)). PVDF-HFP was chosen for the
work carried out by these researchers. The polymer was mixed with ethylene carbonate and propylene carbonate solvents, and tetraethylammonium tetrafluoroborate electrolyte at different concentrations. Both ion conductivity and capacitance increased with concentration, up to 1.0 M, after which a plateau region was observed and no further increases were noted. Above 1.0 M a decline in mechanical strength was also observed. Osaka et al. made two interesting observations; firstly that polymer gelled cells outperformed non-gelled cells, and secondly that increases in specific capacitance with increased current density were higher for polymer gelled cells than non-gelled cells. Both observations were attributed to the close contact between activated carbon particles and polymer gelled electrolyte that was achieved through gelation.

Despite the large number of United States patents already published concerning polymer gels, this topic continues to be of great interest today [104] [105]. A good example of recent industry-related work is a paper published by Sony employees Yamamoto et al [105]. These researchers also used PVDF-HFP with ethylene carbonate and propylene carbonate solvents to form a gel. LiPF₆ was the supporting electrolyte chosen. All chemicals were mixed at 90°C and the hot ‘sol’ coated onto electrodes, with an aim to penetrate the porous matrix of the electrodes. On cooling to room temperature the gel was formed. A picture of the gel is shown in Figure 3.15.

![Figure 3.15. A picture of polymer gelled electrolyte solution](image)

Yamamoto et al. reported that the liquid was successfully trapped within the polymer matrix, and the resulting gel was both structurally stable and highly conducting. During
electrochemical testing, these researchers reported that the polymer-gelled cells helped to overcome a problem with capacity fade. The polymer-gelled cells were also tested for safety, and were found to be successful in this area too.
4 Experimental

The following section describes the experimental procedures and techniques used throughout the thesis, before describing specific experiments in more detail. All chemicals were used as-received, unless otherwise stated. Weighing of materials was carried out using either an Oertling NA 114 sealed balance or an Avery Berkel top-loading balance. Solutions were usually made in 100 cm$^3$ volumetric flasks.

4.1 Electrode Fabrication

4.1.1 Calendered Electrodes

Carbon electrodes used throughout the present study can be described broadly as thick film (typically 3-5 mm) and ultra-thin film electrodes (typically $\ll 1$ mm). The thick film type was manufactured by two different methods; extrusion or calendering. The thin film type was produced by screen-printing. This section first discusses thick film electrode fabrication.

Thick film electrodes were made according to the method used by Schlumberger WCP Ltd for producing their carbon black electrodes for Li-SOCl$_2$ cells. The quantities of materials and the method used to fabricate these electrodes were developed some years ago in industry, and the information remains a trade secret. The industrial recipe was adapted by a previous researcher for use on a laboratory scale [45]. This recipe, as described in Appendix I, incorporated a 1:4 ratio of Ketjenblack 300J (Akzo Nobel) to Shawinigan Acetylene Black 50% compressed (Chevron Phillips). The carbon black materials were stirred briefly before the appropriate volume of solvent was added to wet the carbon materials thus forming a 'slurry'. The solvent was a 2:1 ratio of isopropyl alcohol (Fisher) and triply distilled water, obtained from a Millipore Milli-Q. Isopropyl alcohol has a very low surface tension (20.93 mN/m at 25°C), and hence is highly effective at wetting the carbon surface, which can be hydrophobic. After further mixing to ensure all the carbon had been wetted, 60 wt. % dispersion of polytetrafluoroethylene (PTFE) in water (Aldrich) was added to the mixture, to act as a binder. Upon stirring
the binder into the mixture, a shear thickening phenomenon was noted, and the resulting mixture developed a dough-like consistency. This ‘dough’ was kneaded and then either calendered between two metal rollers onto a PTFE sheet or extruded using an extrusion machine. After being allowed to air-dry overnight, the calendered/extruded material was placed into an oven and dried at 70°C for approximately four hours. To destroy the surfactant within the binder suspension, the temperature of the oven was increased to over 200°C (the industrial method states 207°C). 1.2 cm × 1.2 cm sections of the finished material were cut using a blade and a metal template. A working electrode was made by placing this specimen inside a stainless steel ‘envelope’ or gluing it to a screen-printed electrode using conductive carbon ink. Both the stainless steel and the screen-printed electrode provided a means of connecting the carbon specimen to the potentiostat.

4.1.2 Screen-Printed Electrodes

In previous work carried out at Loughborough University a screen-printing method of electrode production was optimised [106]. Specially designed mesh screens with a negative image were used with a Dek 65 manual screen-printer. Pictures of the screen-printer are shown in Figures 4.01 – 4.03.
Figure 4.01. A Dek 65 manual screen-printer with doctor blade attached, substrate holder underneath screen.
Figure 4.02. A Dek 65 screen-printer (top view) with no doctor blade or screen fitted, allowing observation of substrate holder beneath handle.
The substrate used for screen-printed electrodes was a commercial polymer film (CG 3300, 3M). This film was taped onto the substrate holder; a metal plate that was pushed beneath the mesh screen holder [106]. A mesh screen with a negative image was fitted into the screen printer. Examples of mesh screens used are shown in Figure 4.04.

Figure 4.03. A Dek 65 screen-printer with doctor blade and mesh screen fitted.
A plastic doctor blade was secured between two metal plates and fastened onto a bar above the mesh screen. Ink was placed on top of the screen and initially manually swept across the surface using a metal doctor blade. The plastic blade remained stationary whilst the substrate holder was pulled forward with the mesh screen, thereby allowing the plastic doctor blade to force ink through the screen and onto the substrate, printing a positive image. Four electrodes were printed onto each sheet of substrate, which permitted high through-put testing of different types of modified carbons. A schematic diagram depicting the screen printing action is shown in Figure 4.05.
Printed sheets were cured in an oven at 100°C for various amounts of time. Multilayer electrodes were printed, with each subsequent layer printed on top of the former, after first drying in an oven. Initially, a layer of commercially available silver ink (EI660-136, Ercon) was printed. The purpose of this was to provide a conducting pathway from the test area of the electrode to the contact point of the electrode. Next, a layer of conductive carbon ink was printed on top. The purpose of this was simply to mask the electrochemistry of the silver once in solution. This smooth carbon ink had a low surface area, and so did not contribute significantly to the measured capacitance.

Finally, a 1 cm x 1 cm test area was printed on top of the smooth carbon layer. Test areas were usually printed from in-house inks, made with activated carbon or graphite. In-house inks were made according to the following general formulation: 15% of the solid constituents were binder, which was polyvinylidene fluoride powder (Kynar). This was first dissolved in a given solvent in an agate container. The carbon powder of interest was then added, with a small portion of additional solvent. A lid was placed on the agate container, which was then transferred to a Fritsch Pulverisette 7 planetary ball mill. Mixing speeds used were 200-400 rpm, for durations of 2-4 minutes at a time. Higher mixing speeds (up to 800 rpm) were occasionally used, but this could result in further grinding of activated carbons, thus reducing particle sizes. After mixing the inks were assessed for viscosity (on a trial-and-error basis), and more solvent was added if necessary. When the ink consistency was deemed to be suitable for printing the ink was used in the same way as previously described.

Printed layers typically required approximately 1 hour in the oven to dry. In the case of the conductive carbon layer, 3 – 4 hours was used to ensure good coverage of the substrate had occurred. Individual electrodes were then cut from the sheet. The multilayered structure of the finished working electrode is shown in Figure 4.06.
4.2 Electrochemical Cell Set-Up

Electrochemical testing throughout this thesis involved the set-up of a three-electrode cell consisting of a working electrode, reference electrode and counter electrode. The cell was connected to an Autolab potentiostat (PGSTAT20, Eco Chemie). A potentiostat is essentially an electronic circuit, capable of controlling one parameter whilst measuring another. For example one might control the voltage between the working and reference electrodes whilst recording the current that flows between the working and counter electrodes. The potentiostat was connected to a Viglen Genie computer via an Autolab USB interface. Voltage and current were controlled/measured by using Autolab GPES software.

Two different types of electrochemical cell were used; one type for aqueous solutions and one type for non-aqueous solutions. The cell used for non-aqueous solutions could be sealed more effectively to prevent moisture entering the cell. For aqueous solutions this clearly wasn’t a problem. Although the same type of cell could have been used for aqueous solutions, the one chosen was preferable due to the longer, thinner Luggin probe. The Luggin probe is a capillary drawn out from the reference electrode compartment of the cell. It effectively reduces the distance between the working and reference electrodes, and therefore helps to reduce the $IR$ drop. When large currents are
drawn from the cell, \( IR \) drop is large, which means that the voltage error is large (\( IR \) drop subtracts from the voltage applied by the potentiostat). Some potentiostats can correct for most of the \( IR \) drop, via a voltage feedback loop. Uncompensated resistance can be composed of solution resistivity, cell geometry and resistance in electrical contacts.

A schematic diagram of the cell used for aqueous solutions is shown in Figure 4.07.

![Figure 4.07. A schematic representation of an electrochemical cell.](image)

Although the cell has a Teflon lid, around which may be wrapped a length of Parafilm, the cell is not moisture-proof. The reference electrode compartment is difficult to seal when the reference electrode is placed inside. The cell used for non-aqueous solutions is shown in Figure 4.08. This particular cell has been set-up for a Li-SOCl\(_2\) experiment. Strips of lithium ribbon are held in the reference and counter electrode compartments, and the working electrode in the third compartment is made up of a carbon electrode specimen encased in stainless steel mesh. The cell is sealed by using Subaseals (Fisher), which were found to be chemically resistive during the time-scale of the experiment.
Figure 4.08. A tightly sealed three-electrode cell used for non-aqueous cell solutions.

Contact between the electrochemical cell and the potentiostat was made by attaching crocodile clips (RS) to the potentiostat leads and subsequently attaching these to the wires (Goodfellow) protruding from the cell.

4.2.1 Reference Electrodes

For all experiments conducted in aqueous solutions the mercury/mercurous chloride system was employed as a reference electrode (more properly referred to as a reference ‘half-cell’). This system is known as the Saturated Calomel Electrode (SCE), and consists of mercury coated with a mixture of mercury and solid mercurous chloride, $\text{Hg}_2\text{Cl}_2$, immersed in a saturated solution of KCl. The SCE cannot be used in non-aqueous solutions without introducing a large liquid-junction potential. For this reason a pseudo-reference electrode was employed in organic solutions.
Pseudo-reference electrodes exhibit different potentials in different solutions, but they maintain a constant potential in a given experiment. Typically, they consist of pieces of high-surface-area metal which form a reversible couple with at least one of the ionic components of the cell solution. Throughout the present work in non-aqueous solutions lithium salts (such as LiCF$_3$SO$_3$) were used as the supporting electrolyte. For this reason, a strip of lithium metal could be used as a pseudo reference electrode. Upon immersion of the metallic lithium in a solution of LiCF$_3$SO$_3$, a redox couple was formed. In order to check the stability of the lithium reference electrode, the potential difference was measured between the lithium counter and the lithium reference electrode using a multimeter. Ideally there should not be a difference in potential at all, although minor differences, (up to a few millivolts) were deemed acceptable. This was typically the case. Measurement of potential difference in this case merely served as a 'quality-control' assessment of the lithium, to monitor the stability of the lithium reference electrode.

4.2.2 Electrochemical Techniques

Two electrochemical techniques were used for experiments reported in this thesis. They are discussed briefly in this section.

Chronopotentiometry is the measurement of potential difference as a function of time under constant current. This technique was used under galvanostatic control, which meant that electrical energy expended was measured as chemical reactions took place in the cell. A value for the constant load current was selected, and voltage measured as the experiment proceeded. When the chemical reaction could no longer sustain a certain voltage, a drop in the voltage value was observed. At this stage the experiment was normally terminated, as very low voltages (< 1 V) were not of interest.

Voltammetry techniques measure current within a specified voltage range. Cyclic voltammetry was the particular technique used in this thesis, which involved scanning the specified voltage window in both forward and backward directions. Thus, both oxidative and reductive scans were recorded in one experiment, and the process could be repeated many times by continued cycling. The key parameter in this technique was
scan rate, i.e., how much of the voltage window was scanned in a given time. Cyclic voltammetry is useful for observing redox active species on an electrode (faradaic processes) and noting changes over continued cycling. It was also used in the present study for measuring capacitances of carbon electrodes, as current and scan rate are related by:

\[ I = C \left( \frac{dE}{dt} \right), \]

where \( I \) = current (A), \( C \) = capacitance (F) and \( \frac{dE}{dt} \) = scan rate (V/s).

4.3 Electrode Dead Volume

4.3.1 Visualisation Using Scanning Electron Microscopy (SEM)

SEM is an extremely useful technique for obtaining high resolution, high magnification images. SEM imaging was used in work for this thesis to show the different morphologies of activated carbon and carbon black. It was also used to show before and after images for electrodes used in lithium-sulphur cells.

All SEM images shown in this thesis were taken using a Carl Zeiss 1530 field emission SEM machine, using a secondary electron detector. There are two types of secondary electron detector; ‘in lens’ and ‘SE2’. Both detect the secondary electrons that leave the sample, however the ‘in lens’ detector is situated much closer to the sample than the ‘SE2’ detector, and thus can provide a higher resolution image.

4.3.2 Estimation Using the IPA Test for Dead Volume

Porosity in carbons may take the form of true pores (in activated carbon) or ‘dead volume’ (in carbon blacks). In the latter case the dead volume arises from inter- and intra- aggregate voids. SEM images in Figures 4.09 and 4.10 illustrate this, and show
how intra-aggregate regions of dead volume can have diameters wider than 1 μm. In
activated carbons, pores with diameters larger than 50 nm are classed as macropores.

Figure 4.09. An SEM image of a typical carbon electrode fabricated in the present
study. The inter-aggregate cavities are in excess of 100 μm wide.

Figure 4.10. An SEM image of a typical carbon electrode fabricated in the present
study. The intra-aggregate cavities are in excess of 1 μm wide in some areas.

A standard test (ASTM D 2414-01) is often used to provide ‘dibutyl phthalate (DBP)
absorption numbers’ for carbon materials, indicating their dead volume. This test
measures the volume of dibutyl phthalate or paraffin oil absorbed by a sample of carbon
material, up until the point the carbon/oil mix reaches a pre-determined viscosity. A test
with a similar aim was developed in the present study to measure the dead volume of carbon black electrodes. The test involved submerging a pre-weighed specimen of carbon electrode in a bath of isopropyl alcohol (IPA). IPA was used due to its very low surface tension which enables it to wet the surface of the carbon. The aim was to displace all the air in the dead volume with IPA, thus providing an accurate measure of electrode dead volume. Once air bubbles ceased to rise from the specimen it was removed from the IPA bath, briefly blotted with paper towel and re-weighed. The difference in weight was attributed to the amount of IPA absorbed by the specimen. During the present study, this test has been extensively used. This test is referred to as the IPA Test for Dead Volume. The data analysis has also been developed to provide useful information such as estimation of total electrode volume and the percentage dead volume in the electrode. The estimations obtained for electrode dead volume were compared to literature values of DBP dead volume for a number of carbons, and found to show a strong correlation. In later work, the total electrode volumes estimated using data from the IPA Test for Dead Volume were compared with total electrode volumes calculated using a micrometer to measure electrode thickness, and found to be highly accurate.

Table 4.01 shows a comparison of the DBP and IPA molecules and their surface tensions.

<table>
<thead>
<tr>
<th></th>
<th>DBP</th>
<th>IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>COO(CH₂)₃CH₃</td>
<td>COO(CH₂)₃CH₃</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>33.4 mN m⁻¹</td>
<td>21.7 mN m⁻¹</td>
</tr>
</tbody>
</table>

Table 4.01. A comparison of DBP and IPA molecules and surface tensions.

Not only does IPA have a slightly lower surface tension than DBP, the molecule is also smaller. Although access to dead volume would probably not be size-restricted on a molecular scale, in certain circumstances there may be some benefit to using a less sterically hindered molecule. If IPA molecules could enter more regions of dead volume than DBP molecules, they could provide more accurate measurements of such volumes. The IPA test was initiated to assess dead volumes of composite electrodes, not
just the carbon powder alone. Whilst it is realised that a thorough comparison of the two methods would require the standard test to be carried out with IPA in place of DBP, this is beyond the scope of this thesis. Nevertheless, the IPA test was carried out on a number of samples, and the resulting data compared with DBP data. In terms of health and safety, IPA would certainly be favourable to use in place of DBP; its Permissible Exposure Limit (PEL) is 980 mg/m³, compared to DBPs PEL of 5 mg/m³ (time-weighted averages, over a period of eight hours).

4.4 Differential Scanning Calorimeter (DSC)

Part of the work reported in this thesis aimed to create a novel electrolyte/solvent combination for lithium sulphur batteries. A mix of two solvents was chosen, and it was then of interest to discover the eutectic point of this mix. A useful technique for ascertaining freezing/melting points of mixtures is differential scanning calorimetry.

Calorimetry refers to the measurement of heat. A calorimeter is a device that measures changes in temperature or heat capacity in a sample when a known amount of heat is contributed or taken away from a sample. A definition of DSC is provided by Hühne et. al.: “Differential Scanning Calorimetry (DSC) means the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program” [107]. DSC is different to Differential Thermometry (DT) which measures the change in the difference of the temperature between the sample and the reference material.

The DSC machine used for work in the current study was a power-compensation calorimeter (TA Instruments 2920). This instrument maintains a certain level of power in the system, compensating for heat supplied to the surroundings during bond formation (freezing) or heat removed from the surroundings during bond breaking (melting). The output is a plot of heat capacity (W/g) vs. temperature (°C). Figure 4.11 shows a typical melting point peak in a DSC plot.
The interpolated baseline represents heat flow rates at steady state conditions in the DSC, i.e., when there is an absence of reactions or transitions in the sample. Processes such as melting and crystallisation lead to the production of peaks in the curve, which disturbs the steady state. The peak shown in the graph represents the melting of a solid, which requires heat to be removed from the surroundings and added to the system (therefore more power is supplied). This is an endothermic peak.

4.5 Experimental Details

4.5.1 Mitsubishi Carbons

A selection of highly characterised Mitsubishi carbons was chosen to use in the present study. The aim of experimenting with these carbon materials was to discover useful physical property-electrochemical performance relationships. For example, it is known that the reduction of SOCl\textsubscript{2} in the Li-SOCl\textsubscript{2} battery takes place on the porous carbon electrode surface. However, some researchers state that the battery performance is dependant on electrode porosity, not surface area. Other researchers have stated both factors are important in determining battery capacity. By experimenting with Mitsubishi
carbons with different porosities and surface areas in the present study, it was hoped that further support for one of these theories would be elucidated. Electrodes were fabricated from the carbon powders by the method previously described. Each was then used as a working electrode in a Li-SOCl₂ cell, although it was never intended that these materials be used as real battery electrodes.

Mitsubishi carbons were also used to prove the validity of the IPA test.

4.5.2 Lithium Thionyl Chloride Experiments

Lithium thionyl chloride batteries are produced by Schlumberger WCP Ltd for use in its oil-drilling business. Observation of the manufacturing plant elucidated a problematic area: carbon electrodes would often crack or crumble during the drying process, and thus had to be discarded. One of the main aims of this thesis was to solve this problem, and reduce the number of discarded electrodes. It was thought that the addition of a material to the existing carbon electrode mix would be a preferable approach, as this would be a relatively easy change for a manufacturing plant to accommodate.

Carbon fibre is known worldwide for its excellent properties of strength and flexibility. This has brought about its use in applications within the automotive and aeronautical industries, and also in the building industry where it is used to reinforce concrete. The addition of carbon fibre to carbon electrodes therefore seemed an ideal approach to imparting strength and flexibility, whilst avoiding the introduction of new chemicals to the carbon mix. The important issue to consider was whether or not the addition of carbon fibres would have a negative impact on cell capacity. This might arise due to the change in electrode dead volume or morphology, although adverse effects were not expected. Nevertheless, it was imperative to assess the impact on cell capacity when using fibrous carbon electrodes.

The carbon fibres used in the present study were known as Kreca Chop C-206S (H T Gaddum). Kreca Chop is the brand name of these fibres, which are commonly used in reinforced concrete and asbestos-free gaskets. The fibres were made from a graphite thread and had a tensile intensity of 800 MPa (this is similar in magnitude to some
stainless steel fibres). The volume resistivity of these fibres was 50 $\mu\Omega$-m. The fibres were 14.5 $\mu$m in diameter and 6 mm in length.

Electrode fabrication was carried out as previously described in this chapter, with the addition of carbon fibre taking place before the solvent was added. Four different electrodes were initially made, with different amounts of carbon fibre added. The final percentages of carbon fibre in the dried, finished product were: 4%, 8%, 11% and 14%. Capacity performance was then analysed. Although the fibrous carbon electrodes were undoubtedly stronger than non-fibrous carbon electrodes, more quantitative data was sought. However, it appeared that Schlumberger WCP Ltd did not employ any standard test to measure electrode strength, and so could offer no solutions. Enquiries were also made within Loughborough University’s Materials Characterisation Centre, and efforts were made to test samples using a standard tensile strength instrument. However, the fibrous electrodes were deemed unsuitable by test personnel. Indeed, the samples did not fare well, as they tore around the teeth of the sample holder before any great tension could be applied. A less complicated ‘tear test’ was then attempted, which also failed to yield any useful results. From a qualitative point of view, handling of fibrous electrodes was notably easier than non-fibrous electrodes, and cracking was not observed.

A further problem on the manufacturing plant was that the quantities of isopropyl alcohol (IPA) used were close to UK/EU safety limits. It was therefore necessary that the volume be decreased. Initially, a ratio of 2:1 IPA to water was used as the solvent in the electrode fabrication process. There appeared to be no particular reason for this ratio, but it was certain that IPA was required as it had a low surface tension, and therefore allowed wetting of the carbon surface. The approach to solving this problem also had to be mindful towards allowing a relatively easy-to-implement change for Schlumberger WCP Ltd. For this investigation, 10 electrode mixes were made in the laboratory, each using different ratios of solvents. The first batch used a 9:1 ratio of IPA:water, and the following batches decreased in IPA content, with the ratio changing to 8:2, 7:3... etc. Each carbon electrode was tested in the same way as previously discussed, and the capacity performance analysed.

Schlumberger WCP Ltd currently uses Ketjenblack EC-300J (Akzo Nobel) in their electrode manufacturing process (this will subsequently be referred to as 300J). During
research for this thesis it was discovered that Akzo Nobel produces another type of Ketjenblack, known as EC-600JD (this will subsequently be referred to as 600JD). Some properties of these carbon materials are compared in Table 4.02.

<table>
<thead>
<tr>
<th></th>
<th>300J</th>
<th>600JD</th>
</tr>
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<tbody>
<tr>
<td>B.E.T Surface Area (m²/g)</td>
<td>800</td>
<td>1250</td>
</tr>
<tr>
<td>DBP Dead Volume (cm³/100 g)</td>
<td>250</td>
<td>415</td>
</tr>
<tr>
<td>Volume Resistivity, 10% loading (Ω.cm)</td>
<td>158</td>
<td>3</td>
</tr>
<tr>
<td>Volume Resistivity, 15% loading (Ω.cm)</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.02. Comparison of some Ketjenblack properties [108].

The data indicate that Ketjenblack EC-600JD could enhance the electrode performance, as it has a higher surface area and dead volume than Ketjenblack EC-300J. It also has a lower resistivity than Ketjenblack EC-300J. It was therefore of interest to fabricate electrodes where 300J was replaced with 600JD. The cell capacity values were measured and analysed.

Schlumberger WCP Ltd currently uses an extrusion machine in their electrode manufacturing process. An in-house template is placed in the machine and a foot pedal is used to activate the machine to extrude carbon mix through the template. The resulting electrode strips are laid on metal trays and later placed in an oven at 70°C to dry. The temperature is then ramped to 207°C to ensure the surfactant within the binder suspension has been destroyed. The speed of extrusion, the pressure placed on the foot pedal, the handling of the long strips of wet electrode and the quality of the template are all variables in this process. There does not appear to be a particular reason for using this extrusion machine. Some of the work reported in the present study instead used a calendering technique; rolling the electrode mix between two metal rollers to produce a sheet. This could potentially be a preferred method for electrode fabrication, as it does not involve as many variables as the extrusion technique. Also, large sheets of electrode material may be easier to manipulate than extruded strips, and any future changes to the electrode shape or size could be more easily accommodated. However, tests were needed to see whether the change in electrode production method had any effect on its electrochemical performance in a battery. Different production methods might alter the electrode structure due to application of different compressions. Although it was
predicted that this wouldn’t be the case, tests were carried out to check if this was true. Electrodes produced by the extruded method were labelled ‘L3’ and those produced by calendered method were labelled as ‘L2’.

Unfortunately, whether electrodes were extruded or calendered, variations in thickness along the electrode were noted. Presumably these changes took place as solvent evaporated from the electrodes (electrodes were calendered or extruded at the same thickness). A number of measurements were made in order to estimate the size of this non-uniformity, and to then assess whether this was a significant problem.

In all experiments, electrode specimens of 1.2 x 1.2 cm were cut and placed in a stainless steel mesh envelope, as shown in Figure 4.12.

![Figure 4.12. A working electrode; a carbon specimen in a stainless steel mesh envelope.](image)

This working electrode was then placed in a three compartment glass cell with lithium ribbon counter and reference electrodes. The cell was assembled in a glove box filled with dry argon and sealed with Subaseals (Fisher). The cell was attached to a Schlenk line which first allowed a vacuum pump to be used to evacuate the cell, before the tap was switched to an argon supply, allowing the cell to be filled with argon (BOC). After
this process was complete the cell was injected with 1.4 M LiAlCl$_4$ in SOCl$_2$ (as-
received, Schlumberger WCP Ltd) using a double-tipped needle and positive pressure
from an argon flow. Approximately 60-70 ml electrolyte solution was used for each
experiment (the solution had only to satisfy the requirement to be in excess of the
amount that could be reduced, hence not being the limiting factor). The cell was then
connected to an Autolab PGSTAT20 potentiostat, and the ‘chronopotentiometry,
galvanostatic’ method was selected. All cells were discharged at a current density of
20 mA cm$^{-2}$ until the voltage dropped to 1 V. The value of discharge capacity was
taken at 2 V, because the battery is of little use to industrial applications below this
potential. The reason that potential was allowed to drop as low as 1 V was because the
resulting graphs would then clearly show a typical Li-SOCl$_2$ discharge curve.

4.5.2.1 The Use of Cyclic Voltammetry in Estimating Electrode
Microstructure

Cyclic voltammetry was used to measure the capacitance of electrodes. Capacitance
values were directly proportional to observed current, since:

$$I = C \left( \frac{dE}{dt} \right) = Cv,$$

where $I$ = current (A), $C$ = capacitance (F) and $dE/dt$ = scan rate which is also known as
$v$ (V/s).

Capacitance is also proportional to accessible surface area, since:

$$C = \frac{\varepsilon A}{d},$$

where $C$ = capacitance (F), $\varepsilon$ = permittivity of the medium, $A$ = electrode surface area
($m^2$), and $d$ = distance between capacitor plates (m) (or in this case, the electrode and
solution).
This meant that comparisons in accessible surface area of different electrodes could be estimated by measuring current during cyclic voltammetry experiments. This provided an excellent method of assessing electrode ‘microstructure’ (the accessible internal surface area), and checking how consistent this was between different samples of the same electrode formulation. As such, capacitance values of different samples cut from the same sheet of a particular electrode formulation were used as an assessment of quality control.

However, the correlation between capacitance and surface area is not always perfectly linear. Complications can be introduced by surface groups on carbon, which provide pseudocapacitance. This can skew the correlation between capacitance and surface area. In order to test whether cyclic voltammetry was an appropriate estimation of surface area for carbon black electrodes, the technique was first applied to the highly-characterised Mitsubishi carbon electrodes. The aim was to assess how well electrode capacitance values correlated with carbon B.E.T surface areas. If the correlation was strong, this would support the use of cyclic voltammetry in providing information about quality control in electrode manufacture. If quality control was high, different specimens cut from the same sheet of electrode material would have the same accessible internal surface area, and therefore the same capacitance. If there are significant differences in available surface areas of specimens cut from the same sheet of electrode material, this implies poor quality control. Both repeatability and reproducibility were assessed by this technique. Repeatability is a measure of how consistent the result of a specimen will be when produced and tested under the same conditions by the same person. Reproducibility is a measure of how consistent the result of a specimen will be when produced and tested under the same conditions by two or more people. To test the latter, individual batches of ‘L2’ electrode mix were made and labelled as ‘DP’ and ‘NH’. The electrodes were produced and tested as previously described in this report.

A 1M solution of H$_2$SO$_4$ (98%, Fisher) in distilled deionised water (Millipore) was made. This solution was used for initial capacitance testing because the proton readily penetrates dead volume in carbon electrodes. Protons can effectively access more surface area than other ions via a ‘hopping mechanism’. The cell depicted in Figure 4.07 was used, with a Saturated Calomel Electrode (SCE) as the reference electrode and
a platinum gauze electrode as the counter electrode. 1.2 cm × 1.2 cm areas of Mitsubishi carbon electrode were cut using a template and blade. Stainless steel mesh could not be used in this cell set-up, as it showed electrochemical activity in \( \text{H}_2\text{SO}_4 \). Instead, the electrode specimens were glued to blank screen-printed electrodes, using conductive carbon ink. The working electrodes were dried in an oven at 100°C for approximately one hour prior to testing.

The aqueous system negated the need for vigorous sealing and vacuuming of the cell, as used in Li-SOCl₂ cells. Argon was still used to purge the cell solution however, to remove oxygen. A Teflon lid was placed on the cell and the argon flow was placed just inside this lid, such that a blanket of argon remained over the cell solution. Initial experiments using a blank screen-printed electrode indicated that the potential window was \(-100 \text{ mV to } +300 \text{ mV}\). Outside of this window 'gassing' was observed at the counter electrode, which indicated oxygen or hydrogen evolution due to solvent breakdown. A low scan rate was preferable, as high scan rates cause higher currents to be recorded. Higher currents increase the effect of \( \text{IR} \) drop, and skew the voltammograms. A scan rate of 2 mVs\(^{-1}\) was therefore used.

Finally, cyclic voltammetry was also used to measure capacitance of fibrous electrodes. Having investigated the possibility of adding carbon fibres to 'L2' and 'L3' electrodes and testing them in capacity experiments, it was also of interest to measure their capacitance.

### 4.5.3 Lithium Sulphur Experiments

The aim of this work was to produce a superior performance Li-S cell, by combining a few of the best performance materials used in the existing literature.

Sulphur is an insulator, and so must be mixed with a conducting material to form a working electrode. As shown in the literature review, many researchers favour the mixing of sulphur with carbon to form conducting composite electrodes. This was the method used in the present study. Some researchers also use rather high percentages of sulphur in their composite electrodes, and cite poor sulphur utilisation as a major
problem. In experiments carried out for this thesis, lower percentages of sulphur were used in an attempt to improve utilisation. It was noted by some previous researchers that higher sulphur utilisation was achieved when using lower percentages of sulphur [5].

In order to conduct a brief study into the optimum amount of sulphur that could be used, the screen-printing technique was first used to produce electrodes, with a view to later producing calendered electrodes using the optimum amount of sulphur. Samples of graphite ink were combined with different amounts of elemental sulphur, and mixed via ball-milling. The percentages of sulphur in the finished, dried electrodes were 8%, 14%, 27% and 64%. The screen-printed electrodes were dried in an oven at 100°C. This was close to the melting point of sulphur, which was not ideal, however at lower temperatures the test areas did not cure properly. This led to a problem with the mechanical integrity of the test area, which resulted in detachment from the substrate on contact with solvents. The implications of melting sulphur in the test area were the possibility of re-distribution, and the formation of different types of sulphur crystal forming on cooling. The presence of a few very large sulphur crystals amongst smaller crystals might affect the electrochemical reduction of sulphur.

In later work, when calendered electrodes were made containing sulphur, they were heated only to 70°C to remove excess manufacturing solvent. These electrodes were based on the same formulation as detailed in Appendix I. However, the percentages of solid PTFE and Ketjenblack were fixed, whilst some of the Shawinigan carbon was substituted for sulphur, depending on the percentage required. The PTFE suspension (Aldrich) used for this section of work was the same formulation as previously used, with the exception that the manufacturers no longer defined the particle size. SEM imaging indicated that slightly smaller particles were present in the new formulation. This was not thought to have a significant effect on electrochemical performance.

Previous researchers have experimented in a mixed solvent system of sulfolane and 1,2-dimethoxyethane (also known as monoglyme) [109]. These authors reported higher values of electroconductivity when using the mixed solvents for dissolving salt than when using the individual solvents. The mix of the solvents was a 1:3 volume ratio. It was thought that this mixture of solvents might be ideal for work carried out for this
thesis. However, monoglyme has a relatively low boiling point compared to diglyme (85°C compared to 162°C). Higher boiling point, lower melting point solvents are preferable for battery research, as this broadens the types of application they may be used in. Thus, a 1:3 volume ratio of sulfolane (99%, Aldrich) and diglyme (99%, Acros Organics) was used to create a mixed solvent. According to Clariant, both glymes are suitable as battery solvents [63].

Sulfolane has a relative static permittivity of 43 and is also a polar, aprotic solvent. However, it is solid at room temperature, and so diglyme is ideal to counteract this property. Glymes are inert, aprotic solvents, able to dissolve many organic and inorganic compounds. Aprotic organic solvents have also been shown to be compatible with solid lithium in a cell, whilst being able to dissolve large amounts of lithium discharge products, such as Li₂Sₙ [67].

It was clear that solvents used for lithium batteries should have low melting points, high boiling points, and high values of relative static permittivity. Two solvents were sourced that had both high boiling points and high values of relative static permittivity. They were sulfolane (99%, Aldrich) and ethylene carbonate (>99%, Fluka), and these solvents were mixed to form the second solvent system. Both solvents are solid at room temperature, however, when mixed they remain liquid. Initial investigations into the optimum ratios to mix the solvents yielded a 7:3 (w/w) mix of sulfolane to ethylene carbonate that remained liquid even when placed in a freezer at -7°C. This ratio of solvents was used when making a 1M LiCF₃SO₃ solution in sulfolane/ethylene carbonate. Subsequently, a number of different mixes were made and analysed more precisely using DSC in order to discover the eutectic melting point of the mixture. A similar solvent system was used for electrochemical capacitor research by Morita et al., but this incorporated different solvent ratios and different salts [110].

Finally, a third mixed solvent system was experimented with; previous researchers reported improved cell performance when using a mixed solvent system of tetraglyme and 1,3-dioxolane (1:1 v/v) [61]. For this reason it was of interest to experiment with a 1M solution of LiCF₃SO₃ (Acros Organics) in this mixed solvent system too. Tetraglyme (99%, Acros Organics) and 1,3-dioxolane (>99%, Fluka) were both kept
moisture-free by the addition of 4A molecular sieves (Acros Organics). Structures of all solvents used for this work are shown in Table 4.03.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfolane / Diglyme (also known as 2-methoxyethylether)</td>
</tr>
<tr>
<td>2</td>
<td>Sulfolane / Ethylene carbonate</td>
</tr>
<tr>
<td>3</td>
<td>Tetraglyme (also known as tetraethylene glycol dimethyl ether) / 1,3-Dioxolane</td>
</tr>
</tbody>
</table>

Table 4.03. The three solvent systems used in lithium sulphur experiments.

The electrolyte chosen to be used in all solutions for lithium-sulphur cell experiments for this thesis was LiCF₃SO₃, as this was one of a number of electrolytes used by many researchers.

A three electrode cell set-up was used with lithium ribbon (99.9%, Strem or Aldrich) for the reference electrode and the counter electrode. All electrolyte solutions were purged with dry argon (BOC) once in the cell to remove oxygen. Although carbon is relatively electrochemically inert, it can be oxidised in the cell at very high potentials. In order to find the region in which graphite alone produced a flat voltammogram, i.e., no redox peaks were observed, some blank graphite electrodes were cycled. It was expected that sulphur redox peaks recorded would overcome any peaks seen from graphite electrochemistry; nevertheless, the potential window should be limited to the reaction of interest.

Cyclic voltammograms and discharge profiles were recorded for a number of lithium-sulphur experiments.
4.5.4 Electrochemical Capacitor Experiments

Activated carbons are the most common materials to use in electrochemical capacitor electrodes. This is because they have a high surface area, imparted by their highly porous nature. However, activated carbons are often blended with a small amount of carbon black in order to improve their conductivity. The aggregation of tiny carbon particles in carbon black is sometimes referred to as a 'string of pearls', and this formation allows long-range conductivity. The SEM images shown in Figures 1.03 and 1.04 show that the morphologies of carbon black and activated carbon are quite different, and yet both can have large B.E.T surface areas. It appears that surface area in carbon black may be more accessible as there are no pore size limitations. It was therefore of interest to experiment with electrodes made solely of carbon black materials, for use in electrochemical capacitors.

Electrochemical capacitors can be relatively small devices and may often make use of ultra-thin film electrodes. For developing applications of electrochemical capacitors such as regenerative breaking in electric vehicles and energy management on crane sites, very small devices are not crucial. In fact, larger devices may be preferable as this would allow larger electrodes to be used, which would allow for higher energy storage. It was also preferable to use calendered electrodes for this study because carbon blacks are not suitable materials to use for ultra-thin film electrodes. They tend to absorb large amounts of solvent before forming an ink of the correct consistency. When the agglomerates finally break up, due to the large volume of solvent, the ink consistency rapidly becomes too fluid.

A number of carbon black materials were made into 'L2' type electrodes using the method previously described. The solvent used to disperse the carbon black was a 2:1 mix of IPA and water, as previously used. However, not all carbon blacks needed the same amount of solvent to form a slurry. The actual volumes used were not considered very important, since the only role of the solvent was to disperse the carbon and binder in order to mix them.
1.2 cm × 1.2 cm specimens were cut from each electrode sheet and glued onto screen-printed substrates using conductive carbon ink. Electrodes were placed in an oven to cure for approximately three hours. Two specimens of each material were tested in three different electrolyte solutions. 1M H₂SO₄ (aq) was used because the entire surface area would be penetrated by the proton. 1M KCl (aq) was used for a comparison with H₂SO₄ (aq). As the potassium ion is significantly larger than the proton one would expect that smaller capacitances would be measured using KCl (aq). However, it was of interest to see if carbon blacks would restrict ions of this size. Finally, the novel 1M LiCF₃SO₃ in sulfolane/ethylene carbonate solution developed in the lithium-sulphur work was also experimented with here.

Aqueous cells employed an SCE reference electrode and platinum gauze counter electrode. Non-aqueous cells employed lithium ribbon strips as both the reference and counter electrodes. All cells were purged with argon before testing commenced and all cells were tested using cyclic voltammetry. Aqueous cells were cycled between −0.1 mV and +0.3 mV, and non-aqueous cells were cycled between 2.25 V and 3.25 V. All cells were scanned using a scan rate of 2 mV/s. Capacitances were measured from the cyclic voltammograms according to the following calculation:

\[ C = \frac{(I_{(f)} - I_{(b)})}{2v} \]

Where \( C \) = capacitance (F), \( I_{(f)} \) = forward scan 'steady state' current (A), \( I_{(b)} \) = backward scan 'steady state' current (A) and \( v \) = scan rate (V/s).

In cases where true steady state currents were not obtained (when the \( RC \) time constant was large in magnitude), it should be noted that this calculation provided underestimates of the true capacitance.

Specific capacitances were obtained by dividing capacitance by specimen weight. Energy stored for a particular carbon electrode in a particular solution was obtained using the following equation:
Where \( E = \frac{1}{2} CV^2 \)

4.5.5 Gelled Electrolyte Solutions

PVDF was chosen as the polymer to use in attempts to gel electrolyte solutions, as it had been used successfully in previously reported literature and it was in plentiful supply in the laboratory. Had it not proved successful in the present study, another polymer, such as polymethyl methacrylate perhaps, might have been used instead.

A number of attempts were made at gelling a solution of 1M LiCF_3SO_3 in sulfolane/ethylene carbonate (7:3).

**Attempt No.1.**

PVDF powder was added to the electrolyte solution, constituting 20% by weight of the end product. The PVDF and solution were heated in a beaker stood in an oil bath on a hot plate, whilst being stirred, up to about 60°C. The viscosity of the solution increased, but on cooling the product was found to be too dry. It was clear that too much PVDF had been used, and it appeared that some of the powder had not dissolved in the solution.

**Attempt No.2.**

PVDF powder was added to the electrolyte solution, constituting 10% by weight of the end product. The mixture (in a beaker) was placed in an oven at 100°C for approximately 10 minutes, before being transferred to an oil bath on a hot plate and being stirred. The solution was cooled overnight with continued stirring, as it appeared that not all the polymer had dissolved. The following day there appeared to be a gel surrounding the magnetic bar inside the beaker, although the remainder of the solution was only viscous, not gelled. The solution was heated again; up to approximately 60-70°C, with stirring, before being placed briefly back in the oven at 100°C. After cooling
the solution still had not gelled. The question was raised as to whether or not the polymer had actually dissolved, or simply swelled temporarily.

**Attempt No.3**

PVDF powder was added to the electrolyte solution, constituting 10% by weight of the end product. This time the mixture was ball-milled to mix it, in a Fritsch Pulverisette 7 planetary ball mill. The mixture was placed in an agate container, and ball milled as follows:

1 minute at 100 rpm  
1 minute at 200 rpm  
1 minute at 400 rpm

The slow mixing first allowed gentle combination of the materials, leading to a product of higher viscosity than the pure solvent. Faster mixing speeds were used to more thoroughly mix the contents. Unfortunately the volume of liquid proved to be too much and the solution began to leak from the container. The remaining solution was transferred to a beaker and placed in an oven for 15 minutes, after which it was left to cool. Gelation did not occur.

**Attempt No.4.**

Both the 10% level of PVDF and the ball-milling technique were used again. However, this time PVDF was first ball-milled with a small portion of liquid solution. 1 g PVDF and 2 g electrolyte solution were placed in the agate container and mixed at a much higher speed of 800 rpm (there was now a much lower risk of large volumes of solution leaking from the container). After 2 minutes a white paste had formed. A further 1 g of electrolyte solution was added, and the solution was mixed at 800 rpm for a further 2 minutes. After this time the liquid was beginning to spread around the walls of the container and so it was decided no more solution could be added. The remaining solution was heated in a beaker placed in an oil bath on a hot plate to approximately 50-60°C. The contents of the agate container were then transferred to the beaker and heated together for 10-15 minutes. The solution was cooled. Gelation did not occur. The solution was then covered with a watch glass and transferred to an oven at 100°C for approximately 10 minutes. The slightly opaque solution turned translucent, and on
cooling gelation occurred. It was thought that this attempt was successful firstly because the ball-milling process had thoroughly mixed the polymer with the liquid solution, and secondly because this improved mix was more efficiently heated in the oven.

An attempt at gelling electrolyte solution using only 5% PVDF was made, but this proved to be unsuccessful.

After achieving gelation the next stage was to attempt to gel working electrodes. In making the next gelled solution the same process of ball-milling was repeated. This time the PVDF paste and remaining liquid mix was transferred immediately to the oven for approximately 30 minutes before being poured into individual vials containing working electrodes. These vials were placed in the oven for approximately 1 hour, in order that the gelled electrolyte solution could penetrate the dead volume of the electrode whilst in a hot, liquid state. The aim was that on cooling the gelled electrolyte solution would be present throughout the dead volume of the electrode. The finished gelled working electrodes were removed from glass vials prior to testing, and the excess gel gently removed, leaving a layer around the carbon specimen only (Figure 4.13).

![Figure 4.13. A PVDF-gelled electrolyte solution surrounding a calendered carbon specimen adhered to a screen-printed electrode.](image-url)
The gelled working electrode were then placed in an electrochemical cell and experimented with using cyclic voltammetry as previously described.
5 Results and Discussion: Carbon Electrodes for Use in Lithium Thionyl Batteries

5.1 Overview of Chapter

Lithium thionyl chloride batteries are one of the world’s best primary batteries. However there is a serious problem during manufacture of the carbon electrodes for these cells, as they are prone to cracking. In the present work this problem has been solved by adding carbon fibre. Results of electrochemical testing of these fibrous electrodes suggest they perform better than non-fibrous electrodes.

The total capacity of the lithium thionyl chloride battery is related to its dead volume, i.e., the total quantity of thionyl chloride that may be stored inside the carbon electrode. In the present work an efficient method of estimating the dead volume of carbon electrodes has been developed. This makes use of an immersion technique and does not have to resort to the comparatively inefficient DBP test.

Industry has already determined that IPA is the optimum wetting agent for carbon electrode manufacture. Unfortunately the quantity of IPA currently used on the assembly line approaches UK/EU limits. This problem has been solved in the present study by demonstrating that the volume of IPA may be halved without damaging the microstructure of the electrode. This has very important implications for health and safety on site and has enabled manufacturing to continue, by a simple modification of the standard procedure.

Other work discussed in this chapter includes investigations into repeatability, the possibility of using an improved Ketjenblack material, and the use of SEM imaging to characterise different electrode formulations.
5.2 Discharge Capacity Tests on Baseline and Fibrous Electrodes

5.2.1 Baseline Formulations

The first discharge capacity tests were carried out on authentic Schlumberger WCP Ltd electrodes and electrodes fabricated (using the same formulation) in Loughborough University laboratories. The latter ‘baseline’ electrodes are referred to as ‘L2’. Unless otherwise stated, all extruded or calendered electrodes tested in discharge capacity tests were in cells discharged at a constant current of 28.8 mA. This was equivalent to a current density of 20 mA/cm² applied to full-size Schlumberger WCP Ltd electrodes in a Li-SOCl₂ cell. An example of typical results from this type of test is shown in Figure 5.01, where discharge cell voltage has been plotted versus fractional specific capacity. The sudden drop in potential occurs when the active sites of the carbon electrode have been blocked by LiCl formed during discharge.

![Figure 5.01](image)

*Figure 5.01. Typical fractional specific capacities for an authentic Schlumberger WCP Ltd electrode and an electrode fabricated for the present study using the same formulation (L2) when testing in Li-SOCl₂ cells. Discharged at 28.8 mA constant current for several hours each.*

SEM images of these types of carbon electrode can be seen in Figures 5.02 – 5.05, where two different magnifications are shown for each formulation.
Figure 5.02. An SEM image of the outer surface of a Schlumberger WCP Ltd electrode. The scale bar is at 100 μm.

Figure 5.03. An SEM image of the outer surface of an L2 electrode. The scale bar is at 100 μm. The structure appears more open than seen in the Schlumberger WCP Ltd electrode.
Figure 5.04. An SEM image of the carbon aggregates of a Schlumberger WCP Ltd electrode. The scale bar is at 1 µm. Note the aligned polymer strings.

Figure 5.05. An SEM image of the carbon aggregates of an L2 electrode. The scale bar is at 1 µm. Note the random orientation of polymer strings.

From the SEM images it appears that the electrodes made for the present study have a more open structure than the Schlumberger WCP Ltd electrodes.
Electrodes manufactured at Schlumberger WCP Ltd were extruded using their technique and electrodes manufactured for the present study were, for the main part, calendered. Part way through the present study machinery was supplied to allow electrodes to be extruded, for comparison with calendered electrodes. Electrodes extruded at Loughborough for the present study were referred to as L3 electrodes. SEM images of electrodes extruded for this purpose are shown in Figures 5.06 and 5.07. Figure 5.06 shows a more open structure than observed in Figure 5.02, but Figures 5.07 and 5.04 appear very similar.

Figure 5.06. An SEM image of the outer surface of an L3 electrode. The scale bar is at 100 μm.
5.2.2 The Addition of Carbon Fibres to the Electrode

In industry there is a serious problem during carbon electrode manufacture, as they are prone to cracking. In the present work this problem has been solved by adding carbon fibre to the carbon mix, prior to electrode extrusion. As detailed in Chapter 3, the formulation was adapted to include various percentages of chopped carbon fibre. Carbon fibre is known worldwide for its excellent properties of strength and flexibility. The addition of carbon fibre to carbon electrodes is therefore an ideal approach to imparting strength and flexibility, whilst avoiding the introduction of new chemicals to the carbon mix. The fibre used in the present study was Kreca Chop, which has a tensile intensity of 800 MPa and is widely used in reinforced concrete. SEM images of a fibrous carbon electrode are shown in Figures 5.08 and 5.09.
Figure 5.08. An SEM image of the outer surface of a fibrous L2 electrode. The scale bar is at 100 μm. Note the fibres appearance as scaffolding between the carbon black aggregates.

Figure 5.09. An SEM image of the carbon aggregates of a fibrous L2 electrode. The scale bar is at 1 μm.

Although the fibres were an excellent reinforcing material, it was equally important that they did not damage the specific capacity of the cell. Accordingly, Kreca Chop C-206S fibres were added to the electrode mix in different proportions and the resulting
electrodes were tested electrochemically. Specifically, discharge capacity tests were carried out under constant current and the fall in potential was recorded with time. The average specific capacities are shown in Figure 5.10 in the form of a bar graph.

![Figure 5.10. Comparison of specific capacities of fibre-containing carbon electrodes with a ‘baseline’ L2 electrode (fibre-free) after testing in Li-SOCl₂ cells. All electrodes discharged at 28.8 mA constant current for several hours each.](image)

There is evidence that the addition of carbon fibres to the electrode formulation does not have a detrimental effect on the performance of the electrode in a lithium-thionyl chloride cell. Indeed, there appears to be a slight increase in specific capacity. Whether or not the observed difference in performance was statistically significant was estimated using an unpaired Student’s t-test with $p \leq 0.01$ being significant and $p \leq 0.05$ showing a strong trend towards significance. This test was carried out using the L2 and L2 8%F results. An improvement of 10% was observed ($N=3$, $p=0.01$). This provides evidence that there could be a real improvement in specific capacity when using fibrous electrodes. An unpaired t-test was also used to assess whether there was any discernible difference between different percentages of fibres used in the electrode. However, when comparing L2 4%F and L2 8%F this was not the case ($N=3$, $p=0.49$). Hence, there is reasonable evidence to support the statement that there is no real change in specific capacity with change in percentage fibres, up to 14%.
5.2.3 Discussion

The strength and flexibility of carbon black electrodes has been improved by the addition of carbon fibres. There is statistical evidence to suggest that these fibrous electrodes can perform 10% better than non-fibrous electrodes in discharge capacity tests. The reason for this might be due to the way the fibres separate agglomerates of carbon black to create more dead volume, as seen in the SEM images. This could allow more electrolyte solution to enter the electrode, which leads to an extended discharge capacity.

5.3 IPA Test for Electrode Dead Volume

Industry has already determined that isopropyl alcohol (IPA) is the optimum wetting agent for carbon electrode manufacture. This is probably because IPA has a low surface tension (21.7 mN/m), which allows it to wet even hydrophobic surfaces easily. With this in mind, a new test was developed for estimating electrode dead volume using IPA. The method for this test was described in the Experimental chapter. Briefly, samples of carbon electrode were submerged in a bath of IPA until the dead volume had been filled with IPA. The samples were weighed prior to this, and re-weighed to calculate the mass of IPA absorbed. This was then converted to a volume measurement. The test has been used extensively for carbon black electrodes, and in particular, to carbon black electrodes of the Schlumberger WCP Ltd design.

In some proof-of-concept experiments, the percentage increases in weight that were observed after submerging a series of test electrodes in IPA were calculated. In Figure 5.11, the results have been correlated with the electrodes’ specific capacities.
The internal volumes of the carbon electrodes correlate with their performances in lithium/thionyl chloride batteries. There also appears to be a difference in performance between those electrode manufactured on-site at Schlumberger WCP Ltd, and those produced for the purpose of this thesis. However, the work presented here will focus on those electrodes produced for this thesis (formulations with ‘L’ prefixes).

With further development this test might provide a suitable means of predicting whether or not a particular electrode is good enough for inclusion in a given lithium/thionyl chloride cell. Throughout the present study different carbon electrode formulations are described. The IPA test for dead volume will be used for a number of these formulations in an attempt to provide further characterisation.

5.3.1 Mitsubishi Carbon Blacks

A number of Mitsubishi carbon blacks were selected for experimentation, due to the fact they have been very well characterised. The aim was to use these materials to allow some useful conclusions to be made about how physical properties relate to electrochemical performance. Some of the properties of the selected Mitsubishi carbons are shown in Table 5.01.
<table>
<thead>
<tr>
<th>Mitsubishi Carbon</th>
<th>Particle Size (nm)</th>
<th>B.E.T Surface Area (m²/g)</th>
<th>DBP Absorption (cm³/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 L</td>
<td>24</td>
<td>125</td>
<td>45</td>
</tr>
<tr>
<td>47</td>
<td>23</td>
<td>132</td>
<td>64</td>
</tr>
<tr>
<td>2300</td>
<td>15</td>
<td>320</td>
<td>64</td>
</tr>
<tr>
<td>40</td>
<td>24</td>
<td>115</td>
<td>110</td>
</tr>
<tr>
<td>MA 600</td>
<td>20</td>
<td>140</td>
<td>131</td>
</tr>
</tbody>
</table>

*Table 5.01. Some properties of Mitsubishi carbons.*

Calendered electrodes were made from each carbon material, using the binder to carbon ratio shown in the Schlumberger WCP Ltd formulation (see Appendix I). The final products were difficult to cut into shape due to their inflexible texture, and seemed less ‘spongy’ than Schlumberger WCP Ltd or L2 electrodes.

Capacity tests were run by using the electrode material as a working electrode in a Li-SOCl₂ cell, although it was never intended that these materials would replace the current carbon electrodes. The aim of these capacity tests was to demonstrate whether capacity correlated with B.E.T surface area or DBP dead volume (or neither). Since SOCl₂ is reduced on the carbon surface, one might have expected Mitsubishi carbon 2300 to give the highest capacity. On the other hand due to the LiCl deposition during cell discharge, pore volume is also important and thus one might have expected MA 600 to give the highest capacity. A graph showing specific capacity and B.E.T surface areas overlaid for these materials is shown in Figure 5.12. There is clearly no correlation.
There is no relation between specific capacity and B.E.T surface area. However, as Figure 5.13 shows, there is a relation between specific capacity and DBP dead volume.

The results show that specific capacity of Li-SOCl\(_2\) cells is related to the dead volume available inside the carbon electrodes. This proves that dead volume is more important than surface area in this case.
Mitsubishi carbons were also used to test the validity of the IPA test. The aim was to observe whether values of DBP dead volume correlated with values of IPA dead volume. Figure 5.14 shows that this was generally the case.

![Graph showing DBP and IPA numbers](image)

**Figure 5.14. A comparison of DBP numbers and IPA numbers for a number of highly characterised Mitsubishi carbons. Note the close overlay of values of dead volume in all cases.**

The trends in DBP numbers are mapped by the trends in IPA numbers, although the absolute values are slightly different. One would expect a difference in the absolute values, since the DBP numbers are measured for carbon materials in their loose state, and IPA numbers are measured for electrodes, fabricated with a polymer binder. At the same time, IPA molecules are less sterically hindered than DBP molecules, and as such may be able to access more dead volume.

IPA has a much higher Permissible Exposure Limit (PEL) than DBP (980 and 5 mg/m$^3$ respectively) and thus is preferable to use for large scale industrial measurement of dead volume. Since specific capacities correlate with DBP numbers, they also correlate with IPA numbers. This establishes that the IPA test for dead volume could be employed as a useful (and quick) predictor of specific capacity.

Finally, capacitance tests were run in 1M H$_2$SO$_4$ in order to measure accessible surface area. The proton is a very small ion that can move quickly through solution, and as such...
this solution was ideal for these measurements. The aim of these capacitance tests was to demonstrate whether capacitance correlated with B.E.T surface area or DBP dead volume (or neither). Each electrode was soaked in 1M H$_2$SO$_4$ for 30 minutes before testing, to ensure proper wetting. Some typical capacitance curves are shown in Figure 5.15, where specific current has been plotted versus voltage.

![Figure 5.15. Voltammograms for different types of Mitsubishi carbons tested in 1M H$_2$SO$_4$ versus an SCE reference electrode. Scan rate 2mV/s.](image)

Clearly, the electrode made from Mitsubishi Carbon 2300 displayed the highest capacitance, whereas all the other carbons were similar in magnitude. Figure 5.16 compares the capacitance values with the B.E.T surface areas.
It is clear that cyclic voltammetry provides an accurate and convenient measure of the surface areas of carbon black electrodes.

5.3.2 Discussion

Using a set of well-characterised carbon blacks from Mitsubishi it has been demonstrated that capacitance correlates with B.E.T surface areas and battery capacity correlates with DBP dead volume. It has also been demonstrated that IPA numbers correlate with DBP numbers, which provides conclusive proof that the IPA test can be used as an alternative method of assessing dead volume. The use of IPA in place of DBP is strongly preferred as the former has a higher Permissible Exposure Limit (PEL).

Since the IPA test is a successful predictor of battery specific capacity, it represents a valuable new laboratory-scale quality-control method.
5.4 The Use of Different IPA:H₂O ratios in the Manufacturing Solvent for Electrode Manufacture

According to Schlumberger WCP Ltd, it would be desirable to decrease the amount of IPA released by the manufacturing process. It was therefore of interest in the present study to explore the possibility of decreasing the concentration of IPA in the extrusion mixture. Since the standard industrial procedure made use of only two solvents it was preferable to avoid the introduction of a third. Instead, the ratio of the two solvents was experimented with, with the aim of allowing a relatively easy change to the current manufacturing procedure. A large series of experiments was therefore undertaken to determine if the IPA/water ratio could be decreased without compromising the performance of electrodes, and without compromising their structural integrity.

A large, systematic series of experiments was carried out to determine the effect of the IPA to water ratio on the specific capacity of individual carbon electrodes. A suite of data is plotted in Figure 5.17, derived from calendered electrodes discharged in Li-SOCl₂ cells at 28.8 mA constant current.
A significant upward trend in specific capacity is observed with a decreasing percentage of IPA in the manufacturing solvent. Further experiments were therefore carried out on extruded electrodes of the L3 type, and compared with results from calendered L2 electrodes (Figure 5.18). A similar significant trend was observed.
Figure 5.18. Specific capacity of both L2 and L3 electrodes tested in Li-SOCl₂ cells. Note the increase in specific capacity in both cases as the percentage of IPA in the manufacturing solvent is decreased.

These data confirmed the surprising fact that decreasing the IPA content of the manufacturing solvent actually improved the electrode capacity.

In order to confirm that the increase in electrode capacity was genuine, and not just an artefact caused by swelling of the electrode, it was also necessary to determine the volumetric capacity of electrodes. Volumetric capacity may also be a preferred measure of performance for some manufacturers. Obtaining such data necessitated the accurate determination of electrode volumes. Problems were encountered with estimating electrode volumes, due to their compressibility. In generating the data in Figure 5.19, a micrometer was used to measure electrode thickness, thus allowing calculation of electrode volume. The calculated volumetric capacities are presented in Figure 5.19. The trends are very similar to trends observed in specific capacity. This suggests that the increase in electrode capacity is genuine, and not simply due to swelling of the electrode.
Finally, a further observation was made during these experiments. At high percentages of water (above 70%) the finished electrodes lost some tensile strength, and this caused them to tear more easily. Clearly this was undesirable, but this weakness was rectified by the addition of 8% (w/w) chopped carbon fibres. Four replicate discharge capacity experiments were then carried out; the average result was 2206 mAh/g. This compares favourably with previous performances of carbon black electrodes in lithium thionyl chloride cells (approximately 2100 mAh/g), and demonstrates that neither the new manufacturing solvent composition nor the addition of fibres had any detrimental effect on specific capacity.

5.4.1 Discussion

These experiments have shown conclusively that it is possible to decrease the amount of IPA in the manufacturing solvent, without compromising the electrode performance. Making this change to the solvent composition will allow the continuation of electrode manufacture, whilst not exceeding environmental discharge limits on the manufacturing plant.
It is interesting to consider how the improvement in specific electrode capacity is related to the water content of the manufacturing solvent. When the percentage of water in the manufacturing solvent is increased, a more open structure develops inside the calendered carbon electrode, i.e., there is a smaller mass of carbon per unit volume. This is due to the way in which the solvent evaporates from the electrode after calendering. Most likely, the IPA fraction evaporates first, leaving the water fraction behind. At some point a de-wetting transition must take place. This involves the increasingly-pure water withdrawing from the hydrophobic carbon black particles, leaving behind a less dense structure. The idea that a less dense structure develops at higher percentages of water is consistent with the observation that electrodes lose some tensile strength when the percentage of water exceeds 70%.

Multiple tests were also carried out on both the baseline formulation (L3 made with 67% IPA in the manufacturing solvent), and an L3 electrode made with just 30% IPA in the manufacturing solvent. The results (Figure 5.20) show a comparison of 5 tests carried out on carbon electrodes made using both the standard manufacturing solvent and the new manufacturing solvent composition. The error bars are at the 1 sigma level of significance (± 1σ).
The mean specific capacities are:

- L3 67% IPA (baseline): $1891 \pm 104 \text{ mAh g}^{-1}$
- L3 30% IPA: $2091 \pm 132 \text{ mAh g}^{-1}$

The key point to note is that these tests confirm the use of a lower IPA:water ratio does not have a detrimental effect on electrode specific capacity. In fact, there is evidence to support a statistically significant ($N = 5, p = 0.03$) improvement in specific capacity by using only 30% IPA in the manufacturing solvent.

### 5.5 Estimation of Electrode Volume

In view of the fact that work carried out thus far had revealed difficulties with accurate electrode volume measurement (Figure 5.19), efforts were made to address this. The use of a micrometer tended to compress the samples being measured, but it was later
realised that data derived from the IPA Test for Dead Volume could also be employed to estimate the total electrode volume without any compressing problems. These two independent methods could then be compared:

1. **The IPA Test for Dead Volume method.** This measured the mass of IPA absorbed by the electrode, and then combined the data with the known densities and masses of the other materials to estimate the total volume of the electrode.

2. **The micrometer method.** This measured the thickness of the electrode, and then combined the data with the cross-sectional area to estimate the total volume of the electrode.

Due to the possible swelling of electrodes, the IPA method generated *overestimates* of the electrode volumes. Due to the possible compression of electrodes the micrometer method generated *underestimates* of the electrode volumes. A further point should be taken into account when using the IPA Test for Dead Volume method; the “true” density of carbon black particles is difficult to estimate. This is because there are vacancies and inclusions inside the solid material, which can severely complicate density measurements. To avoid this problem, the density of pure graphite (2.26 g/cm³) was adopted as the well-defined upper limit on the density of carbon black.

The results of the two methods are compared in Figure 5.21 for a number of 1.2 cm x 1.2 cm L2 (calendered) specimens of varying thickness (3.5 – 4.0 mm, depending on where the sample was cut from the sheet of calendered material). The data correspond very well, but with an absolute difference of < 0.2 cm³.
Overall, apart from a numerical factor the data superimpose. The average volume of a carbon electrode sample was $0.6 \text{ cm}^3 \pm 0.1$.

Finally, upper and lower bounds on the volumetric capacities are shown in Figure 5.22, as calculated by the micrometer measurement and the IPA measurement. The very important conclusion is that decreasing the IPA content of the manufacturing solvent did not damage the electrochemical performance of electrodes.
5.51 Effect of IPA/Water Ratio on Electrode Dead Volume

Although the IPA/H$_2$O ratio had a significant effect on the specific capacity and the volumetric capacity of electrodes, the effect on the electrode dead volume was surprisingly small.

Dead volume measurements were carried out on the L3 suite of electrodes described previously, in which the IPA/H$_2$O ratio was changed during the manufacturing process. Dry samples from each electrode were submerged in a bath of IPA, and their weight gain was recorded. The increase in weight is due to the IPA occupying the dead volume within each electrode. The tests were performed in duplicate, the volumes calculated, and the average value presented in Table 5.02.
Table 5.02. Dead volume measurements carried out on the L3 suite of electrodes described previously, in which the IPA/H₂O ratio was changed during the manufacturing process.

<table>
<thead>
<tr>
<th>% IPA</th>
<th>% Dead Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>88</td>
</tr>
<tr>
<td>50</td>
<td>88</td>
</tr>
<tr>
<td>40</td>
<td>89</td>
</tr>
<tr>
<td>30</td>
<td>89</td>
</tr>
<tr>
<td>20</td>
<td>89</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

The dead volume increased from 88% to 90% of the total electrode volume as the percentage of IPA in the manufacturing solvent was decreased. Despite this apparently small increase in dead volume, the specific capacity increased significantly. This is because the small increase in dead volume translates as a relatively large decrease in the mass of the electrode, and hence a large increase in the specific capacity.

It may be concluded from these considerations that the IPA/H₂O ratio is exerting its influence principally through the microstructure of the solid constituents (carbon and binder) of the electrode.

5.6 Comparing Extruded/Calendered Electrodes

In the early part of the present study the carbon electrodes were manufactured by calendering (rolling). Later on, after the installation of the extrusion apparatus, the electrodes were also manufactured by extrusion through a special template (Figure 5.23). Due to the different surface profiles produced by the two different methods (the calendered electrodes were flat whereas the extruded electrodes were ridged), it was important to compare their electrochemical performances.
A 2 × 2 matrix of electrode experiments was therefore designed (see Table 5.03) involving the two types of manufacturing process (calendering and extruding), and also two types of Ketjenblack. Schlumberger WCP Ltd currently uses Ketjenblack 300J and Shawinigan carbon black in a ratio of 1:4 for the manufacture of carbon electrodes. During the present study a different type of Ketjenblack was identified; Ketjenblack 600JD. This material has a higher DBP dead volume, and it was therefore of interest to experiment with using this material in place of ‘300J’ (maintaining the 1:4 ratio with Shawinigan). A large increase in specific capacity was predicted.

<table>
<thead>
<tr>
<th></th>
<th>Ketjenblack 300J</th>
<th>Ketjenblack 600JD</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2 (calendered)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>L3 (extruded)</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 5.03. The matrix of electrode experiments.

The whole matrix of electrodes was then discharged in lithium thionyl chloride cells under galvanostatic control, using a constant current of 28.8 mA, and their capacities were calculated from the time taken for the voltage to fall to 2 V.

The results are shown in Figures 5.24 and 5.25. Three specimens of each electrode were run and the average result is shown here, with error bars at ± 1 standard deviation.
For electrodes made with both types of Ketjenblack there were increases in measured specific capacities upon changing the manufacturing process from calendering to extruding. In the case of Ketjenblack 300J this increase was 7\% and in the case of Ketjenblack 600JD this increase was 13\%.

The effect of changing the type of Ketjenblack is shown in Figure 5.25.

Figure 5.24. Comparison of performance of calendered (L2) and extruded (L3) electrodes. Performances from electrodes made with Ketjenblack 300J are on the left, those made with Ketjenblack 600JD are on the right (both used in a ratio of 1:4 Ketjenblack:Shawinigan). Data are the average of three measurements each. The error bars indicate ± 1 standard deviation.
For both methods of electrode manufacture there was an increase in measured specific capacity upon changing from Ketjenblack 300J to Ketjenblack 600JD. In the case of calendered electrodes this increase was 14%, and in the case of extruded electrodes this increase was 20%.

The coefficients of variation for all electrode formulations are collected in Table 5.04. None of the coefficients of variation is greater than 9%.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Coefficient of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2 300J</td>
<td>3%</td>
</tr>
<tr>
<td>L2 600JD</td>
<td>9%</td>
</tr>
<tr>
<td>L3 300J</td>
<td>7%</td>
</tr>
<tr>
<td>L3 600JD</td>
<td>6%</td>
</tr>
</tbody>
</table>

Table 5.04. Coefficients of variation for L2 and L3 electrodes made with different Ketjenblack materials run in Li-SOCl₂ cells.

In order to assess whether or not the increases in measured specific capacities were statistically significant, an unpaired Student’s t-test was carried out on the data. The resulting p-values are collected in Table 5.05, where $p \leq 0.05$ indicates a statistically significant result.
Electrode Formulation Comparison  

<table>
<thead>
<tr>
<th>Comparison</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2 300J vs. L2 600JD</td>
<td>0.100</td>
</tr>
<tr>
<td>L3 300J vs. L3 600JD</td>
<td>0.029</td>
</tr>
<tr>
<td>L2 300J vs. L3 300J</td>
<td>0.204</td>
</tr>
<tr>
<td>L2 600JD vs. L3 600JD</td>
<td>0.116</td>
</tr>
</tbody>
</table>

Table 5.05. *p*-values for each of the electrode formulations, as calculated from an unpaired Student’s *t*-test (N=3). Smaller *p*-values indicate higher significance.

The results in Table 5.05 show that a statistically significant improvement was observed when 600JD was used in place of 300J for extruded (L3) electrodes. A 20% increase ($N = 3, p = 0.029$) was observed. The *p*-value of 0.100 for L2 300J vs. L2 600JD shows a strong trend towards significance. Values of $>0.100$ indicate a weak trend towards significance. This data shows that a significant increase in measured specific capacity was observed when Ketjenblack 600JD was used in place of Ketjenblack 300J. A significant difference between calendered and extruded electrodes was not observed.

5.6.1 Discussion

Schlumberger currently manufacture carbon electrodes by extrusion of a wet carbon mixture. In the present work it has been shown that the specific capacity of these electrodes in lithium thionyl chloride batteries cannot be improved by calendering them. Since no significant difference was observed between extruded and calendered electrodes, the method of electrode production could be changed to allow for changes in electrode size/shape. Should calendering be incorporated into electrode manufacturing it would also negate the need for specialist templates to be made.

Schlumberger currently uses Ketjenblack 300J in the manufacture of their carbon electrodes. This material has a dead volume of 250 cm$^3$/100g. By contrast, Ketjenblack 600JD has a dead volume of 415 cm$^3$/100g. This increase in dead volume translates into a 20% increase in the specific capacity of extruded electrodes; a very significant improvement in battery performance.
5.7 Development of a Quality Control Method for Electrode Manufacture

5.7.1 The Use of Capacitance Measurements in Repeatability Estimation

Various uncontrolled factors during manufacturing can result in two formally identical electrodes behaving differently. For example, insufficient mixing may cause a non-uniform dispersion of the components of the extrusion mixture. At present there is no quick method of estimating the size of such fluctuations. In the present work a method was developed based on the measurement of electrode capacitance using cyclic voltammetry in sulphuric acid. Since electrode capacitance is proportional to the electrochemically active surface area, this is a very good probe of electrode microstructure.

The capacitances of carbon black electrodes are made up of two components; double layer capacitance and pseudocapacitance (refer to section 3.3 of the present study). Both are proportional to surface area. By carrying out repeat capacitance tests, statistical estimates of the fluctuation in electrode area can be made.

The mean specific capacitances of four specimens tested from four different electrode formulations cycled in 1M H_2SO_4 (aq) are shown in Figure 5.26. The error bars are at the 1 sigma level of significance.
Figure 5.26. Mean specific capacitances for different electrode formulations cycled in 1M H₂SO₄ (aq) versus an SCE reference electrode. The error bars indicate ±1 standard deviation. Note the large improvement with the fibrous electrode.

Given the size of the error bars, no significance can be attached to the small differences between the Schlumberger WCP Ltd electrodes, the Loughborough L3 baseline electrodes, and the new electrodes extruded with 30% IPA. However, there was a significant increase in capacitance when 4% carbon fibres were included in the L3 mix.

The coefficient of variation was also calculated for each formulation as a percentage, according to:

\[
\text{Coefficient of Variation (\%)} = \left( \frac{\sigma}{\text{mean}} \right) \times 100
\]

The coefficient of variation indicates the relative spread of data about the mean. The parameter therefore indicates how far there has been a loss of quality control in the manufacturing process. It is clear from the data in Table 5.06 that the addition of 4% chopped carbon fibre to the extrusion mixture yields a more consistent product. Four samples of each electrode were tested.
<table>
<thead>
<tr>
<th>Electrode Formulation</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3 4% F</td>
<td>3</td>
</tr>
<tr>
<td>L3 30% IPA</td>
<td>6</td>
</tr>
<tr>
<td>Schlumberger WCP Ltd Inner</td>
<td>8</td>
</tr>
<tr>
<td>L3 baseline</td>
<td>12</td>
</tr>
</tbody>
</table>

*Table 5.06. Coefficients of variation for capacitance measurements on different electrode formulations cycled in 1M H₂SO₄(aq).*

### 5.7.2 Electrode Thickness Uniformity

All electrodes were extruded or calendered at a constant thickness. During the drying process, very slight changes in this thickness occurred throughout the electrode. From a quality control point of view it was important to obtain an estimation of how large the fluctuation of electrode thickness was.

A number of different electrode formulations were investigated, mostly derived from the large set manufactured during the present study, but also including an authentic Schlumberger WCP Ltd commercial electrode. A micrometer was used to take eight measurements at random points on each electrode. Calculations were then carried out to determine the coefficient of variation in each case, thus providing an estimation of the fluctuation level in electrode thickness.

Tables 5.07 and 5.08 are compilations of data (for non-fibrous and fibrous formulations respectively) related to the thickness measurements. None of the electrode formulations had a co-efficient of variation greater than 5%, proving that a high degree of quality control was achieved in all cases. Extruded electrodes generally exhibited higher coefficients of variation than calendered electrodes. 5% can be taken to be the maximum level of fluctuation in electrode thickness.
<table>
<thead>
<tr>
<th>Electrode Formulation</th>
<th>Schlumberger Inner Formulation</th>
<th>L2 300J CALENDERED</th>
<th>L3 300J EXTRUDED</th>
<th>L2 600JD CALENDERED</th>
<th>L3 600JD EXTRUDED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXTRUDED</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.34</td>
<td>4.51</td>
<td>3.51</td>
<td>4.71</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>3.33</td>
<td>4.47</td>
<td>3.46</td>
<td>4.65</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td>3.47</td>
<td>4.47</td>
<td>3.40</td>
<td>4.61</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>3.54</td>
<td>4.34</td>
<td>3.37</td>
<td>4.52</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>3.57</td>
<td>4.44</td>
<td><strong>3.53</strong></td>
<td>4.57</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>3.32</td>
<td>4.50</td>
<td>3.07</td>
<td>4.65</td>
<td>3.43</td>
<td></td>
</tr>
<tr>
<td>3.69</td>
<td>4.43</td>
<td>3.15</td>
<td>4.63</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td>3.55</td>
<td>4.42</td>
<td>3.37</td>
<td>4.67</td>
<td>3.52</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.07. Thickness measurements for a selection of rolled and extruded electrodes. The largest and smallest values measured are shown by red and blue respectively.

<table>
<thead>
<tr>
<th>Electrode Formulation</th>
<th>L2 4%F CALENDERED</th>
<th>L3 4%F EXTRUDED</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.02</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>3.92</td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>4.23</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td><strong>4.27</strong></td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>3.99</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td><strong>3.00</strong></td>
<td></td>
</tr>
<tr>
<td>3.93</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>

| Mean | 4.05 | 2.80 |
| Range | 0.35 | 0.37 |
| Standard Deviation | **0.13** | **0.12** |
| Co-efficient of Variation (%) | 3 | 4 |

Table 5.08. Thickness measurements for fibrous electrodes. The largest and smallest values measured are shown by red and blue respectively.
5.7.3 Discussion

In the present study, the use of cyclic voltammetry to measure electrode capacitances in sulphuric acid has been proved to an excellent method of estimating the quality control of electrodes. This is because it provides a quick assessment of electrode microstructure. The coefficient of variation of the electrode capacitance is a good measure of the fluctuations that may occur. In the present study it was discovered that addition of chopped carbon fibres produced a more reliable product, since capacitance measurements of fibrous electrodes had a small coefficient of variation.

Electrode thickness is slightly non-uniform regardless of whether electrodes are rolled or extruded, and regardless of whether the electrodes contain carbon fibre or not. The highest measured coefficient of variation was only 5%, proving that a high degree of quality control was achieved. Generally extruded electrodes had larger coefficients than calendered, which provides evidence that thickness varies more in these electrodes.

5.8 Further Development of Quality Control Methods Using Capacitance Measurements

5.8.1 Testing of Accessible Surface Area in Low IPA Industrially Manufactured Electrodes

Having recommended to Schlumberger WCP Ltd that a lower IPA/water ratio be adopted to allow improved health and safety on the manufacturing plant, (also having a lower cost), a large set of electrodes was later produced on their site for testing. These were made with a 1:2 IPA/water ratio. The aim was to assess whether the microstructure of the electrodes was the same for ‘original’ electrodes (manufactured with the original manufacturing solvent composition) and ‘low IPA’ electrodes (made with a 1:2 ratio of IPA:H$_2$O). Two different electrode designs were made at the company, namely ‘Arc 5’ electrodes and ‘FDA’ electrodes; the latter being approximately twice the thickness of the former. These names indicate the different types of cells the electrodes are designed for. Forty electrode samples were received from Schlumberger WCP Ltd and run in capacitance tests in 1M H$_2$SO$_4$. Since
capacitance is proportional to surface area, these measurements allowed comparison of different formulation microstructures. If low IPA samples had the same accessible surface area as the original electrodes it would be a good indication that electrode microstructure had not been altered. This would support the use of low IPA electrodes on the manufacturing plant. $\text{H}_2\text{SO}_4$ (aq) was selected as the electrolyte solution due to the small size of the proton, so that even small regions of dead volume within the electrode would be accessed.

A series of small test samples (1.2 x 1.2 cm) was cut from Schlumberger WCP Ltd’s electrodes, and tested under electrochemical capacitor conditions as a rapid means of assessing accessible surface area. Working electrodes consisted of 1.2 cm x 1.2 cm samples of extruded test material glued to a screen-printed electrode by a conducting carbon adhesive. The latter had a very low surface area compared to that of the test electrode, so did not interfere with the test. A potential window of $-0.1$ V to $+0.3$ V was scanned, at a scan rate of 2 mV s$^{-1}$. The height of each voltammogram was then measured in order to calculate the capacitance in Farads. Figure 5.27 shows the mean average specific capacitances from 10 electrodes of each type. Each data bar has an error bar of ± 1 standard deviation.

![Figure 5.27. Mean specific capacitances measured in 1M $\text{H}_2\text{SO}_4$ (aq) of ten samples each of four different electrode formulations. Arc 5 and FDA are the names of two different geometries of cell electrode. Scan rate 2 mV/s.](image-url)
Despite the fact that the FDA electrodes were approximately twice as thick as the Arc 5 electrodes (~5.5mm versus ~2.5mm), their specific capacitances were similar, which provides strong evidence that the interiors of both electrodes were fully accessible to the electrolyte solutions. However, the crucial point is that the change in formulation of the manufacturing solvent did not significantly affect the electrochemical performance of the finished electrodes.

The coefficients of variation were also calculated for Arc 5 and FDA electrodes, and the values are presented in Table 5.09.

<table>
<thead>
<tr>
<th>Electrode Type (manufacturing solvent)</th>
<th>Mean Specific capacitance (F/g)</th>
<th>Coefficient of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Arc 5” (IPA/water, 2:1)</td>
<td>5.5</td>
<td>6 %</td>
</tr>
<tr>
<td>“Arc 5” (IPA/water, 1:2)</td>
<td>5.6</td>
<td>4 %</td>
</tr>
<tr>
<td>“FDA” (IPA/water, 2:1)</td>
<td>5.2</td>
<td>3 %</td>
</tr>
<tr>
<td>“FDA” (IPA/water, 1:2)</td>
<td>5.2</td>
<td>2 %</td>
</tr>
</tbody>
</table>

Table 5.09. Specific capacitances and coefficients of variation of commercial (Schlumberger WCP Ltd) electrodes. Some were manufactured using a 2:1 ratio of IPA to water, and others using a 1:2 ratio of IPA to water.

None of the coefficients of variation exceeded 6%. It is interesting to notice that the electrodes made with less IPA in the manufacturing solvent have lower coefficients of variation. This provides further evidence that low IPA electrodes are more consistent than the original electrode formulation.

5.8.1.1 Discussion

Extensive testing on low IPA electrodes manufactured at Schlumberger WCP Ltd (according to the formulation developed in the present study) indicates that they perform just as well as electrodes made using larger volumes of IPA. Given that the coefficients of variation are smaller for ‘low IPA’ electrodes there is the added benefit that incorporating a new manufacturing solvent will also produce a more consistent product.
The Use of Capacitance to Confirm Manufacturing Reproducibility

In order to gain some estimation of electrode reproducibility, two independent batches of ‘L2’ electrode material were prepared (acknowledgement to D. Phillips for making the second batch of electrodes). The electrodes were then cycled in 1M H₂SO₄ as previously described in this chapter. The different electrodes are labelled as ‘NH’ (the author) and ‘DP’ (an undergraduate student). Two electrodes of each batch were tested.

To eliminate sampling errors in the manufacture of the test electrodes, all the voltammetric currents were normalised by the test electrode mass. Hence Figure 5.28 shows the specific current density in units of mA/g. The specific capacitances are given in Table 5.10.

![Figure 5.28. Voltammetry of electrodes ‘baseline’ L2 electrodes made by two different personnel (NH; the author and DP; an undergraduate student). Scan rate 10 mV/s.](image)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP1</td>
<td>3.1</td>
</tr>
<tr>
<td>DP2</td>
<td>2.7</td>
</tr>
<tr>
<td>NH1</td>
<td>2.7</td>
</tr>
<tr>
<td>NH2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Table 5.10. Specific capacitances of ‘DP’ and ‘NH’ electrodes cycled in 1M H₂SO₄.*
Unfortunately even after normalisation, some electrodes still showed residual differences (up to 15%) in capacitance. It could be said that $\pm 15\%$ probably represents the limit of reproducibility attainable with present-day techniques.

5.9 Closing Discussion and Overall Findings

Chopped carbon fibres can be added to the electrode formulation to impart strength and flexibility without compromising the cell capacity. There is reasonable evidence to suggest that the specific capacity is improved upon using fibrous electrodes.

Despite the need for reducing the volume of isopropyl alcohol used in manufacture, this solvent has proved to be very useful in developing a test for estimating electrode dead volume. Since its use in this test would involve relatively small volumes, it is feasible for this test to be used in industry. This could remove the need for using dibutyl phthalate in the DBP test, which is difficult to implement.

The large quantities of isopropyl alcohol used in the electrode manufacturing procedure can be drastically decreased. This does not alter the surface area of electrodes, or the specific capacity. This discovery is extremely important for the manufacturing company, because it will allow them to continue to operate within UK and EU safety limits.

Further research carried out on the carbon electrodes used in lithium thionyl chloride cells included assessing electrode thickness variability, which was found to have a coefficient of variation no higher than 5% for the formulations tested. No significant differences in specific capacity were observed between calendered and extruded electrodes, suggesting that the extrusion process could be changed in the future to eliminate the need for specialist instruments and in-house templates. An investigation was also carried out into using a new Ketjenblack carbon of higher DBP dead volume. The results suggested that significant improvements in specific capacity were possible when using the new Ketjenblack.
Finally, a number of attempts were made to fabricate a carbon electrode using activated carbon rather than carbon black. Because the reduction of SOCl₂ takes place on the surface of carbon, it was thought that activated carbon might allow more contact between SOCl₂ molecules and carbon surface, thereby sustaining the reduction of SOCl₂ for a longer period of time. Since activated carbon is highly porous it was thought there would be ample space for discharge product deposition. A number of different activated carbons were experimented with, but all failed either during manufacture (would not bind together to form an electrode) or during capacity tests.

The reason that activated carbon systematically failed electrode capacity tests was probably due to one of the following reasons: non-wetting of activated carbon pores with solution, pores being too small for SOCl₂ molecules to penetrate, or resistivity of activated carbon. Upon using a Multimeter to measure the electrical resistance of electrodes, all the activated carbon electrodes turned out to be highly resistive. For example, an Elorit test material had a resistance of approximately 400 Ω, whereas a standard L2 test material had a resistance of only 6 Ω.
6 Results and Discussion: Carbon Electrodes and Electrolyte Solutions for Use in Lithium Sulphur Batteries

6.1 Overview of Chapter

The lithium sulphur battery is a leading candidate for next generation high-energy density rechargeable batteries [5] [52]. In principle it is cheap and recyclable, but it suffers from low sulphur utilisation and long-term capacity loss.

In the present study, a three-electrode bench-top apparatus was developed for the screening of calendered porous carbon electrodes in different solvent systems. This allowed single electrode discharge curves to be recorded. Sulphur was dispersed within the carbon matrix, and reduced upon discharge of the cell. Screen-printed electrodes were also used. Three different electrolyte solutions were made, including a novel electrolyte solution of 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate (7:3, w/w).

The work presented in this chapter contributes to the extensive research carried out on this battery system, and shows that even in novel electrolyte solutions the problem of rechargeability still exists.

6.2 Electrodes and Electrolyte Solutions

Throughout work on the lithium sulphur cell both screen-printed and calendered electrodes were used. In all cases, sulphur was dispersed throughout the carbon electrode. In screen-printed electrodes sulphur was mixed with graphite powder and binder during ink formation. In calendered electrodes sulphur was mixed with the dry carbon blacks before the addition of solvent and the binder solution.

Three different electrolyte solutions were used throughout this work. The electrolyte used remained a constant; 1M LiCF$_3$SO$_3$. The solvent systems are summarised in the Table 6.01.
<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfolane / Diglyme (also known as 2-methoxyethylether)</td>
</tr>
<tr>
<td>2</td>
<td>Sulfolane / Ethylene carbonate</td>
</tr>
<tr>
<td>3</td>
<td>Tetraglyme (also known as tetraethylene glycol dimethyl ether) / 1,3-Dioxolane</td>
</tr>
</tbody>
</table>

**Table 6.01. Three solvent systems used in experiments on the lithium sulphur cell in the present study.**

Solvent system 1 was chosen because previous researchers had found sulfolane mixed with monoglyme to be effective at allowing a higher conductivity solution to be achieved than that obtained when using the individual solvents [109]. For the present study diglyme was used instead of monoglyme, because diglyme has a much higher boiling point (162°C) than monoglyme (85°C), and ultimately a battery system capable of operating at high temperature was preferred.

Solvent system 2 was a novel system created for the purpose of the present study. The aim was to combine two high relative static permittivity, high boiling point solvents in order to form a solvent system capable of fully dissolving large amounts of electrolyte, thus allowing a less resistive solution. It was also desirable to have a solution stable at high temperatures. Despite both sulfolane and ethylene carbonate being solid at room temperature, they form a liquid when mixed.

Solvent system 3 was chosen due to the fact that previous researchers had reported improved cell performance using such a system [61].
Sulfolane is polar (\( \varepsilon_r = 43 \)), due to the two S=O double bonds. Although it is unlikely that many interactions take place between sulfolane and diglyme, some dipole-dipole interactions must occur between sulfolane and ethylene carbonate (\( \varepsilon_r = 89 \)). With regard to the salt, LiCF\(_3\)SO\(_3\), the triflate anion does not have a high charge density because the single negative charge delocalises over all three oxygen atoms. Triflate anions are often not highly solvated. However, the lithium cation has a high charge density, and attracts the negatively charged oxygen atoms of polar groups. Thus, it is likely that lone pairs on the oxygen atoms in diglyme and sulfolane coordinate lithium to some extent.

6.3 Sulfolane/Diglyme

6.3.1 Overview

Both cyclic voltammetry and discharge capacity techniques have been used in the present study to investigate the lithium sulphur battery system. The results indicate that the sulphur system may be recharged during fast cycling, but cannot be recharged during slower discharge capacity tests. The widely acknowledged problem of sulphur utilisation was also found to be a challenge in the present study.

6.3.2 The Use of Cyclic Voltammetry

Cyclic voltammetry was used as a rapid way of learning about the redox chemistry of the sulphur, using screen-printed electrodes. First, an ‘in-house’ graphite ink was made using graphite powder, PVDF binder and propylene carbonate solvent. Electrodes made from this graphite ink were then tested using cyclic voltammetry. The current was measured whilst the potential window was scanned at a rate of 100 mV/s. The potential window of 2 V was the range in which the solvent was stable; no faradaic electrochemistry was seen when using a blank graphite electrode in this range. This is depicted in Figure 6.01.
Next, a screen-printed working electrode with 8% sulphur in graphite was tested in the sulfolane/diglyme solvent. Three voltammograms from sequential scans of the same electrode are shown in Figure 6.02. Current density is plotted against voltage. Sulphur is reduced when scanning in the negative direction, at potentials less than 2.5 V. On the reverse scan, the sulphur discharge products (probably Li$_2$S and various polysulfide products) are reoxidised.

The scans almost track each other, indicating the redox active species has not been lost during the experiment. This is true for all percentages of sulphur, as shown in Figures 6.03 – 6.04.
Figure 6.03. Voltammograms from sequential scans of in-house graphite ink with 14% sulphur electrode scanned at 100 mV/s in 1M LiCF$_3$SO$_3$ in sulfolane/diglyme.

Note that in all voltammograms the reduction peak lacks hysteresis, unlike the broad oxidation peak. This is because there is such a large quantity of solid sulphur available to be reduced, that the reduction does not become a diffusion-limited process (on this timescale). During the oxidation the process is diffusion-controlled, and hence a broad peak is observed.

The aim of using screen-printed electrodes was to learn quickly about the lithium-sulphur system, and ascertain the best performing electrodes based on the highest currents recorded in cyclic voltammetry tests. A comparison of data using different
amounts of sulphur produced inconclusive results as to the optimum percentage (see Figures 6.05 and 6.06).

**Figure 6.05.** Comparison of the third scans from different amounts of sulphur in graphite ink electrodes; first set of results. All electrodes cycled in 1M LiCF$_3$SO$_3$ in sulfolane/diglyme. 27% sulphur produced the largest currents.

**Figure 6.06.** Comparison of third scans from different amounts of sulphur in graphite ink electrodes; second set of results. All electrodes cycled in 1M LiCF$_3$SO$_3$ in sulfolane/diglyme. 14% sulphur produced the largest currents.
6.3.3 Discharge Capacity Tests

Screen printed electrodes were also used in discharge capacity tests. These electrodes were used in a three-electrode arrangement, with lithium metal counter electrodes and lithium metal reference electrodes. Cells were discharged at 2 mA constant current. The first discharge curves obtained for sulphur electrodes in 1M LiCF$_3$SO$_3$ dissolved in a sulfolane/diglyme are shown in Figures 6.07 – 6.08 for 8% and 14% sulphur electrodes. The ‘in-house graphite ink’ serves as the blank, baseline electrode.

![Figure 6.07](image)

**Figure 6.07.** Assessment of rechargeability with a screen-printed electrode containing 8% sulphur in graphite ink, discharged at 2 mA/cm$^2$ in 1M LiCF$_3$SO$_3$ in sulfolane/diglyme.
Discharge profiles of both 8% and 14% sulphur show that there was no sulphur to reduce upon the second discharge. After reducing the sulphur to polysulfide products, it was clearly not easy to re-oxidise back to sulphur. This is evident by the lack of reduction plateaus in the second discharge. Figure 6.09 compares the first discharge profiles of each.
Upon comparing the discharge capacities for 8% and 14% sulphur, the increase in discharge time is not equal to the increase in sulphur. This suggests that not all of the additional sulphur is being accessed, thus there is a problem with sulphur utilisation.

6.3.4 Discussion

Sulphur was successfully reduced in a graphite matrix, but it was not possible to produce a fully rechargeable system. There were several possible reasons for this. The polysulfide discharge products might have had time to diffuse away, or perhaps the lithium polysulfide products were insoluble and had precipitated from solution. Yet another possibility was that the electrolyte solution had not fully penetrated (wetted) the graphite/sulphur network. If this had occurred, the reaction would have been confined to the outer surface of the electrode. Finally, it was also conceivable that the system had failed during re-oxidation, such that the polysulfide products had successfully re-oxidised back to sulphur, but this had then failed to adhere to the electrode.
Better results might be obtained if calendered electrodes were used, as perhaps the polysulfide products would become trapped within the dead volume of the electrode, hence prevented from escaping on the time-scale of the experiment.

6.4 Sulfolane/Ethylene Carbonate

6.4.1 Overview

A solvent of higher relative static permittivity ($\varepsilon_r$) allows greater dissolution of salts, since it shields the ion charges from each other. If the electrolyte solution contained high relative static permittivity solvents this might also shield charges of lithium polysulfide discharge products, hence allowing them to dissolve in solution. The aim is then to have free polysulfide ions in solution which might be more readily re-oxidised to sulphur. The new solvent system therefore made use of two high relative static permittivity solvents; sulfolane ($\varepsilon_r = 43$) and ethylene carbonate ($\varepsilon_r = 89$). Both of these also have high boiling points (285°C and 247°C respectively), which is useful for a high temperature battery. Initial investigations into the optimum ratios to mix the solvents yielded a 7:3 (w/w) mix of sulfolane to ethylene carbonate that remained liquid even when placed in a freezer at -7°C. This ratio of solvents was used when making a 1M LiCF$_3$SO$_3$ solution in sulfolane/ethylene carbonate. Later, a number of different mixes were made and analysed more precisely using DSC in order to discover the minimum melting point of the mixture. This was found to be approximately -25°C (the full results can be found in Appendix II).

Calendered electrodes were experimented with in addition to screen-printed electrodes. It was found that the use of high relative static permittivity solvents resulted in dissolution of the sulphur reduction products (polysulfides). This forced the recharge process onto a diffusional time scale, effectively making the sulphur cell irreversible. Some interesting peaks were noted however, when experimenting with calendered electrodes. Some discussion is provided regarding the nature of these peaks.
6.4.2 Discharge Voltage Comparison

Figures 6.10 and 6.11 show a comparison of discharge curves recorded when using sulphur/graphite screen-printed electrodes in both solvent systems discussed so far.

![Comparison of discharge curves](image)

Figure 6.10. Comparison of first discharges of screen-printed electrodes containing 8% sulphur in graphite ink in two different electrolyte solutions. Discharged at 2 mA/cm².
Despite the sulfolane/ethylene carbonate solvent system showing a lower discharge voltage than sulfolane/diglyme initially, it sustains a higher voltage in the latter stages of discharge. Figure 6.12 shows the increasing discharge time with increasing percentage sulphur.

Figure 6.11. Comparison of first discharges of screen-printed electrodes containing 14% sulphur in graphite ink in two different electrolyte solutions. Discharged at 2 mA/cm².

Figure 6.12. Comparison of first discharges of screen-printed electrodes with different amounts of sulphur. Run in 1M LiCF₃SO₃ in sulfolane/ethylene carbonate. Discharged at 2 mA/cm².
Discharge time increases with the increase in sulphur content. It is interesting to note that an electrode containing 64% sulphur has a lower starting (and discharging) potential than the other electrodes.

6.4.3 The Use of Cyclic Voltammetry

Using the new solvent system, a wider electrochemical window could be used. A blank electrode showed no faradaic electrochemistry over a voltage range of 2.5 V, as depicted in Figure 6.13.

![Voltammogram](image.png)

*Figure 6.13. Voltammogram of in-house graphite ink run in 1M LiCF₃SO₃ in sulfolane/ethylene carbonate. Scan rate 100 mV/s.*

The voltammograms were similar to those seen previously and also showed the system could be recharged on a fast time-scale, as seen in Figures 6.14 – 6.16. The scan rate in all cases was 100 mV/s.
Figure 6.14. Voltammograms of sequential scans of a screen-printed electrode containing 8% sulphur in graphite ink cycled in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at a scan rate of 100 mV/s.

Figure 6.15. Voltammograms of sequential scans of a screen-printed electrode containing 27% sulphur in graphite ink cycled in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at a scan rate of 100 mV/s.
Figure 6.16. Voltammograms of sequential scans of a screen-printed electrode containing 64% sulphur in graphite ink cycled in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at a scan rate of 100 mV/s.

The third scans of each electrode of different sulphur-loading have been overlaid to allow comparison. This is shown in Figure 6.17.

Figure 6.17. Third scans for screen-printed sulphur/graphite electrodes with different amounts of sulphur cycled in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at a scan rate of 100 mV/s.

The data indicate that using a sulphur level of 64% is not effective, as the peak currents are smaller than observed with the 27% sulphur electrode. Since only one sample of the electrode containing 64% sulphur was tested, further tests would be required to ensure the observed phenomenon was repeatable.
It is possible that 64% sulphur is too much to be fully accessed in a composite electrode. Low sulphur utilisation with high percentage sulphur levels has also observed by other researchers. For this reason no further experimentation was carried out using 64% sulphur.

6.4.4 Calendered Electrodes in Discharge Capacity Tests

The next step was to use Schlumberger WCP Ltd-type calendered sulphur/carbon electrodes, in an attempt to minimise the diffusion of reduction products away from the carbon surface, thus allowing recharging after discharge. It was hypothesised that the sulphur would be reduced within the dead volume of the carbon electrode, and the polysulfide discharge products would then be held within the dead volume. If using calendered Schlumberger WCP Ltd-type electrodes could prevent diffusion of polysulfide products away from the electrode surface then it might be easier to re-oxidise them back to sulphur. Accordingly, lithium sulphur cells were made using calendered carbon/sulphur electrodes, and lithium ribbon reference and counter electrodes.

For the electrode manufacture, some Shawinigan was substituted for powdered sulphur at the relevant percentage, and the dry components mixed. The addition of solvent and the remainder of the electrode manufacturing process were the same as described previously. As the working electrodes would now be tested inside stainless steel mesh envelopes (as in Li-SOCl₂ cells reported earlier), it was necessary to ensure this was not electrochemically active in this solution. Scanning a wide potential window using a ‘blank’ stainless steel electrode did not produce any significant electrochemical activity, as shown in Figure 6.18.
The currents measured from a blank stainless steel mesh envelope were very small; less than 1 mA. This did not interfere with analysis of sulphur/carbon electrodes.

Carbon black electrodes containing 14% and 27% sulphur by weight were calendered. A standard “L2” formulation (sulphur-free) was also run for comparison. Discharge voltage was measured versus Li/Li⁺ in the same electrolyte solution (1M LiCF₃SO₃ in sulfolane/ethylene carbonate), under 28.8 mA constant current.

It was first necessary to test how easily the extruded sulphur/carbon-black electrodes were wetted by the solution of 1M LiCF₃SO₃ in sulfolane/ethylene carbonate. Initially the electrode was not pre-soaked, but this clearly affected the discharge of the cell, as seen in Figure 6.19.
It is clear that pre-soaking the electrode affected both the discharge voltage and the discharge time. Practically, the lack of proper wetting meant that air was not readily displaced from the interior of the electrode when assembling the cell. Since L2 electrodes required soaking time, it suggested that the lack of 'wettability' was more connected with the carbon than with the sulphur. It was also interesting to observe that there was an unknown discharge reaction that supplied a stable discharge voltage of 1V. The nature of this process is unknown.

14% sulphur electrodes were then soaked in the cell solution for different periods of time, and the effect on the discharge curves was recorded. The results from a number of cells are shown in Figure 6.20, where voltage has been plotted against specific capacity, and R indicates the run number. The end-point of the discharge curves was determined either by the fall in voltage or by the run-time.
Despite the fact that all discharge curves seen in Figure 6.20 are from 14% sulphur electrodes, they appear quite different. Whether or not there is a substantial difference between soaking for 0.5 h (R2) or 3h (R3) is not clear, as the overall discharge curves appear quite different. Initially R2 sustains a higher voltage than R3, as the latter suffers from a delay (~1200 seconds) in reaching the expected discharge potential of ~ 2V. After about 3000 seconds the discharge voltage of R2 begins to fall, whereas the discharge voltage of R3 remains around 2V. Figure 6.21 highlights the problem of repeatability.

Figure 6.20. Discharge curves for L2 electrodes containing 14% w/w sulphur, soaked for different periods of time (indicated), discharged in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at 28.8 mA constant current.
Even two electrodes containing the same amount of sulphur, soaked for the same period of time give different results. The curve that begins with a peak in voltage is the one that maintains a longer discharge capacity.

An electrode containing 27% sulphur was also run in the same cell set-up. The specific capacity obtained on discharge is shown in Figure 6.22, where results from 14% sulphur have also been plotted to allow comparison. A constant current of 28.8 mA was used in all experiments and the discharge voltage was measured against Li/Li⁺ in the same electrolyte solution.
Figure 6.22. Effect of different sulphur loadings on the discharge curves. Electrodes discharged in 1M LiCF<sub>3</sub>SO<sub>3</sub> in sulfolane/ethylene carbonate at 28.8 mA constant current.

Seemingly, no extra capacity was gained by increasing the percentage sulphur from 14% to 27%. The reason for this is most likely to be due to low sulphur utilisation, and/or poor conductivity of the 27% sulphur electrode. Low sulphur utilisation would explain why the discharge curve appears so similar to that of L2 with 14% sulphur (no extra sulphur is being consumed). Poor conductivity might also play a role in preventing the entire electrode material from partaking in the reaction, thus limiting the capacity.

6.4.5 Discussion of Peak Observation

The rationale behind the observation of a peak in the discharge curve of R3 is unclear, but there are two possible explanations. Firstly, the peak might signify the existence of a passivating film on the lithium electrodes, which introduces a voltage delay. This is a known problem with other lithium batteries such as lithium thionyl chloride, but usually occurs after a period of storage. Although the lithium sulphur cells reported here have not been kept in storage prior to testing, the lithium electrodes might nevertheless develop a passivating film on their surface upon submerging into the electrolyte solution, and this could cause a brief voltage delay. In the case of lithium-sulphur work presented in this thesis, a passivation layer could be LiCF<sub>3</sub>SO<sub>3</sub>, since the triflate counter
ions are readily available in the electrolyte solution. However, the high relative static permittivity of the solvents might prevent the formation of this salt, since it is also the supporting electrolyte which has been dissolved in the solvent.

A passivation layer might also be formed by the breakdown of ethylene carbonate, via a ring-opening mechanism. This kind of behaviour was described by Kim et al., who claimed that a similar solvent stabilised the lithium surface by breaking down (via a ring-opening reaction) to form a layer upon the lithium [68]. These authors used 1,3-dioxolane and claimed that altering the proportions of different solvents resulted in alterations to polysulfide stability in solution.

The other possible explanation is that the peak indicates nucleation kinetics. The initial drop in voltage followed by a recovery in voltage is characteristic of a nucleation type process. In this particular case, the nucleation might be due to the uncovering of a large cluster of sulphur crystals, and could be explained as follows: voltage drops initially because only a small surface of the sulphur crystals is available to reduce, thereby sustaining the current required. As the reduction proceeds and sulphur is converted into polysulfide discharge products, voltage begins to fall. Following the reduction of all the exposed sulphur, a larger surface area of sulphur crystals is exposed. Now the voltage increases, as suddenly a large surface area of sulphur is available to reduce, and the system does not have to search for another reaction to sustain the required current. After the rise in voltage it stabilises, gradually dropping as the sulphur is consumed in the reduction reaction.

Since the observed peak was not present in all discharge curves it is difficult to satisfactorily assign one of the previous explanations to the cause of it. All explanations would imply that this phenomenon should be observed in all discharge curves, but in reality this was not the case.

6.4.6 Assessing Rechargeability

This section presents discharge profiles of the individual electrodes tested in Figures 6.23 – 6.26. The first and second discharges are compared for each electrode. 'R' denotes the run number of each electrode formulation. It is interesting to note that in all
cases there seem to be problems with either repeatability or recharging of the lithium sulphur cell, or a combination of the two.

Figure 6.23. Run 2 of an L2 14% sulphur electrode specimen discharged in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at 28.8 mA constant current.

Figure 6.24. Run 3 of an L2 14% sulphur electrode specimen discharged in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at 28.8 mA constant current.
The third specimen (in Figure 6.24) of the calendered electrode containing 14% sulphur (L2 14% R3) shows that even if the cell is not discharged to lower voltages (~ 1.5 V); the capacity still fades rapidly on the second discharge.

*Figure 6.25. L2 14% sulphur R4 discharged in 1M LiCF₃SO₃ in sulfolane/ethylene carbonate at 28.8 mA constant current.*

*Figure 6.26. Run 1 of an L2 27%S electrode specimen discharged in 1M LiCF₃SO₃ in sulfolane/ethylene carbonate at 28.8 mA constant current.*
Having increased the relative static permittivity of the solvent system to prevent insoluble lithium polysulfides from forming, it now seems likely that the polysulfide discharge products are completely dissolving, and hence are not available to oxidise back to sulphur.

6.4.7 Discussion

Overall, it is clear that there is a severe problem at the heart of the lithium/sulphur system. A solvent having a high relative static permittivity must be used to dissolve the supporting electrolyte, in order to maintain a low internal resistance inside the battery. At the same time, any solvent that has a high relative static permittivity also dissolves the products of the sulphur reduction process (polysulfides), which forces the recharge process onto a diffusional time scale. This unfortunate combination of characteristics has the effect of making the sulphur cell effectively irreversible.

Several strategies can be suggested for improving the performance of lithium sulphur cells. (i) One could possibly revert to lower relative static permittivity solvents (e.g. by using glymes), in order to render the polysulfides less soluble. However, this might be at the cost of lower electrolyte solubility and hence higher cell resistance. (ii) A saturated solution of supporting electrolyte might be tried, in order to depress the solubility of the polysulfides. This could have negative cost implications, however, and could also impact the conductivity of the solution, due to ion pair formation. (iii) The free volume of electrolyte solution might be drastically reduced. This might be accomplished by tightly compressing the cell components, so that any dissolved polysulfides would not have to diffuse very far in order to recharge. Unfortunately very high compression cells (such as coin cells) were not available for the present study.

6.5 A Compressed Cell

Attempts were made to manufacture a smaller (compressed) cell than previously used, in which the free volume of solvent in the cell could be drastically decreased. It should be noted that if extremely small volumes of solution are used this may result in solution starvation. In the present study, the original cell set-up was compressed by fitting both
the sulphur/carbon electrode and the lithium electrode into a glass sample vial. A filter paper was wrapped around and between the two electrodes, thereby holding them together but preventing them from touching each other. This cell used approximately one third of the solution previously used in larger cells. This small-cell was then tested in the same way as previously described for larger cells. The discharge profile is shown in Figure 6.27.

![Discharge profile](image)

**Figure 6.27.** Attempt to create a small cell to reduce the volume of solution required, such that the rechargeability might improve. 14% sulphur in a calendered electrode discharged in 1M LiCF₃SO₃ in sulfolane/ethylene carbonate at 28.8 mA constant current.

The specific capacity recorded for the compressed cell was almost 40 mAh/g. This is much lower than specific capacities recorded for larger cells, which approached values of 250 mAh/g. In addition, the problem of rechargeability was not solved by compressing the cell. This is shown by the relatively rapid failure of the cell during the second and third discharges.

After failure of the compressed cell the electrodes were removed from the filter paper wrapping and placed in the original, non-compressed three-electrode cell used in earlier work. Another attempt at discharging the cell was made, and found to be successful.
Figure 6.28 shows the same discharge profile seen in Figure 6.27 from the compressed cell, with the addition of the final discharge in the non-compressed cell.

![Graph](image)

*Figure 6.28. Discharge profile of the small, wrapped cell including the discharge curve recorded after being unwrapped and run as a normal cell, discharged in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at 28.8 mA constant current.*

Amazingly, despite the lack of capacity observed from the second and third discharges in the compressed-cell, a much larger specific capacity was recorded after placing the same electrodes in the non-compressed cell. It is possible that the filter paper used as a separator in the compressed cell restricted access of the electrolyte solution to the electrode surfaces. This may have been due to the close proximity of the filter paper, or due to trapped air bubbles between the filter paper and electrodes. Removal of the filter paper separator may have allowed better surface access, hence the capacity was improved.

The compression of the lithium sulphur cell in the present study did not prove to be a successful method of improving rechargeability of the cell. This was probably due to an inappropriate separator and cell set-up.
6.6 Tetraglyme/1,3-Dioxolane

6.6.1 Overview

Having discovered problems with recharging of the lithium sulphur cell using (1) a sulfolane/diglyme solvent system and (2) a sulfolane/ethylene carbonate solvent system, experiments were then conducted in a third solvent system. This mixed solvent system comprised a 1:1 mixed system of tetraglyme and 1,3-dioxolane (refer to page 160 for further details). The electrolyte was not changed (1M LiCF$_3$SO$_3$). Since this solvent system had been investigated by previous researchers, it was of interest to use it to assess rechargeability of the novel calendered electrodes described in the present study. The calendered 14% sulphur electrodes were tested in the same way as previously described.

6.6.2 Discharge Capacity Tests

As Figure 6.29 shows, stainless steel mesh was stable in 1M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane. Although some electrochemical activity was seen at voltages below 2.4 V, the currents were very small (-0.2 mA) and were masked by sulphur redox chemistry.
Figure 6.29. Cyclic voltammogram of stainless steel mesh, scanned at a rate of 10 mV/s in 1M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane.

Figure 6.30 shows some of the discharge curves of sulphur/carbon electrodes containing 14% sulphur run in 1M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane. Discharge was terminated when the discharge potential fell below 1.6 V. Potential has been plotted against fractional specific capacity, and several discharge curves were recorded from the same cell, indicating successful recharging of the cell.

Figure 6.30. Specific capacities measured for some discharges of 14% sulphur L2 electrodes in 1M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane at 28.8 mA constant current.
Figure 6.30 shows that the cell was recharged, since several discharge curves could be recorded. This is in stark contrast to the discharge curves recorded when discharging a 14% sulphur calendered electrode in sulfolane/ethylene carbonate (Figure 6.23). This means that the reduced material was re-oxidised successfully in the tetraglyme/1,3-dioxolane cell solution.

Figure 6.31 shows the total number of discharge curves recorded from this experiment, where potential has been plotted against time. For ease of comparison, discharge curves 1 – 5 have been cut-off at the same time, so that the differences in discharge potential may be observed clearly for all curves. As the number of discharges increased, the discharge was allowed to run to lower voltages, and thus in some cases the voltage cut-off point was lowered to 1 V.

It is not clear why the discharge potentials of the fourth and fifth discharges are slightly higher than the preceding discharges. It is clear that after the seventh discharge the cell could no longer be recharged.
Unlike some of the discharge curves observed from the sulfolane/ethylene carbonate system (Figure 6.21), there was no sign of any possible voltage delay/nucleation behaviour in this solvent system.

The discharge experiments were run again, using a fresh electrode. The resulting discharge profile is shown in Figure 6.32. The first discharge was run to a cut-off potential of 1.6 V. Subsequent discharge curves were run to 1.5 V.

![Fractional Specific Capacity vs. Discharge](image)

**Figure 6.32.** Fractional specific capacity for some discharge curves from Figure 6.32. *Note the decreasing value of discharge potential with increasing discharge number.*

The results shown in Figure 6.32 show that the discharge potential decreases with the increasing number of discharges. Overall, the discharge potentials observed (even for the first discharge) are significantly lower than those observed in Figure 6.30.

Figure 6.33 shows the discharge profile from Figure 6.32 with the final discharge curve overlaid. The discharge potential fell very quickly during the fifth discharge, and thus the experiment was allowed to run to 1 V to allow observation of the end of the cell life.
The lithium sulphur cell has successfully been recharged, as can be observed by the recording of at least four discharge curves running at a discharge potential of >1.5 V. However, both discharge potential and specific capacity decrease with each subsequent discharge.

It should be noted that there is a very clear difference in the discharge potentials of the cell tested in Figure 6.30 (R2) and the cell tested in Figure 6.32 (R3). This is depicted more clearly in Figure 6.34, which shows the beginning of the discharge only. L2 14%S R2 maintains a comparatively high potential whilst L2 14%S R3 falls rapidly in discharge potential (and hence reaches the cut-off point sooner). This indicates a problem with repeatability of lithium sulphur cell performance.
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0 10 20 30 40 50 60
Fractional Specific Capacity / mAh/g

L2 14% S R2
L2 14% S R3

Figure 6.34. A comparison of the first discharge curves for R2 and R3 when tested under the same conditions. Note the lower discharge potential for run 3 of L2 14\% sulphur.

It is also interesting to observe that the starting potential was lower for R3 than for R2. It is difficult to explain why this is the case, since both electrodes contained the same sulphur loading, and were tested in the same solution, against a lithium electrode.

6.6.3 Discussion

The lithium sulphur cell containing calendered sulphur/carbon electrodes has been successfully recharged in the tetraglyme/1,3-dioxolane solvent system to some extent. This shows some future promise for the use of novel, thick film calendered electrodes in such cells.

6.7 An SEM Study of Sulphur/Carbon Electrodes in Lithium Sulphur Cells

SEM images were taken of a sulphur/carbon electrode with 14\% sulphur loading before and after a discharge capacity test. Images were also taken of a sulphur/carbon electrode in which the sulphur had been melted in an oven at 200\degree C and then cooled. It was of interest to observe how the sulphur became redistributed throughout the carbon matrix.
Firstly a sulphur/carbon electrode containing 14% sulphur prior to testing is shown in Figure 6.35. The white areas indicate poorly conducting material.

Figure 6.35. A 14% sulphur L2 electrode before testing. The scale bar is 1 μm. This image appears very similar to previously seen images of carbon black electrodes (for example, in Figure 1.03).

Figure 6.36 shows an electrode of the same type, after being run in a discharge capacity test in 1 M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane.
The aggregates of carbon have now been covered. Due to the electrostatic charging of this film during SEM it is likely that this substance is poorly-conducting. This suggests it could be made up of sulphur and/or polysulfides. These discharge products appear to have covered the electrode surface in a film.

Figures 6.37 and 6.38 show two different images of a sulphur/carbon electrode which had been in an oven at 200°C. This electrode therefore contains sulphur that has melted and re-crystallised inside the electrode. These images are very different to the discharged electrode image.
Figure 6.37. A sulphur/carbon electrode in which sulphur had been melted and re-crystallised. The scale bar is 1 μm. Note the large agglomerates that appear distinct from the other carbon black clusters.

Figure 6.38. Another image of a sulphur/carbon electrode in which sulphur had been melted and re-crystallised. The scale bar is 1 μm. Note the unusual structures on the electrode surface.

These images are not the same as those from a discharged electrode. In the latter, a film appears to cover the carbon aggregates. In the melted sulphur electrode, carbon
aggregates can still be seen, and so the melted sulphur did not distribute itself over the entire surface area. It is known that sulphur crystals can change in size and shape after being melted, and indeed some interesting crystals may be observed in the SEM images.

6.8 Closing Discussion and Overall Findings

A three-electrode test cell was developed for the screening of calendered porous carbon electrodes in different solvent systems. This allowed single electrode discharge curves to be recorded.

In the sulfolane/diglyme system screen-printed electrodes were successfully cycled on a fast scan rate during cyclic voltammetry experiments. In discharge experiments on the other hand, it was found that the cell could not be recharged. It was thought that insoluble lithium polysulfide products might be forming, thus rendering the re-oxidation reaction impossible.

In the sulfolane/ethylene carbonate system it was hoped the increased relative static permittivity would allow dissolution of lithium polysulfide salts, thus allowing re-oxidation of polysulfides. However, recharging of the cell could still not be achieved in discharge capacity experiments.

In the tetraglyme/1,3-dioxolane solvent system recharging of the cell was achieved for several cycles.
Results and Discussion: Carbon Electrodes for Electrochemical Capacitors

7.1 Overview

Globally there is a need for storing large quantities of energy [1] [6]. Current research efforts continue to search for more efficient and cost-effective ways of solving this problem. In the present study the possibility of using carbon-based electrochemical capacitors has been explored. A number of carbon materials were used to make ‘Schlumberger WCP Ltd type’ calendered electrodes (as previously described in this thesis). Carbon blacks were found to perform significantly better than activated carbons when used in thick film electrodes (film thickness > 3 mm). This was attributed to their distinctive morphology and high dead volume allowing better surface access. The best performing carbon black had a specific capacitance of 38 F/g at a thickness of 3.5 mm.

The present study has shown that carbon blacks are excellent candidates for electrodes to use on next generation, large scale devices for energy storage. This concept may also be of interest to Schlumberger WCP Ltd, as electrochemical capacitors might be incorporated into lithium-thionyl chloride battery packs to provide power during voltage delay.
7.2 Comparison of Activated Carbon and Carbon Black Morphologies

In the fabrication of electrodes for industrial electrochemical capacitors, the material of choice is usually activated carbon. This is because activated carbon contains large numbers of pores that confer a high surface area on the finished product. An example of this is illustrated by the SEM image in Figure 7.01, where some of the larger pores can be observed.

Figure 7.01. Some of the larger pore openings in a granule of activated carbon from an electrode sample. The scale bar is 200 nm.

A lower magnification SEM image of activated carbon is presented in Figure 7.02. This activated carbon is DLC Supra 30; a material recommended by manufacturers (Norit) for use in electrochemical capacitor electrodes. Here the individual particles of activated carbon can be observed. They are irregularly shaped and have rough edges and surfaces.
Figure 7.02. An SEM image showing the rough particles of DLC Supra 30. The scale bar is 1 μm.

In contrast with the image of activated carbon, SEM images of some carbon blacks are shown in Figures 7.03 – 7.04. Carbon blacks form aggregates, which in turn form agglomerates. These are made up of clusters of carbon black particles, sometimes referred to as ‘strings of pearls’.

Figure 7.03. An SEM image of the carbon black aggregates/agglomerates of a Ketjenblack 300J electrode. The scale bar is 1 μm.
In the present study carbon blacks were tested as electrode materials for electrochemical capacitors. Electrodes were made according to the method previously described in this thesis, such that a number of thick film calendered electrodes were created using different carbon blacks. It is necessary to distinguish these electrodes from the thin film electrodes used in present-day electrochemical devices. The aim was to experiment with thick film electrodes to see if they could provide high capacitance. These thick film electrodes might then be useful for large electrochemical devices. Such devices could play a significant role in future applications for energy storage and energy management on industrial sites.

7.3 The Use of Cyclic Voltammetry

A number of different carbon blacks were investigated using cyclic voltammetry. Each was tested in two different aqueous systems; 1M H₂SO₄ and 1M KCl. Samples of the carbon black electrodes were also tested in a solution of 1M LiCF₃SO₃ in sulfolane/ethylene carbonate. Organic solvents are generally stable over a much wider
potential window than aqueous solutions. It was found that thick film carbon electrodes could be cycled over a 0.4 V window in aqueous systems and over a 1 V window in the organic system. The scan rate in all cases was 2 mV/s.

### 7.3.1 Capacitance Measurement

Eight different types of carbon black were used, namely: Black Pearls 2000 (BP2), Ensaco 250P (E2), Ensaco 350GR (E3), Ketjenblack 300J (Kb), Regal 400R (R4), Soltex 50% compressed (S3), Soltex 75% compressed (S2) and Soltex 100% compressed (S1). In aqueous solutions the working electrodes were cycled against a Saturated Calomel Electrode (S.C.E) with a platinum gauze counter electrode. In organic solvents, separate strips of lithium metal served as reference and counter electrodes. Two specimens of each electrode were tested, and some of the voltammograms obtained are shown in Figures 7.05 – 7.08, where specific current density \( i \), has been plotted against potential \( E \).

![Figure 7.05. Black Pearls 2000 electrodes cycled in 1M H_2SO_4 at a rate of 2 mV/s. The voltammograms are very close to overlapping each other, indicating good repeatability.](image)

\[ E / V \]

\[ i / \text{mA g}^{-1} \]

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Figure 7.06. Black Pearls 2000 electrodes cycled in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate at a rate of 2 mV/s. Note the increased IR drop altering the voltammogram shape.

Figure 7.07. Ketjenblack 300J electrodes cycled in 1M H$_2$SO$_4$ at a rate of 2 mV/s. The voltammograms are very close to overlapping each other, indicating good repeatability.
There is a significant difference in the cyclic voltammograms recorded in aqueous and non-aqueous solutions. In the latter there is more \textit{IR} drop, as can be seen by the slope of the voltammograms.

All forty-eight results are collated in Figure 7.09, where the mean specific capacitance of each electrode in each solution is plotted in a three dimensional bar chart.
Specific Capacitance (F g\(^{-1}\))

H\textsubscript{2}SO\textsubscript{4} aq
KCl aq
LiCF\textsubscript{3}SO\textsubscript{3} organic

Figure 7.09. The specific capacitances for different carbon blacks in three different electrolyte solutions (collation of 48 individual experiments). The carbon blacks are: Soltex 100% compressed (S1), Soltex 75% compressed (S2), Soltex 50% compressed (S3), Enscao 250P (E2), Regal 400R (R4), Ensaco 350GR (E3), Ketjenblack 300J (Kb) and Black Pearls 2000 (BP2).

Note that the trend of which carbon materials give higher specific capacitances is not always the same. The best-performing system was Black Pearls 2000 in aqueous sulphuric acid (38 F/g). In the novel lithium triflate solution, it was found that the best-performing carbon black was Ketjenblack 300J (the mean result was 14 F/g, although this was poorly reproducible; experimental values ranged from 8 to 19 F/g. Black Pearls 2000 was next best, with 10 F/g).

7.3.2 Explanation of Capacitances Measured

It is expected that the capacitances measured will be different for each carbon black, since each carbon black has a different surface area. Figure 7.10 shows that there is a good correlation between measured capacitance and carbon black B.E.T surface area in aqueous sulphuric acid.
This strong correlation suggests that the full surface area of the carbon has been accessed by the protons, thus allowing maximum capacitance to be measured. However, since the trends in measured capacitance in Figure 7.09 are different for each electrolyte solution, there must be other phenomena to consider. The usual explanation for this difference in trends in activated carbon electrodes is that ‘size filtration’ takes place inside the micropores. This cannot explain the different responses from carbon blacks, as they lack microporosity. There may be different amounts of interaction between ions in solution and functional groups (such as carbonyls and phenols) on the carbon surface. This would provide additional pseudocapacitance to the measured double layer capacitance, and could explain the changing trends in measured capacitance.

The reason that much larger capacitances can be measured using aqueous sulphuric acid is explained by the unique behaviour of the proton. H\(^+\) tends to protonate water in a solution of H\(_2\)SO\(_4\), forming H\(_3\)O\(^+\). This allows the proton to effectively travel very quickly through solution, exhibiting a type of tunnelling behaviour known as ‘proton-hopping’, attributed to von Grotthuss [32] [111]. This accounts for its comparatively fast penetration of pores and voids, and hence the measurement of comparatively large specific capacitances.
7.3.3 Energy Storage

The voltage window has a profound impact upon the energy $E$ (measured in Joules) stored in an electrochemical capacitor material:

$$E = CV^2$$

where $C =$ capacitance (F) and $V =$ voltage (V). Clearly, a wider potential window will increase the energy that can be stored.

The energies from the previously shown carbon electrodes in each of the three solvents have been calculated. The data are presented in Figure 7.11.

![Figure 7.11. The specific energies for different carbon blacks in three different electrolyte solutions (collation of 48 individual experiments). The carbon blacks are: Soltex 100% compressed (S1), Soltex 75% compressed (S2), Soltex 50% compressed (S3), Ensaco 250P (E2), Regal 400R (R4), Ensaco 350GR (E3), Ketjenblack 300J (Kb) and Black Pearls 2000 (BP2).](image)

Note that the order of ‘best performance’ has now changed. The LiCF$_3$SO$_3$ (org) system allows for much more energy storage in carbon materials than the aqueous systems. This is due to the wider voltage window available for the organic solvents, and is true for all carbon materials tested.
7.3.4 Comparison with L2

It was also of interest to compare the performance of an L2 electrode with other carbon blacks. Recall that an L2 electrode is one made according to the Schlumberger formulation (1:4 ratio of Ketjenblack 300J to Shawinigan) and is calendered into a thick film electrode. This formulation has been widely used in previous sections of the thesis, and represents Schlumberger WCP Ltd’s standard electrode mix. The three-dimensional bar chart for specific capacitance is reproduced in Figure 7.12 with the addition of the L2 experiments. Each of the bars represents the average specific capacitance of two samples tested.

![Figure 7.12. The specific capacitances for different carbon blacks and L2 in three different electrolyte solutions. The carbon blacks are: Soltex 100% compressed (S1), Soltex 75% compressed (S2), Soltex 50% compressed (S3), Ensaco 250P (E2), Schlumberger standard formula (L2), Regal 400R (R4), Ensaco 350GR (E3), Ketjenblack 300J (Kb) and Black Pearls 2000 (BP2).](image)

In both aqueous systems the capacitance of L2 is relatively low, and it falls in between Ensaco 250P (E2) and Regal 400R (R4). In the organic system however, the capacitance of L2 is higher than both of these carbon blacks and is closer in performance to Ensaco 350GR (E3). This appears to be an anomalous result, which is further magnified when comparing values of specific energy, as seen in Figure 7.13.
Further tests using an L2 electrode in this particular solution would be required to obtain a better measurement of its true performance.

Overall, the L2 electrode showed an intermediate performance in comparison with the other carbon black electrodes. If Schlumberger WCP Ltd required an electrochemical capacitor device to support their lithium thionyl chloride batteries they might be able to use the same electrodes. However, this would depend on the amount of energy required from such a device.

### 7.4 Comparison of Activated Carbon and Carbon Black Capacitances

#### 7.4.1 Screen-Printed Electrodes

After measuring capacitances of numerous carbon blacks, the capacitances of two activated carbons were then measured. Those selected were:

![Figure 7.13. The specific energies for different carbon blacks and L2 in three different electrolyte solutions. The carbon blacks are: Soltex 100% compressed (S1), Soltex 75% compressed (S2), Soltex 50% compressed (S3), Enscao 250P (E2), Schlumberger standard formula (L2), Regal 400R (R4), Ensaco 350GR (E3), Ketjenblack 300J (Kb) and Black Pearls 2000 (BP2).]
Elorit; an activated carbon recommended by Norit for the manufacture of dry-cell batteries. It has a B.E.T surface area of 700 m$^2$/g.

DLC Supra 30; an activated carbon specifically recommended by Norit for the manufacture of double layer capacitors. It has a B.E.T surface area of 1900 m$^2$/g.

Initially, each activated carbon was ball-milled into a viscous paste with a solvent and binder. These mixtures were then screen-printed, cured, and finally cycled voltammetrically in 1 M H$_2$SO$_4$ at a scan rate of 2 mV/s. On the (reasonable) assumption that the screen-printed layers were of the same thickness (since the same experimental conditions were used), the DLC Supra 30 was found to have a capacitance approximately twice that of the Elorit. This can be seen in Figure 7.14.

![Figure 7.14. Cyclic voltammograms of different screen-printed activated carbons in 1 M H$_2$SO$_4$ at 2 mV/s. Note the comparatively better performance of DLC Supra 30.](image)

Interestingly, this difference in capacitances is in the same ratio as their B.E.T surface areas, once again implying a correlation between B.E.T surface area and electrochemical capacitance. (This is analogous to the case of the carbon blacks shown in Figure 7.10.)

In the case of the screen-printed activated carbons it would have been useful to measure their specific capacitances to a high degree of accuracy. Unfortunately this was ruled
out by the difficulties of weighing ultra-thin screen-printed layers, which required a highly precise balance. Nevertheless, based on a statistical sample of electrodes (eight samples), it was estimated that the median specific capacitance of DLC Supra 30 electrodes was in the region of $65 \pm 15 \, \text{F/g}$. This was significantly greater than the specific capacitance of the best carbon-black electrodes (Black Pearls 2000) which was only $38 \, \text{F/g}$. Thus, DLC Supra 30 out-performed all the carbon blacks when used in the thin-film geometry. However, this did not mean that carbon blacks were unworthy of study as thick-film electrodes, because their higher dead volume might have given them some advantages in that case.

Before turning to thick film electrodes, it is necessary to briefly discuss the attempts made to screen-print Black Pearls 2000. Disappointingly, this material was poorly adherent due to its propensity to form agglomerates. This is shown in Figure 7.15. For comparison, the equivalent image of highly adherent DLC Supra 30 is shown in Figure 7.16. DLC Supra 30 does not form agglomerates since the activated carbon grains do not aggregate. The reason that activated carbon particles do not aggregate could be explained by the size of the particles. The activated carbon particles in Figure 7.02 are much larger than the carbon black particles in Figure 7.03 (page 184), and this may prevent attractive interactions that lead to aggregate formation.

![Figure 7.15. Black Pearls 2000 as a thin film electrode (screen-printed). The formation of agglomerates prevents an even surface coverage.](image)
It is clear that the Black Pearls 2000 has not adhered to the surface in an even layer, and has therefore not been screen-printed successfully as a thin-film electrode.

### 7.4.2 Calendered ‘Thick Film’ Electrodes

The standard method of preparing thick-film electrodes in the present study was to calender them (to press between rollers) in order to ensure consistent electrode thickness. Two different electrode thickness were used for activated carbon calendered electrodes; 4.5 mm and 1.7 mm. These were about 100 times thicker than the screen-printed electrodes discussed in Section 7.4.1. One advantage of using such thick electrodes was that their mass was very easy to measure. In a typical experiment, 1.2 × 1.2 cm areas were cut from a calendered sheet, and weighed using an ordinary laboratory balance. These were then attached to screen-printed substrates using a conductive carbon ink. An S.E.M image of the finished product (DLC Supra 30) is shown in Figure 7.17.
Figure 7.17. DLC Supra 30 as a thick film electrode (calendered).

Electrochemically, calendered thick-film electrodes were cycled in 1M H$_2$SO$_4$ over a range of 0.4 V, at a scan rate of 2 mV/s. Some typical results are shown in Figures 7.18 – 7.19, where specific currents have been plotted on the vertical axis. Voltammograms from four samples of each type of electrode are shown.

Figure 7.18. A repeatability test; voltammograms from cycling four different samples of 4.5 mm thick calendered DLC Supra 30 electrodes in 1M H$_2$SO$_4$ at 2 mV/s.
Figure 7.19. A repeatability test; voltammograms from cycling four different samples of 1.7 mm thick calendered DLC Supra 30 electrodes in 1M H₂SO₄ at 2 mV/s.

Despite normalisation of the currents recorded the data remain poorly repeatable. This may be due to the different extents of penetration of the electrode by the solution. Corroborative evidence in favour of this hypothesis is that the specific currents observed from the 1.7 mm electrodes are about three times greater than the specific currents from the 4.5 mm electrodes, suggesting that deeper levels of thicker electrodes are simply not responding. Likewise, the average specific capacitances are 6 F/g for the 1.7 mm electrodes and 2 F/g for the 4.5 mm electrodes. This implies that only the outer layer of the thick-film electrodes is actually reacting; below that the electrode is ‘dead’. Overall it may be concluded that solution penetration of thick-film electrodes is strongly inhibited in the case of activated carbons.

No such limitations are observed in the case of carbon blacks. For example, Black Pearls 2000 far out-performs DLC Supra 30 in the thick-film geometry, as seen in Figure 7.20. This is a major discovery, because it suggests that carbon blacks can form the basis of a new generation of electrochemical capacitors for bulk energy storage.
Figure 7.20. A comparison of DLC Supra 30 and Black Pearls 2000 specific currents recorded during cyclic voltammetry in 1M $H_2SO_4$ at 2 mV/s.

Analogous results for Ketjenblack 300J (which is a standard material used in Schlumberger battery electrodes) are shown in Figure 7.21. Remarkably these electrodes are perfectly serviceable as electrochemical capacitor electrodes for bulk energy storage, although they were not quite the best ones discovered.

A comparison of the average values of specific capacitances of a variety of carbon blacks is shown in Figure 7.22. It is clear they out-perform DLC Supra 30 in this thick-
film geometry. Since Black Pearls 2000 has the highest specific capacitance in the present study, it is recommended that this material should form the basis of next-generation thick-film electrodes.

![Graph showing specific capacitance comparison]

*Figure 7.22: A comparison of average values of specific capacitance of DLC Supra 30 and some carbon blacks measured in 1M H$_2$SO$_4$ at 2 mV/s.*

The large capacitance differences between the activated carbon DLC Supra 30 and high surface-area carbon blacks can probably be explained by the very different morphologies of activated carbon and carbon black. Since activated carbon is a highly porous material it takes time for ions in solution to diffuse into the pores and access all the surface area. Carbon blacks on the other hand have high dead volume, created by the spaces in-between aggregates and agglomerates. Since the inter-agglomerate distances are hundreds of nanometres wide they by far exceed the largest pore diameters in activated carbon. This permits rapid ingress of ions, thus allowing more rapid and easy access to the available surface area.

### 7.5 The Addition of Carbon Fibres

#### 7.5.1 Addition of Carbon Fibres to Activated Carbon Thick-Film Electrodes

In an attempt to overcome the poor utilisation of DLC Supra 30 activated carbon in the calendered thick-film electrodes, 10 wt.% of chopped carbon fibre was added to the
electrode mixture before rolling out. The activated carbon and the fibres did not calender very well, giving a very uneven surface, but the product was nevertheless mechanically strong. The final average thickness was 3.9 mm. The electrodes were tested in the same way as previously described, and some typical voltammograms are shown in Figure 7.23. Remarkably, the voltammograms repeated each other very well.

Figures 7.24 - 7.25 show these same voltammograms overlaid on top of voltammograms obtained without carbon fibre. It can be seen that the specific capacitance of the fibrous electrodes is much larger than the specific capacitances of the non-fibrous electrodes, doubtless because the fibres have created a more open electrode structure. It is very unlikely that the carbon fibres could have affected the internal structure of the activated carbon, but they certainly help to produce a better internal structure of the electrode as a whole.
Figure 7.24. A comparison of fibrous DLC Supra 30 electrodes with non-fibrous 4.5 mm thick DLC Supra 30 electrodes cycled in 1M H$_2$SO$_4$ at 2 mV/s.

Figure 7.25. A comparison of fibrous DLC Supra 30 electrodes with non-fibrous 1.7 mm thick electrodes cycled in 1M H$_2$SO$_4$ at 2 mV/s.

A comparison of the average specific capacitances obtained from each type of DLC Supra 30 electrode is shown in Figure 7.26.
Figure 7.26. A comparison of the average specific capacitances measured in 1M H$_2$SO$_4$ of DLC Supra 30 4.5 mm thick, 1.7 mm thick and DLC Supra 30 made with 10% fibres.

Figure 7.26 clearly shows that the average specific capacitance of the fibrous electrodes is much larger than the specific capacitances of the non-fibrous electrodes. The fibres create a more open electrode structure, which allows better ingress of electrolyte solution. Thus, it is discovered that carbon fibres help to produce a better internal electrode structure in this case.

7.5.2 Addition of Carbon Fibres to Carbon Black Thick Film Electrodes

Having observed an increase in specific capacitance when chopped carbon fibres were added to activated carbon electrodes, investigations were next undertaken to establish what effect (if any) the addition of chopped carbon fibre might have on the carbon electrodes used in this study. A smaller effect was predicted, because it was clear that carbon black electrodes were already operating close to their maximum performance. Nevertheless it was of interest to see what might happen.

For carbon blacks such as Ketjenblack 300J and Shawinigan the fibrous and non-fibrous thick-film electrodes were virtually indistinguishable (Figures 7.27 and 7.28, where ‘F’ denotes the fibrous electrodes). However for Black Pearls 2000 the thick-film electrodes showed much improved rise times (i.e. the electrode time constant $\tau$ was significantly decreased). This is shown in Figure 7.29.
Figure 7.27. Voltammograms from cycling fibrous and non-fibrous Ketjenblack 300J electrodes in 1M H$_2$SO$_4$ at a scan rate of 2 mV/s, versus an S.C.E reference electrode. The counter electrode was a platinum gauze electrode. All voltammograms appear similar.

Figure 7.28. Voltammograms from cycling fibrous and non-fibrous Shawinigan electrodes in 1M H$_2$SO$_4$ at a scan rate of 2 mV/s, versus an S.C.E reference electrode. The counter electrode was a platinum gauze electrode. The voltammograms almost map each other.
Figure 7.29. Voltammograms from cycling fibrous and non-fibrous Black Pearls 2000 electrodes in 1M H$_2$SO$_4$ at a scan rate of 2 mV/s, versus an S.C.E reference electrode. The counter electrode was a platinum gauze electrode. Note the improvement in the rise times (RC time constants) with the addition of carbon fibres.

Since the rise time $\tau$ was the product of resistance $R$ and capacitance $C$, and since $C$ was actually slightly larger in the presence of fibres, it followed that the smaller value of $\tau$ was due to a smaller value of $R$. In other words, the addition of the carbon fibres improved both the capacitance and the conductivity of thick-film electrodes of Black Pearls 2000. A summary graph of the effects of chopped carbon fibre on the specific capacitances of thick-film electrodes is shown in Figure 7.30. It is concluded that the chopped carbon fibres can significantly improve the internal accessibility and conductivity of some carbon black electrodes (but not all).
Finally, in Figure 7.31 the best-performing thick-film electrodes made from a carbon black (Black Pearls 2000) are compared with the best-performing thick-film electrodes made from activated carbon (DLC Supra 30). Both are in the presence of 10 wt.% chopped carbon fibres. Once again it can be observed that Black Pearls 2000 outperformed its rival.

**Figure 7.30.** Average specific capacitances measured in 1M H$_2$SO$_4$ for fibrous and non-fibrous carbon black electrodes.

**Figure 7.31.** A comparison of fibrous DLC Supra 30 and Black Pearls 2000 electrodes, all cycled in 1M H$_2$SO$_4$ at 2 mV/s.
Some SEM images were taken before and after cycling a fibrous Black Pearls 2000 electrode in 1M H$_2$SO$_4$. Over 200 cycles of this electrode were carried out, while the capacitance remained constant. Figures 7.32 – 7.33 show low magnification images of the electrode before and after cycling. Clearly there is not much difference between the specimens as a result of cycling.

Figure 7.32. SEM image of a fibrous Black Pearls 2000 electrode before cycling. The scale bar is 100 μm. Note the carbon fibres running across and in-between carbon agglomerates.
Figure 7.33. SEM image of a fibrous Black Pearls 2000 electrode after cycling. The scale bar is 100 μm. Note the fibres are still holding carbon agglomerates together, and providing electrical pathways throughout the electrode.

7.7 Gelled Electrolyte Solution

Gelling electrolyte solutions can be an effective way of improving safety of electrochemical devices containing potentially harmful solvents. In the event of accidental cell damage it would be preferable to have harmful solvents trapped within a gel network. This reduces the exposure of personnel to the harmful effects of the solvents.

A number of attempts were made to gel the novel lithium triflate/organic solvent electrolyte solution using polyvinylidene fluoride (PVDF). Eventually a successful gelled solution was obtained using 10 wt.% PVDF and a combination of ball-milling and heating. This procedure was used to create a gelled electrolyte solution around an L2 electrode adhered to a screen-printed substrate. A representation of this working electrode is shown in Figure 4.13 (page 104).

The aim of creating such working electrodes was to test whether the capacitance measurements would be similar to non-gelled working electrodes. Gelled calendered,
thick-film electrodes were tested in cyclic voltammetry experiments, run in 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate. It was not known if these electrodes would still require some pre-wetting with acetonitrile. Since time had been allowed for hot PVDF gelled electrolyte solution to ingress into the electrode dead volume before cooling, it was hoped pre-wetting would not be required. Figure 7.34 shows a voltammogram obtained from one gelled electrode that was pre-wetted, and one that was tested without pre-wetting.

![Figure 7.34: Cyclic voltammograms obtained from testing L2 electrodes in PVDF-gelled 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate. Scan rate 2 mV/s.](image)

Pre-wetting with acetonitrile did not affect the electrochemical performance of the gelled L2 electrodes. Figure 7.35 shows a comparison between a typical non-gelled L2 electrode and a typical PVDF-gelled L2 electrode.
The pseudo-steady state currents of gelled and non-gelled L2 electrodes are very close in value. The rise times (the $RC$ time constants) are very different, however. The PVDF-gelled L2 electrode has a larger rise time than the non-gelled L2 electrode, indicating that the resistance has increased. Nevertheless, the present study proved that ‘Schlumberger WCP Ltd-type electrodes’ can be successfully gelled using PVDF. This is an important discovery, as it could form the basis of further work to develop gelled electrolyte solutions for practical devices. Indeed, it is a good indication that safer devices might be produced in the future.

7.8 Closing Discussion and Overall Findings

Overall, the specific capacitance and specific energy of carbon black materials such as Black Pearls 2000 and Ketjenblack 300J greatly exceeded that of the activated carbon (DLC Supra 30) in thick film electrodes. This is a very important discovery, and should have significant impact on the design of electrodes for next generation electrochemical capacitor devices.
The inclusion of chopped carbon fibres in a DLC Supra 30 electrode produced a substantially increased specific capacitance. However, this specific capacitance was still not as large as that of Black Pearls 2000.

Inclusion of fibres in some carbon black electrodes did not seem to have a very noticeable effect on specific capacitance. The capacitance of Black Pearls 2000 was increased slightly with the inclusion of fibres. However, more notable was the improvement in the $RC$ time constant, $\tau$. This indicated that the fibres decreased the resistance within the electrode.

Additionally it was noted that thinner calendered DLC Supra 30 electrodes had a higher specific capacitance than thicker calendered electrodes. This is interesting, since such a disparity in specific capacitance was not observed in calendered carbon black electrodes. This could mean that electrolyte solution can penetrate all the available space, even in a thick carbon black electrode, but not in an activated carbon electrode.

PVDF-gelled L2 electrodes were successfully cycled. However, the resistance was somewhat elevated by the inclusion of the gel, and this is not desirable.
8 Conclusions and Further Work

This thesis has described a materials electrochemistry approach to solving problems with lithium thionyl chloride batteries, lithium sulphur batteries, and carbon-based electrochemical capacitors. Work carried out on all of these cells has made use of ‘thick film’ carbon electrodes prepared by calendering or extrusion. The most important discoveries are as follows:

♦ Carbon electrodes manufactured for use in lithium thionyl chloride batteries tend to crack during manufacture. Carbon fibres may be added to the electrode mix to improve electrode strength and flexibility whilst not diminishing specific capacity. Schlumberger WCP Ltd are currently interested in this idea, and have made prototype cells on site with fibrous electrodes.

♦ The quantity of isopropyl alcohol (IPA) currently used in the electrode manufacturing process approaches UK/EU regulations. It has been proved that the volume of IPA needed for the electrode manufacturing process can be halved without affecting electrode microstructure or specific capacity. This has very important implications for environmental impact and has enabled manufacturing to continue.

♦ Enhanced performance of lithium-sulphur cells was not achieved, as the novel sulphur/carbon electrodes combined with the novel electrolyte solutions still suffered from the widely acknowledged problem of non-rechargeability.

♦ The possibility of using carbon electrodes for industrial-scale electricity storage devices was explored. Surprisingly, it was discovered that some carbon blacks have a far superior specific capacitance to industry-recommended activated carbons when used in thick film electrodes. As such they are excellent candidates for next generation energy storage devices.

♦ A novel electrolyte solution (1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate) was successfully gelled using polyvinylidene fluoride. A working electrode submerged in
this gel and tested electrochemically was found to perform almost as well as a non-gelled electrode.

Throughout this thesis, ‘thick film’ electrodes have been experimented with for use in three different electrochemical devices.

Lithium thionyl chloride batteries are one of the world’s best primary batteries. There is a serious problem during manufacture due to the tendency of the carbon electrodes to crack. This problem has been solved in the present study by the addition of carbon fibres to the electrode mix, with the intention of improving the flexibility and strength of the electrodes. Although many attempts were made to characterise the fibrous electrodes mechanically there was no test available that was sensitive enough. Qualitatively, the observation was made that electrodes containing fibres were much easier to handle, and had more flexibility than non-fibrous electrodes. Fibrous electrodes did not crack, and there was also evidence to suggest that they could perform better electrochemically than non-fibrous electrodes. Schlumberger WCP Ltd has shown great interest in fibrous electrodes, and has begun testing such electrodes in cells produced on-site. Future work in this area should focus on an appropriate mechanical test for carbon electrodes.

Other research carried out in the present study on the lithium thionyl chloride battery resulted in developing an efficient method of estimating the dead volume of carbon electrodes. This test is referred to as the IPA Test for Dead Volume, and allows dead volume to be estimated using an immersion technique, instead of having to resort to the DBP test. If this test could be automated it could prove to be a useful and efficient predictor of electrode performance, since dead volume has been found to correlate with specific capacity.

Another problem has been solved that also concerns the manufacture of carbon electrodes for lithium thionyl chloride batteries. The volume of IPA used in the production of carbon electrodes at Schlumberger WCP Ltd’s site was close to exceeding UK/EU regulations. The present study has solved this problem by halving the volume of IPA required, thus allowing production to continue. This change in the manufacturing method does not damage the microstructure of the finished product, and
does not diminish the specific capacity of the electrode when placed in a cell. This minimises the environmental impact, by an easy-to-accommodate change to the manufacturing procedure.

Further research carried out on the carbon electrodes used in lithium thionyl chloride cells included assessing electrode thickness variability, which was found to have a coefficient of variation no higher than 5% for the formulations tested. No significant differences in specific capacity were observed between calendered and extruded electrodes, suggesting that the extrusion process could be changed in the future to negate the need for specialist instruments and in-house templates. An investigation was also carried out into using a new Ketjenblack carbon of higher DBP dead volume. The results suggested that improvements in specific capacity were possible when using the new Ketjenblack.

Investigations into the lithium sulphur battery have ultimately resulted in further support for claims that there are problems with rechargeability of the cell. The present work developed a three-electrode bench top apparatus that allowed single discharge curves of calendered electrodes to be recorded. Recharging of the cell was successful in one of the three electrolyte solutions tested, but even this was limited. Further work in this area should focus on the use of calendered electrodes in more highly compressed cells, in an attempt to improve rechargeability of such cells.

Electrochemical capacitors are likely to play an important role in the future of energy management and regeneration on industrial sites. Devices for such large scale applications will require appropriately scaled electrodes. The present study therefore investigated the possibility of using thick film electrodes made from different carbon blacks. It was discovered that some carbon blacks, such as Black Pearls 2000 and Ketjenblack 300J had higher specific capacitances than the industry-recommended material for use in current electrochemical capacitors. Carbon fibres were also included in some electrode formulations, and were found to decrease the rise times (the $RC$ time constant) in some cases. The fibres imparted high conductivity to the electrode, hence decreasing the $RC$ time constant. Future work should assess the limit of cycling such electrodes, and should also focus on their use in larger scale devices.
Finally, a solution of 1M LiCF$_3$SO$_3$ in sulfolane/ethylene carbonate was successfully gelled using polyvinylidene fluoride. Working electrodes were then soaked in this gelled electrolyte solution prior to testing electrochemically. The gelled electrode compared favourably with a non-gelled electrode, but resistance appeared to increase. Future work should test the feasibility of creating a completely gelled cell of this type, whilst also attempting to reduce the resistance of the gel.
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<td>130</td>
</tr>
<tr>
<td>5.03</td>
<td>The matrix of electrode experiments.</td>
<td>131</td>
</tr>
<tr>
<td>5.04</td>
<td>Coefficients of variation for L2 and L3 electrodes made with different Ketjenblack materials run in Li-SOCl$_2$ cells.</td>
<td>133</td>
</tr>
<tr>
<td>5.05</td>
<td>$p$-values for each of the electrode formulations, as calculated from an unpaired Student’s t-test (N=3). Smaller $p$-values indicate higher significance.</td>
<td>134</td>
</tr>
<tr>
<td>5.06</td>
<td>Coefficients of variation for capacitance measurements on different electrode formulations cycled in 1M H$_2$SO$_4$ (aq).</td>
<td>137</td>
</tr>
<tr>
<td>5.07</td>
<td>Thickness measurements for a selection of rolled and extruded electrodes. The largest and smallest values measured are</td>
<td>138</td>
</tr>
</tbody>
</table>
shown by red and blue respectively.

5.08 Thickness measurements for fibrous electrodes. The largest and smallest values measured are shown by red and blue respectively.

5.09 Specific capacitances and coefficients of variation of commercial (Schlumberger WCP Ltd) electrodes. Some were manufactured using a 2:1 ratio of IPA to water, and others using a 1:2 ratio of IPA to water.

5.10 Specific capacitances of ‘DP’ and ‘NH’ electrodes cycled in 1M H₂SO₄.

6.01 Three solvent systems used in experiments on the lithium sulphur cell in the present study.

AI.01 The formulation used for standard mix electrodes (L2 and L3).

AII.01 DSC data collected for pure sulfolane, pure ethylene carbonate, and five mixtures of the two solvents.
Appendix I  Standard Carbon Electrode Formulation for Lithium Thionyl Chloride Cells.

This formulation was adapted by a previous researcher from the original Schlumberger WCP Ltd formulation to be used for small-scale quantities (acknowledgment to N. van Dijk).

<table>
<thead>
<tr>
<th>Loughborough Mix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent</strong></td>
</tr>
<tr>
<td>63.2 ml of IPA</td>
</tr>
<tr>
<td>31.6 ml of H₂O</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
</tr>
<tr>
<td>8.0 g of SAB</td>
</tr>
<tr>
<td>2.0 g of Ketjenblack</td>
</tr>
<tr>
<td><strong>Binder</strong></td>
</tr>
<tr>
<td>3.7 g of Teflon Solution</td>
</tr>
<tr>
<td>1.1 ml of water</td>
</tr>
</tbody>
</table>

*Table A1. 01. The formulation used for standard mix electrodes (L2 and L3).*
Appendix II  Differential Scanning Calorimetry (DSC) Data

In order to learn more about the mixed system of sulfolane and ethylene carbonate, a number of samples were analysed using DSC. It was of interest to obtain the minimum temperature that different sulfolane/ethylene carbonate mixes melted at. It was also of interest to see if this solvent system had a deep eutectic point, or if the melting point was fairly constant over a wide range of different mixes (thus presenting a 'eutectic line'). The DSC results are shown in Table AII.02.

<table>
<thead>
<tr>
<th>Sample (sulfolane:ethylene carbonate ratio)</th>
<th>Melting Temperature (°C) Peak Max</th>
<th>Melting Temperature (°C) Extrapolated Peak Onset</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% Ethylene carbonate</td>
<td>35 *</td>
<td></td>
</tr>
<tr>
<td>1:9</td>
<td>-22.61</td>
<td>-24.58</td>
</tr>
<tr>
<td>3:7</td>
<td>-18.79</td>
<td>-24.53</td>
</tr>
<tr>
<td>1:1</td>
<td>-14.82</td>
<td>-24.73</td>
</tr>
<tr>
<td>7:3</td>
<td>-17.88</td>
<td>-24.84</td>
</tr>
<tr>
<td>9:1</td>
<td>-21.81</td>
<td>-24.81</td>
</tr>
<tr>
<td>100% Sulfolane</td>
<td>25 *</td>
<td></td>
</tr>
<tr>
<td><strong>Repeated Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% Ethylene carbonate</td>
<td>39.71</td>
<td>32.89</td>
</tr>
<tr>
<td>1:9</td>
<td>-23.50</td>
<td>-25.23</td>
</tr>
<tr>
<td>3:7</td>
<td>-16.84</td>
<td>-26.20</td>
</tr>
<tr>
<td>1:1</td>
<td>-15.57</td>
<td>-26.45</td>
</tr>
<tr>
<td>7:3</td>
<td>-12.98</td>
<td>-20.26</td>
</tr>
<tr>
<td>9:1</td>
<td>-23.22</td>
<td>-25.60</td>
</tr>
<tr>
<td>100% Sulfolane</td>
<td>17.35</td>
<td>13.28</td>
</tr>
</tbody>
</table>

* data obtained from MSDS

During DSC analysis, broad peaks were observed, signifying crystals with a range of melting points. This is possibly because the dipoles of the polar sulfolane molecule lead to the collecting of sulfolane molecules together. Some will also cluster with ethylene
carbonate, and so a wide range of crystals are formed. This leads to a wide range of melting points, hence broad melting peaks.

The peak onset values represent the melting of the eutectic mixture, and this is shown as a linear region in Figure AII.01, where the temperature has been plotted against increasing percentage of sulfolane. The melting point of the eutectic mixture is between -25°C and -26°C.

There is an anomaly in the second set of measurements, and the reason for this is unknown. Both individual solvents and a mixture of the two were analysed using NMR and mass spectrometry techniques to ensure no solvent degradation had occurred. The NMR spectra for the individual solvents matched those provided by the manufacturers. The mixed solvent spectra from both techniques did not show any indication of solvent degradation.

In Figure AII.02 the melting peak maximum values are plotted for increasing percentage of sulfolane.

Figure AII.01. Peak onset values from DSC analysis of sulfolane/ethylene carbonate mixtures. Note the eutectic region at approximately -25°C.
Figure AII.02 shows that the peak maximum values fluctuated between $-23^\circ C$ and $-13^\circ C$ for all mixtures of sulfolane and ethylene carbonate. Unfortunately there is no simple correlation between increasing sulfolane percentage and peak maximum melting point. More narrow melting regions were obtained when using both 10% and 90% sulfolane, whilst intermediate mixtures had broader melting regions.