Characterisation of nickel electrodes by electrochemical impedance spectroscopy

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CHARACTERISATION OF NICKEL ELECTRODES BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

BY

RAYMOND TERENCE BARTON

Supervisor: Dr. P.J. Mitchell

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

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SYNOPSIS

The thesis describes an electrochemical investigation of different types of nickel electrode used in nickel-cadmium cells, which are available commercially or currently under development. Impedance spectroscopy has been used to determine the electrochemical characteristics of these electrodes. The electrochemistry of the nickel electrodes was modelled by the electrical analogue method. Allowance was made within the model for porosity and adsorption effects. Component values were initially estimated by graphical techniques and the computer fitting procedure was then completed by an iterative process to provide kinetic parameters which were used to compare and contrast the characteristics of the nickel sintered, pocket and plastic bonded electrodes.

The technological target of this work was establish a possible method by which the residual capacity remaining within nickel-cadmium cells could be determined. The kinetic parameters generated by the electrical analogue technique have provided data on which to base a measurement for the prediction of the state of charge in nickel-cadmium cells.
ACKNOWLEDGEMENTS

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To Janet, Stephen and David
## CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTER 1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td>The electrochemical impedance spectroscopy technique</td>
<td>4</td>
</tr>
<tr>
<td>CHAPTER 3</td>
<td>Review</td>
<td>22</td>
</tr>
<tr>
<td>CHAPTER 4</td>
<td>Electrochemical impedance spectroscopy of sintered nickel and cadmium electrodes</td>
<td>30</td>
</tr>
<tr>
<td>CHAPTER 5</td>
<td>Electrochemical impedance spectroscopy of plastic bonded nickel electrodes</td>
<td>45</td>
</tr>
<tr>
<td>CHAPTER 6</td>
<td>Electrochemical impedance spectroscopy of pocket nickel electrodes</td>
<td>54</td>
</tr>
<tr>
<td>CHAPTER 7</td>
<td>Overall conclusions</td>
<td>63</td>
</tr>
<tr>
<td>APPENDIX 1</td>
<td>The electrotechnology of the nickel positive electrode</td>
<td>65</td>
</tr>
<tr>
<td>APPENDIX 2</td>
<td>Cadmium. A review of the recent literature</td>
<td>66</td>
</tr>
<tr>
<td>APPENDIX 3</td>
<td>Publications</td>
<td>67</td>
</tr>
</tbody>
</table>

REFERENCES 69
CHAPTER 1

INTRODUCTION

The nickel oxide electrode was first used in the 1890s by Jungner in the nickel-cadmium cell and around the same time Edison used the electrode in the nickel-iron cell. The nickel oxide electrode has subsequently been used to construct couples such as nickel-zinc and nickel-hydrogen. However, the nickel-cadmium cell still remains the most popular system, even though the use of cadmium has become a focus of attention for environmentalists. Nickel-cadmium cells constructed with pocket type electrodes are used mainly by industry for traction and standby power for example. Large cells using the sintered electrode technology are used principally in military applications. Small nickel-cadmium cells (D size and smaller) constructed from sintered electrodes are available to the domestic consumer. These have recently become more attractive because of the development of intelligent chargers capable of fast recharge. The different fabrication methods of electrodes offers various qualities, including high reliability and cycle life. The choice of technology is determined by application and cost. New materials are continuously being studied as suitable replacements of the pocket and sintered nickel electrodes, these include foam, fibres and plastic bonded electrodes.

Two particular behavioural conditions of nickel-cadmium cells are continually being investigated. The first is a problem which limits the residual capacity, namely the 'memory effect'. The effect is well understood, unfortunately
however, the cause is not. The effect can in certain cases, be avoided or overcome. An investigation of the 'memory effect' using electrochemical impedance spectroscopy is described in section 6.3. The estimation of residual capacity is the second perennial problem associated with nickel-cadmium cells. Residual capacity is an important parameter to know, especially for military purposes and traction applications. It has however, proved a difficult parameter to determine. When compared with the lead-acid cell the nickel-cadmium cell has no readily available characteristic on which to base a state of charge measurement. The residual capacity in lead/acid cells can be determined by measurement of the open circuit potential and specific gravity of the sulphuric acid electrolyte. The determination of the residual capacity in lead-acid cells has become more difficult since the introduction of valve regulated lead-acid cells, in which the electrolyte is completely absorbed within the plates and separator and as a consequence is inaccessible for specific gravity measurements.

This problem has been addressed by the author and co-workers using the technique of electrochemical impedance spectroscopy. The technique had already been successfully employed by the Loughborough electrochemistry group to determine the residual capacity in some primary cells. Investigations of the problem provided a satisfactory determination of the residual capacity in both 2.5Ah [1] and 25Ah [2] valve regulated lead-acid cells. Further work [3], again using the same technique has provided a useful method for determining the residual capacity in lead acid monoblocs ranging in capacity from 1 to 100Ah capacity.

The success of electrochemical impedance spectroscopy in providing a method for determining the residual capacity in such cells led to the use of the technique in elucidating a parameter on which to base a measurement of residual
capacity in nickel-cadmium cells. The work reported here describes the usefulness of the technique for such determinations.

After limited success with initial experiments on 23Ah nickel-cadmium cells with sintered electrodes, further studies were undertaken on single electrodes and subsequently on small electrodes of 1cm² area in order to elucidate the nature of the kinetic and other rate determining processes. The electrical analogue technique was used to model the a.c. response of the electrodes. The simplest possible electrical analogues were chosen after careful consideration of the electrochemical reactions occurring at the electrodes. A porosity factor was included which enabled some high quality fitted data to be obtained. This factor has previously been omitted by researchers when investigating porous electrodes.

The primary aim of this research was to provide the M.o.D. with a suitable method for the prediction of residual capacity in nickel-cadmium cells with sintered nickel electrodes, unfortunately initial impedance measurements showed that neither the nickel nor the cadmium electrode dominated the cell impedance spectrum. Therefore, it was essential to determine the impedance and a suitable electrical analogue for both electrodes. It was hoped that the two analogues could then be combined and convoluted to provide the impedance response of the whole cell.

The opportunity was taken to study the nickel plastic bonded and pocket electrodes. This would allow a further test of the correctness of the electrical analogue developed for the sintered nickel electrode. These additional electrodes were studied using the technique on 1cm² electrodes and the resultant information of all three electrode types was compared and contrasted. It was borne in mind that the technological target of the work was to establish a parameter on which to base a state of charge measurement.
CHAPTER 2

THE A.C. IMPEDANCE TECHNIQUE

2.1 INTRODUCTION

Study of the a.c. impedance characteristics of an electrochemical system allows measurements of the kinetic parameters of the cell. These parameters can give indications of the type of reaction and transport mechanisms involved. The application of a.c. theory to liquid metal electrodes has led to a better understanding of electrode reaction mechanisms. Reproducible values for exchange current densities and transfer coefficients have been obtained for simple charge transfer processes. The method has also been successful in evaluating more complex processes involving specific adsorption of reactants or products and to chemical reactions preceding or following the charge transfer process.

Industrial investigations of electrode processes are usually concerned with solid or more often porous electrodes, for example, those in fuel cells, batteries, electrochemical synthesis and electrolysis. Although the results obtained on liquid metal electrodes are of limited use for these systems, the theoretical principles have been established for the interpretation of these measurements in terms of structure, exchange current density, double layer capacity and surface area.

For conventional electrochemical techniques, the voltage applied to the electrochemical system is essentially kept constant during the measurement of current. In the alternating current technique however, an alternating voltage (V) of relatively small amplitude (3mV) is superimposed on the potential difference and the current
contains an alternating component of amplitude (i). When the amplitude of the alternating voltage varies sinusoidally with time (t) and frequency (f) we may write:

\[ \omega = 2\pi f \]  \hspace{1cm} (2.1)

\[ v = V_{\text{max}} \sin \omega t \]  \hspace{1cm} (2.2)

\[ i = I_{\text{max}} \sin (\omega t - \phi) \]  \hspace{1cm} (2.3)

and

\[ Z = \frac{V_{\text{max}} \arg \phi}{I_{\text{max}}} \]  \hspace{1cm} (2.4)

\[ = |Z| \arg \phi \]  \hspace{1cm} (2.5)

where \( Z \) is the impedance of the cell and \( \phi \) is the phase angle between the current and voltage.

When \( \phi \) is a negative quantity the current leads the voltage and the impedance can be represented by a network of resistors and capacitors. Conversely, when \( \phi \) is positive the current lags the voltage and the impedance may be represented by an inductive-resistive circuit. The impedance can be plotted in conventional complex form on an Argand diagram, however, the reactances most often encountered in electrochemistry are capacitive giving a negative quantity on the Argand diagram. Hence, it has become standard practice to use the first quadrant of the complex plane for their representation (Sluyters plot). The impedance may be resolved into resistive and capacitive components which are plotted against \( \omega^{-1/2} \) (Randles plot). Both methods give detailed information about the electrochemistry and will be used exclusively in this thesis.
2.2 THE EXPERIMENTAL SET UP FOR IMPEDANCE MEASUREMENTS

Impedance measurements were determined using microprocessor based Solartron 1170 or 1250 frequency response analysers (F.R.A.) which are now established instruments for the determination of electrochemical impedance data [4,5]. The F.R.A. essentially consists of a programmable generator that provides the perturbing sinusoidal signal, a correlator to analyse the response of the system and a display, to present the results. The fundamental response of a system to a sinusoidal perturbation of the form, $\Delta E\sin(\omega t)$, will be of the form $A\sin(\omega t + \phi)$. The F.R.A. has the advantage of rejecting all harmonics present in the output of the system and minimises the effect of random noise. A single measurement at a particular frequency can be made by programming the generator with the required frequency and signal amplitude. More usually the generator is programmed to sweep through a large frequency range i.e. 60kHz to 0.1mHz, where measurements per decade were made sequentially on a logarithmic scale. The response is given once a measurement has been completed and can be displayed in one of three possible notations, amplitude (A) and phase angle (\phi) relative to the output signal; log(A) and \phi or the real and imaginary parts of the impedance. The results together with the measurement frequency are then transferred to a data logging device whilst simultaneously, the results are plotted on an X-Y recorder. Alternatively data are transferred to a floppy disk and the results shown directly on a V.D.U. Data collected is then transferred directly to a data analysis package for subsequent analysis.

The time required for the F.R.A. to make a single measurement is equal to the period of the signal (i.e. 1 second at 1Hz) and this becomes a major contribution to the total experimental time at low frequencies. In most practical applications a certain amount of random noise is invariably superimposed on the signal to be analysed and this may significantly affect the measurement accuracy. Since this is essentially an
averaging instrument, when noise is troublesome greater accuracy can be achieved by increasing the integration time, and with frequencies below 10Hz by introducing a low pass filter.

The Solartron 1186 electrochemical interface provides the interfacing requirements for the control and measurement of the cell characteristics using a F.R.A. It does this by superimposing its sine wave on an internally generated polarisation voltage. Since the interface also acts as a potentiostat, both a.c. and d.c. measurements can be made. Operation of the electrochemical interface in the two terminal mode is made possible by externally shorting the secondary electrode (SE) with the reference electrode (RE1) and the working electrode (WE) with the remaining reference electrode (RE2). The cell was driven in the potentiostatic mode in which voltage feedback was used to hold a constant voltage across the reference RE1 and the working electrode. The impedance of the cell was then obtained directly by measuring the current on the X terminal of the F.R.A. and the voltage on the Y terminal with the correlator operating in the Y/X mode.

The a.c. perturbation generated by the F.R.A. is small in comparison with the d.c. polarisation voltage and although the interface enables the d.c. content to be backed off, the real part of the signal may remain high relative to the imaginary component. In such cases the resolution of the correlator can be improved by subtracting a known amount, proportional to the current, from the voltage. The net effect of this is to move the response curve closer to the origin, allowing the analyser to be switched to a more sensitive range.
2.3 FARADAIC IMPEDANCE MEASUREMENTS OF SMALL MAGNITUDES

For accurate measurements of the cell impedance it is necessary to select a sense resistor of the same order of magnitude as the cell under test. The lowest sense resistor incorporated in the Solartron 1186 electrochemical interface is $10\Omega$, it is therefore necessary to use an external sense resistor of the correct magnitude. Karunathilaka et al. [6] have established that the lowest sense resistor which can possibly be used with this device as being $0.123\Omega$. This sense resistor is in fact simply a shorting bar. The value of $0.123\Omega$ is a reactance due to the impedance of the electronic path within the 1186 interface which leads up to the socket to which the external 'sense resistor' is connected. This 'sense resistor' is also frequency dependent above 300Hz and hence needs calibrating. Data collected using the 'shorting bar-sense resistance' were correlated prior to permanent storage using the procedure described by Karunathilaka et al. [6].

2.4 THE IMPEDANCE ANALOGUE METHOD FOR THE STUDY OF ELECTROCHEMICAL REACTIONS

In the derivation of an expression for the electrode impedance for the redox reaction $O + n e = R$, it is necessary to assume that Ficks Law is independently applicable to each diffusing species, mass transfer takes place only by planar diffusion, i.e. transfer due to migration and convection is negligible, charge transfer involves only one rate determining step, a steady state is achieved in the a.c. concentration profile and that the double-layer charging process can be separated from the faradaic process.

Eyring et al. [7] derived an equation relating the current, $i$, flowing across an electrode-electrolyte interface of unit area to the potential across the interface i.e.

$$i = nFK_s \left[ C_R^o \exp\left(\frac{\alpha nF(E-E_0)}{RT}\right) - C_O^o \exp\left(\frac{(1-\alpha)nF(E-E_0)}{RT}\right) \right] \quad (2.6)$$
where \( K_s \) is the specific heterogeneous rate constant for the electron transfer reaction and \( \alpha \) is the charge-transfer coefficient. \( C_R^0 \) and \( C_C^0 \) are the surface concentrations of the reductant and the oxidant respectively.

The surface concentrations can be evaluated by solving Fick's Laws of diffusion with the appropriate boundary conditions.

\[
\frac{\delta C}{\delta t} = \frac{D \delta^2 C}{\delta x^2} \quad (2.7)
\]

\[
DnF\left(\frac{\delta C}{\delta x}\right) = i \\
x=0
\]

\[
i = \bar{i} + \Delta i \sin \alpha t \quad (2.9)
\]

where,
- \( D \) = diffusion coefficient
- \( x \) = distance from the electrode
- \( \bar{i} \) = the direct current flowing
- \( \Delta i \) = the amplitude of the alternating current

Randles [8] solved these equations in the case of zero direct current. Others [9-11] have attempted to solve the equations in the more general case. The most successful has been the semi-infinite linear diffusion theory developed by Delahay [11] and extended by Rangarajan and Doss [12]. In this theory the surface concentrations for reversible systems are given by:

\[
C_0^0 = \frac{(C_R^0 + \sqrt{d} C_O^0)}{1 + \sqrt{d} e^{-\alpha}} \quad (2.10)
\]
\[ C_R^0 = \frac{(C_O^* + \sqrt{d} C_R^*)}{e^\phi + \sqrt{d}} \]  

(2.11)

where,  
\[ \phi = nF \frac{(E - E_O)}{RT} \]  

(2.12)

\[ d = \frac{D_R}{D_O} \]  

(2.13)

\( C_R^* \) and \( C_C^* \) are the bulk concentrations

Values of the surface concentrations were also found from steady-state theory by Gerischer [13] using the following expressions:

\[ C_O^0 = C_O^* + \frac{\delta}{nD_O} \mathbf{i} \]  

(2.14)

\[ C_R^0 = C_R^* - \frac{\delta}{nD_R} \mathbf{i} \]  

(2.15)

which can be related to the d.c. voltage by substitution in equation (2.6).

The electrode impedance described by the equivalent circuit shown in fig.2.1 was proposed by Randles [14]. The Randles equivalent circuit incorporates a Warburg impedance \( \sigma \), which accounts for the diffusion of the charged species under an electric field. \( R \Omega \) represents the ohmic resistance of the electrolyte. Within the circuit \( C_L \) denotes the double-layer capacitance which varies with the d.c. voltage in a manner which depends on the concentration and nature of the electrolyte [15], \( \theta \) is the charge-transfer resistance which is related to the exchange current density by:

\[ i_o = \frac{1}{\theta} \cdot \frac{RT}{nF} \]  

(2.16)
FIG. 2.1 RANDLE'S EQUIVALENT CIRCUIT
The following expressions were derived by Randles for the charge-transfer resistance and the Warburg impedance:

\[ \theta = \frac{RT}{n^2F^2k_s} \cdot (C_O^\alpha (C_R^{1-\alpha}) \]  (2.17)

\[ W = \sigma \frac{1}{\sqrt{\omega}} - j\sigma \frac{1}{\sqrt{\omega}} \]  (2.18)

where \[ \sigma = \frac{RT}{n^2F^2\gamma z} \left( \frac{1}{C_O^{\gamma D_O}} + \frac{1}{\gamma D_R^{\gamma D_R}} \right) \]  (2.19)

\[ \theta \] and \[ \sigma \] can be obtained in terms of their bulk concentrations from equations (2.10, 2.11, 2.17 and 2.19)

\[ \theta = \frac{RT}{n^2F^2k_s(C_O^* \gamma D_C + \gamma d C_R^*)} (e^{-\gamma d} + \gamma d e^{-\gamma d}) \]  (2.20)

\[ \sigma = \frac{RT}{n^2F^2\gamma z D_O(C_O^* \gamma D_C + \gamma d C_R^*)} (e^{\gamma d} + d e^{\gamma d})^2 \]  (2.21)

\[ d = \frac{D_R}{D_O} \]  (2.22)

The expressions derived from steady-state theory are similar to those obtained above except that \( d \) is replaced by \( d^2 \) in the equations. Since \( d \) is the ratio of the coefficients of the reduced species to oxidised species, which is normally close to 1, there is no significant difference between the values of the respective expressions. However, comparison of results obtained from amalgam formation in molten salts
and polarographic measurements show that the semi-infinite diffusion equations are more realistic than those obtained from the steady-state theory.

2.5 EVALUATION OF THE KINETIC PARAMETERS DESCRIBED BY THE RANDLES EQUIVALENT CIRCUIT

In the case of the Randles equivalent circuit fig.2.1 the impedance contains a faradaic \((Z_f)\) and a non-faradaic \((Z_D)\) component where:

\[
Z_f = \theta + \sigma_R \frac{1}{\sqrt{\omega}} - j\sigma_C \frac{1}{\sqrt{\omega}}
\]  (2.23)

\[
Z_D = \frac{1}{j\omega C}
\]  (2.24)

The total impedance of the cell is given by:

\[
Z_T = \frac{1}{\frac{1}{Z_f} + \frac{1}{Z_D} + R_\Omega}
\]  (2.25)

where \(R_\Omega\) represents the ohmic resistance of the cell i.e. electrolyte and current collector contacts.

\[
Z_T = Z_A + R_\Omega
\]  (2.26)

\[
\frac{1}{Z_A} = \frac{1}{Z_f} + \frac{1}{Z_D}
\]  (2.27)

\[
\frac{1}{Z_A} = \frac{1}{Z_f} + j\omega C
\]  (2.28)

\[
\frac{1}{Z_A} = \frac{1}{(\theta + \sigma R \frac{1}{\sqrt{\omega}}) - (j\sigma C \frac{1}{\sqrt{\omega}})} + j\omega C
\]  (2.29)
\[
\frac{1}{Z_A} = \frac{1 + j\omega C (\theta + \sigma\omega \frac{1}{2} - j\sigma\omega \frac{1}{2})}{\theta + \sigma\omega \frac{1}{2} - j\sigma\omega \frac{1}{2}} \tag{2.30}
\]

\[
\frac{1}{Z_A} = \frac{1 + j\omega C \theta + \sigma C\omega^2 + j\sigma C\omega^2}{\theta + \sigma\omega \frac{1}{2} - j\sigma\omega \frac{1}{2}} \tag{2.31}
\]

Inverting equation (2.31) gives:

\[
Z_A = \frac{\theta + \sigma\omega \frac{1}{2} - j\sigma\omega \frac{1}{2}}{1 + j\omega C \theta + \sigma C\omega^2 + j\sigma C\omega^2} \tag{2.32}
\]

To separate the real and imaginary components of \(Z_A\) equation (2.32) is multiplied by its complex conjugate to give:

\[
Z_A = \frac{\theta + \sigma\omega \frac{1}{2} - j\sigma\omega \frac{1}{2}}{1 + \omega^2 \sigma C + j (\omega C\theta + \omega^2 C\sigma)} \times \frac{1 + \omega^2 \sigma C - j (\omega C\theta + \omega^2 C\sigma)}{1 + \omega^2 \sigma C - j (\omega C\theta + \omega^2 C\sigma)} \tag{2.33}
\]

Solving for the denominator:

\[
(1 + \omega^2 \sigma C)^2 + (\omega C\theta + \omega^2 \sigma C)^2 = (1 + \omega^2 \sigma C) + \omega^2 C^2 (\theta + \sigma \omega \frac{1}{2})^2 \tag{2.34}
\]

Similarly for the numerator:
\[
\theta + \frac{1}{2} \sigma C \theta - j (\omega C \theta + \frac{1}{2} \sigma C \theta) = \theta + \frac{1}{2} \sigma C \theta - j \omega C \theta - j \omega^2 C \theta + \\
\frac{1}{2} \sigma \theta - j \sigma C - j \omega \frac{1}{2} - j \sigma C - \omega^2 \sigma C \theta - \sigma \theta^2
\]

(2.35)

Combining equations (2.34) and (2.35) yields:

\[
Z_A = \frac{\theta + \sigma \omega \frac{1}{2}}{(C \sigma \omega^2 + 1) + \omega C^2 (\theta + \omega \sigma \frac{1}{2})} - \\
\frac{j \left[ \omega C \left( \theta + \frac{1}{2} \sigma C \theta + \sigma \omega \frac{1}{2} \right) + \sigma \omega \frac{1}{2} \right]}{(C \sigma \omega^2 + 1) + \omega C^2 (\theta + \omega \sigma \frac{1}{2})} \\
\frac{\theta + \sigma \omega \frac{1}{2}}{(C \sigma \omega^2 + 1) + \omega C^2 (\theta + \omega \sigma \frac{1}{2})} - \\
\frac{j \left[ \omega C \left( \theta + \sigma \omega \frac{1}{2} \right)^2 + \sigma \omega \frac{1}{2} \right]}{(C \sigma \omega^2 + 1) + \omega C^2 (\theta + \omega \sigma \frac{1}{2})} \tag{2.36}
\]

\[
Z_{\text{total}} = -j \left[ \omega C \left( \theta + \sigma \omega \frac{1}{2} \right)^2 + \sigma \omega \frac{1}{2} \right] + \\
\left( 1 + \sigma \omega \frac{1}{2} \right)^2 \tag{2.36}
\]
\[ R_{\Omega} + \frac{(\theta + \frac{1}{\sigma \omega^{\frac{1}{2}}})}{(1 + \sigma \omega^{\frac{1}{2}})^2 + \omega^2 \left( \theta + \frac{1}{\sigma \omega^{\frac{1}{2}}} \right)^2} \quad (2.37) \]

From equation (2.37) it can be seen that the impedance of the cell consists of a real and imaginary components. The real part may be expressed in terms of the \( R \) equation.

\[ R_{\text{cell}} = R_{\Omega} + \frac{(\theta + \frac{1}{\sigma \omega^{\frac{1}{2}}})}{(1 + \sigma \omega^{\frac{1}{2}})^2 + \omega^2 \left( \theta + \frac{1}{\sigma \omega^{\frac{1}{2}}} \right)^2} \quad (2.38) \]

whilst the imaginary part is expressed in terms of the \( C \) equation.

\[ \frac{1}{\omega C_{\text{cell}}} = \frac{\omega C \left( \theta + \frac{1}{\sigma \omega^{\frac{1}{2}}} \right) + \frac{1}{\sigma \omega^{\frac{1}{2}}} \left( \frac{1}{\sigma \omega^{\frac{1}{2}}} + 1 \right)}{(1 + \sigma \omega^{\frac{1}{2}})^2 + \omega^2 \left( \theta + \frac{1}{\sigma \omega^{\frac{1}{2}}} \right)^2} \quad (2.39) \]

which rearranges to give:

\[ \frac{1}{C_{\text{cell}}} = \frac{1}{C} \left[ 1 - \frac{(\sigma \omega^{\frac{1}{2}} + 1)}{(1 + \sigma \omega^{\frac{1}{2}})^2 + \omega^2 \left( \theta + \frac{1}{\sigma \omega^{\frac{1}{2}}} \right)^2} \right] \quad (2.40) \]

Although equation (2.37) is complex, the two limiting frequencies yield important results. Firstly, at low frequencies the \( \sigma \omega \bar{C} \) terms can be omitted and as a result equation (2.37) reduces to:

\[ Z_{\text{total}} = R_{\Omega} + \theta + \sigma \omega^{\frac{1}{2}} - j(\sigma \omega^{\frac{1}{2}} + 2\sigma \bar{C}) \quad (2.41) \]
When the real and imaginary parts are plotted against each other a straight line of unit slope is obtained, fig.2.2. Equation (2.41) reveals, even at low frequencies, the influence of the double-layer capacitance on the cell impedance is not completely eliminated. This is a surprising result for at first sight it is plausible to neglect double-layer terms at low frequencies where the charging current is small compared to the faradaic current.

Secondly, at high frequencies when dealing with a fairly irreversible reaction the Warburg impedance can be ignored, since \( \sigma \omega^{\frac{1}{2}} < \theta \). Equation (2.37) then reduces to:

\[
Z_{\text{total}} = R_\Omega + \frac{\theta}{1 + \omega C^2 \theta} - \frac{j\omega C \theta^2}{1 + \omega C^2 \theta^2} \quad (2.42)
\]

When the real and imaginary parts are plotted against each other a semi-circle is the result, fig.2.3. At lower frequencies the Warburg impedance predominates. This gives rise to a distortion of the semi-circle, fig.2.4, which eventually relaxes to a line subtending an angle of \( 45^\circ \) to the real axis.

### 2.6 Randles Method

Randles [8, 14] proposed that the faradaic resistance \( (R_f) \) and faradaic reactance \( (X_f) \) could be calculated from the measured cell impedance (series RC) using the formulae described by Hills [16]. The double-layer capacitance, in the general case, can be determined by carrying out an experiment in the absence of the electroactive species. The electrolyte resistance can also be determined with the
Fig. 2.2 DIFFUSION CONTROL
Fig. 2.3 CHARGE TRANSFER CONTROL

\[ \omega = \frac{1}{\theta} C_L \]

[Diagram showing a semicircle with annotations for \( Z'' \) (imaginary), \( Z' \) (real), and \( R_\Omega \), \( R_\Omega + \theta \).]
Fig. 2.4 MIXED CONTROL
double-layer capacitance. The Warburg coefficient and the charge-transfer resistance are related to the faradaic resistance and reactance by:

\[
R_f = \theta + \sigma \omega^{-\frac{1}{2}}
\]

\[
X_f = \sigma \omega^{-\frac{1}{2}}
\]

The Randles representation of impedance data is shown in fig.2.5. The calculated values of \( R_f \) and \( X_f \) are plotted against \( \omega^{-1/2} \). The rate constant and the exchange current density can be obtained from \( \theta \) and the diffusion coefficient of the reacting species from \( \sigma \). It is assumed that the electroactive species does not specifically adsorb at the electrode surface, thereby changing the double-layer capacitance, and also that the 'a priori' separation of the double-layer charging process and the faradaic process is justified.

2.7 SLUYTERS METHOD

Sluyters and Sluyters-Rehbach [17] devised an elegant method of calculating \( \theta, C_L \) and \( \sigma \) at different concentrations from the measured values of \( R \) and \( C \). The method allows calculation of \( \theta \) and \( \sigma \) without prior knowledge of \( C_L \) and also to calculate \( C_L \) in the presence of an electroactive species. A plot of the real versus the imaginary components of the cell impedance in the frequency plane will directly reveal the values of \( R_E, \theta, \sigma \) and \( C_L \).

Other methods have also been proposed for the determination of kinetic parameters. Gerischer [18] presented a treatment in which he neglected the imaginary part of the Warburg impedance and Vetter [19] corrected the cell impedance for the double-layer capacitance and the ohmic resistance of the electrolyte. However, the results presented in this thesis are graphically represented in terms of the Randles and
Fig. 2.5 RANDLES REPRESENTATION OF IMPEDANCE DATA
Sluyters (complex-plane) plots. In the mathematical modelling treatment, the Randles plot reveals the excellence of the matched data as both the real and imaginary components are plotted separately against the frequency as $\omega^{-1/2}$. The Sluyters plot represents a summing exercise, and as such cannot reveal as much about the quality of the fit obtained with a particular model.

Modification of a Randles circuit, so that it can be applied to reactions involving both adsorbed and soluble intermediates, may become so complex that there may be no graphical method capable of recovering the values of the circuit parameters. In such cases a numerical method must be used and indeed such a method may prove advantageous even when the simple Randles circuit is used.

2.8 THE EFFECT OF POROSITY ON THE ELECTRODE PROCESSES

Solid electrodes behave differently electrochemically to liquid electrodes, and they behave equally different to porous electrodes. The distinction between solid electrodes and porous electrodes is rather arbitrary, depending on the relative magnitude of the pores and surface irregularities. Several attempts [20] have been made to consider the theoretical potential distribution at surfaces with an idealised roughness consisting of 'u' or 'v' shaped parallel grooves or sinusoidal shapes, [21,22] and in the case of:

1) an ohmic controlled potential distribution - representing an infinitely fast electrode and mass transport processes.
2) a diffusion controlled potential distribution.

Investigations revealed that the frequency response for a reaction at a solid electrode was complex. The charge-transfer resistance is directly proportional to the true surface area. The Warburg impedance depends on both the surface roughness and the frequency, and at high frequencies it approaches a value corresponding to the
apparent surface area. The double-layer capacitance is also frequency dependent. At high frequencies the reactance of the double-layer capacitance approaches zero and the charging current approaches ohmic control. At low frequencies the double-layer impedance increases and the current density is more evenly distributed. Adsorption of species is a complicating feature. The effect of adsorption is usually to modify the double-layer capacitance and the charge-transfer resistance. The rate of adsorption and desorption will depend on the degree of roughness of the electrode and is much slower than for a liquid electrode.

The analysis of the impedance data from porous systems is complicated. The reason for this is the inherently complex structure of most porous electrodes and the consequent need for a relatively complex model for a theoretical analysis. Difficulties arise from the recognition that, in principle, for a planar electrode the current lines are perpendicular to the surface, whereas for porous electrodes they are effectively parallel to it. De Levie [20] has, however, developed a simple theory relating the a.c. behaviour of a pore to that of a corresponding planar electrode. The pore of length $l$ behaves as an impedance given by:

$$\frac{E}{i(o)} = \left(\frac{RZ}{Z}\right)^{\frac{1}{2}} \coth \left(\frac{R}{Z}\right)^{\frac{1}{2}} l$$

(2.45)

where $i(o)$ is the total current entering the pore. When $l \to \infty$; the cotanh term may be ignored and the apparent impedance $Z_a = \sqrt{ZR}$.

It follows that for a porous electrode with semi-infinite pores that the phase angle of the impedance is half that of the equivalent planar electrode and that the absolute magnitude of the impedance is proportional to the square root of the equivalent planar electrode.
De Levie defined a penetration depth $\lambda$ which is a quantitative measure of the fraction of the pore effectively involved in the a.c. measurements.

$$\lambda = \frac{\sqrt{ZR}}{R \cos \frac{1}{2} \phi}$$  \hspace{1cm} (2.46)

where $R$ is the electrolyte resistance per unit pore length.

He also showed that if the pore length $l$ was equal to or greater than $3\lambda$ then the pore could behave as a semi-infinite one at high frequencies. This length which varies with the mechanism of current control defines the distance to which a reaction can penetrate a porous electrode [23,24]. This length indicates the optimum thickness for a porous electrode and has considerable significance since electrodes much thinner than the penetration depth behave like planar electrodes of enhanced surface area, whilst those much thicker than the penetration depth are highly inefficient.

For an ideal polarised electrode where,

$$Z = \frac{1}{j\omega C_L}$$  \hspace{1cm} (2.47)

a complex plane plot obtained by plotting the imaginary part of the component $\sqrt{ZR}$ versus its resistive component at different frequencies would give a straight line at 45° to the real axis (90° in the case of a planar electrode). If $Z$ contains a Warburg impedance in parallel with the double-layer capacitance a straight line at 22.5° to the real axis will be obtained, whilst in the case of a planar electrode a line at 45° would result.
2.9 INDUCTIVE REACTANCES

Impedance measurements, on secondary cells containing porous electrodes, in the frequency range above 10 Hz contain a significant inductive component. This has been reported by Brodd and De Wane [25] and Zimmerman [26] for sealed NiCd cells and by Hughes et al [27,2] in the case of vented NiCd and fully sealed lead/acid cells. Gutman [28] ascribed it to geometrical effects of the electrode pores and to the physical structure of the internal cell conditions. It was suggested that the inductive reactance arose due to the time elapsed between the arrival of the signal at the mouth of the electrode pore and it reaching the bottom. Darby [29] showed that inductive reactance could arise when mass transfer and electrochemical reactions occur simultaneously over a distributed region of the electrode. Clearly both processes are responsible for this inductive behaviour, but care is necessary in the correct interpretation of this inductive portion for it has been shown that these inductive effects can arise from the measuring equipment being used with sense resistors which have not been calibrated for low impedance measurements [6].
CHAPTER 3

REVIEW

INTRODUCTION

The electrotechnology of nickel electrodes has been reviewed over the period 1981 to 1985. This publication is presented in appendix 1 and highlights aspects of fabrication, effect of additives, electrometric measurements and modes of failure. Appendix 2 contains a review of cadmium electrochemistry, which was considered pertinent to this research. Below is a selective overview which highlights the work on nickel electrodes since the comprehensive update published by McBreen [30] in 1990. This is followed by a review of the reaction mechanisms of the nickel electrode.

OVERVIEW OF LITERATURE SINCE MCBREEN

ELECTRODE STRUCTURE

Improvements in performance are continually being sought, this has led to the development of lightweight nickel fibre substrates [31,32]. Polypropylene fibres have been metallised both chemically and electrochemically after a special fabric pre-treatment [33]. Johnson et al. [34] have developed and demonstrated improved performance using nickel fibre composite electrodes containing a mixture of fibres as small as 2μm. They compared their results with a commercially available nickel mat (Fibrex™), with nickel fibres of about 30μ.

Saft, Industrial Battery Group [35] have developed a high performance nickel-cadmium cell for electric vehicles. The cell incorporates a hybrid combination of a nickel fibre electrode and a plastic bonded cadmium electrode. This is considered a sensible compromise in terms of specific energy and power, energy and power density, energy efficiency, life and reliability before the commercial development of the nickel-hydrogen cell.
ACTIVE MATERIAL CHARACTERISATION

The chemical state of the active material is still not well understood especially when modified by additions. Several physical studies have been undertaken to improve this knowledge. These have included, scanning electron microscopy [36], Infra-red spectroscopy [37,38], X-ray diffraction, thermal gravimetric analysis, ultraviolet/visible spectroscopy [39,40] and Raman spectroscopy [41].

ADDITIVES

Unates et al. [42] has shown that the addition of cobalt increases the reversibility of the Ni(II)/Ni(III) reaction and hinders ageing effects involving unstable nickel hydroxide. Also, the presence of both cobalt and zinc ions in the metal hydroxide layer has a beneficial influence for the long term stability and efficiency. In addition they found that cadmium hydroxide increases the polarisation of the oxygen evolution reaction. However, Krejci and Vanycek [43] suggest the presence of zinc or iron after formation resulted in a decrease in charge acceptance. This has been confirmed by Demourges-Guerlou [44,45] and that the effect becomes more pronounced at higher concentrations of iron. Visintin et al. [46] have utilised scanning electron microscopy and energy dispersive X-ray analysis to determine the distribution of cobalt and cadmium additions throughout the thickness of the electrode. Lim and Doty [47] have used X-ray techniques to map the distribution of cobalt within the electrode before and after cycling. Cobalt was uniformly distributed when new, but was found to become depleted near the interface between the active material and the nickel metal substrate and migrates into the bulk of the active material.

ELECTROCHEMISTRY MEASUREMENTS

Cycle life and capacity retention of nickel oxide electrodes are areas of necessary improvement for use in nickel-hydrogen cells. Electrochemical impedance
spectroscopy [48,49] and constant potential methods [50] have been employed to characterise self discharge.

A new apparatus [51] for the measurement of self discharge has been developed. The device uses a zinc-oxide cell to determine oxygen gas evolved during self discharge. The device has been adapted [52] to study the formation process of the nickel oxide electrode.

A non-destructive technique [53] has been developed for the determination of impedance parameters of individual electrodes and internal resistance of sealed batteries. In this method the battery is discharged at a constant current of about 2000hr rate for a few seconds. The discharge transient of voltage against time is analysed theoretically to give effective double layer capacitances and charge transfer resistances of both battery cathode and anode separately, as well as the internal resistance of the battery.

An investigation [54] of the discharge performance on the electrode ternary intercalation compounds of graphite with nickel hydroxides, showed that the activation energy for the discharge reaction on the intercalated electrode was lower than on a conventional nickel hydroxide electrode. Water absorption [55] was found to cause a strong increase in the electrical conductivity of uncycled and reduced electrodes.

Double layer impedance measurements of nickel oxide electrodes at low states of charge [56], reveal that porosity does not significantly affect the impedance of the electrode below 100Hz. Even then the double layer impedance can not simply be represented by a pure capacitor. A voltammetric study [57] of hydrous oxide films on nickel in alkali, showed that the majority (80-90%) of the oxide was reduced in the Ni(III)/Ni(II) transition almost reversibly at potentials where the higher oxide was
formed while, depending on the potential of formation, about 10-20% of the NiOOH was irreversibly reduced in the potential region of the hydrogen evolution reaction.

**SIMULATIONS**

Weidner and Timmerman [58] have developed a simulation, which is in good qualitative agreement with experimental data, for the effect of proton diffusion, electron conductivity and charge transfer resistance on nickel hydroxide discharge curves. Mao et al. [59] have presented a theoretical treatment of the discharge performance of a nickel-hydrogen cell which can be used to predict the two discharge plateau behaviour of the nickel electrode.

**A REVIEW OF THE REACTION MECHANISMS OF THE NICKEL ELECTRODE IN ALKALI.**

The simplest overall reaction can be represented as:

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (3.1)
\]

The electrochemical characteristics of nickel electrodes in alkali have been reviewed by Milner and Thomas [60]; they caution that the interpretation of the charge/discharge measurements on nickel are complicated by three phenomenon, namely the oxidation state of nickel is not an integer value in either the charged (III) or discharged (II) state, the equilibrium potential exhibits a hysteresis making its determination difficult and electrode behaviour is sensitive to previous history.

The existence of Ni(OH)\(_2\) and β-NiOOH as the usual discharged and charged materials has been confirmed by X-ray powder diffraction patterns [61-63]. The presence of other structural forms have also been observed, in different electrolytes and under unusual cycling conditions. Tuomi [64,65] has noted that the crystalline structural variability of the divalent nickel hydroxide depended on preparative procedure and that after prolonged overcharge of β-NiOOH in concentrated
potassium hydroxide an $\alpha$-phase was formed. The formation of $\alpha$-phase was eliminated in the presence of lithium hydroxide.

A crystallographic study of the nickel electrode carried out by Bode [66] showed that the charge/discharge process cannot be represented by one equation. At least two reactions can be formulated, which could take place simultaneously, based on different materials as well as different end products. Using potentiostatic and galvanostatic methods they were able to elucidate the part played by these compounds at the nickel electrode as:

$$\beta-\text{Ni(OH)}_2 \quad \text{Transformation in KOH} \quad 3\alpha-\text{Ni(OH)}_2\cdot2\text{H}_2\text{O}$$

Using $\beta$-NiOOH and $\gamma$-NiOOH, they were able to elucidate the part played by these compounds at the nickel electrode as:

$$\begin{align*}
\beta-\text{NiOOH} \quad \beta-\text{NiOOH} \quad \text{Overcharge in KOH} \quad \gamma-\text{NiOOH} \quad \gamma-\text{NiOOH} \\
(\text{more positive by 100mV}) & \quad (\text{more positive by 60mV})
\end{align*}$$

Harivel and associates [67] found that at low potassium hydroxide concentrations, low rates of charge and low overcharge, the $\beta$-NiOOH product is formed. At higher concentrations of potassium hydroxide, higher rates and longer overcharge, the $\gamma$-component is favoured. The $\alpha$-component ($3\text{Ni(OH)}_2\cdot2\text{H}_2\text{O}$) clearly indicates that water is an integral part of the structure and increases the lattice distance between the hydroxide ions greater than the $\beta$ compound. Salkind and Bruins [68] identified a compound that was produced during long overcharge. The form of the compound was suggested by Bode [66] as $[\text{Ni}_4\text{O}_4\text{(OH)}_4]_1\text{O}_{1.5}\text{(OH)}_{0.5}\text{K}$, the $\gamma$-form. A single crystal investigation of nickel using a slow voltage scan [69], found that only a few layers of product are formed in low concentrations of...
potassium hydroxide and that the individual current - voltage peaks were identified relative to the following reactions:

\[
\begin{align*}
\text{Ni} + 2\text{OH}^- & \rightarrow \text{Ni(OH)}_2 + 2e^- \quad (3.3) \\
\text{Ni(OH)}_2 + \text{OH}^- & \rightarrow \text{NiOOH} + H_2O + e^- \quad (3.4) \\
\text{Ni} + 3\text{OH}^- & \rightarrow \text{NiOOH} + H_2O + 3e^- \quad (3.5)
\end{align*}
\]

Reaction 3.3 reflects the conversion of nickel metal to the hydroxide. The active material in the cell is therefore increased and hence the electrode capacity. This oxidation process is related to the corrosion of the nickel current collector. Reaction 3.4 is the oxidation-reduction process occurring in the active material. Reaction 3.5 occurs significantly at higher potentials where oxygen is evolved. The current resulting from these reactions masks the Ni(III) to Ni(IV) reaction. Different oxidation processes have been shown to take place simultaneously at the solid/liquid interface of Ni(OH)\(_2\) [70,71]. On discharge, NiOOH exists over a wide range of compositions which compete for reduction to the discharged species. It is suggested that electrochemical activity takes place at the interface between the conducting NiOOH and non-conducting Ni(OH)\(_2\).

Proton diffusion has been discussed as an alternative mechanism for the nickel oxide electrode [72], Ni(OH)\(_2\) was found to be a good proton conductor but a poor electron conductor. The reaction between \(\alpha\)-3Ni(OH)\(_2\).2H\(_2\)O and \(\gamma\)-NiOOH and subsequent reduction was observed by Briggs and Fleischmann [70,71]. They reported that the discharge and recharge of full layers of NiOOH follows a composite pattern controlled by diffusion of a species through the layers. An infra-red investigation by Kober [73,74] showed that a sintered nickel electrode on discharge has a D\(_{3d}\) structure. The hydroxide ions are parallel to the c axis of the crystal and are
free (hydrogen bonding is absent). Co-ordinate covalent bonds trap a small amount of water in the lattice and upon charging the structure develops a high degree of crystal symmetry. The electrochemical capacity was found to be related to the relative intensity of hydrogen bonding in the charged state.

A linear scan voltammetric investigation [75] on electrochemically prepared nickel hydroxide suggested the following half cell reactions.

\[
2[3\text{Ni(OH)}_2\cdot 2\text{H}_2\text{O}] + 6\text{OH}^- + \frac{3}{2}\text{KOH}
\]

\[
\uparrow
\uparrow
\]

\[
2\left[3\text{NiOOH}_{\frac{7}{2}}\cdot 2\text{H}_2\text{O}_{\frac{3}{4}}\cdot \text{KOH}\right] + 3\text{H}_2\text{O} + 6e^- 
\]

A model was used for the reaction in the nickel oxide electrode including a reversible charge transfer step at the nickel ion site in the lattice. A proton is released at the site and diffuses to the surface on charging and returns to the nickel site during discharge. The proton diffusion is suggested as the limiting step in the reaction. A modification to the Bode reaction has been suggested by Schreiber-Guzman et al. [76-79] as:-

\[
\begin{align*}
[\text{Ni(OH)}_2]_u &\rightleftharpoons [\text{NiOOH}]_s + \text{H}^+ + e^- \\
[\text{Ni(OH)}_2] &\rightleftharpoons [\text{NiOOH}]_u + \text{H}^+ + e^- 
\end{align*}
\]
where \([\text{Ni(OH)}_2]^*\) is a hypothetical intermediate bridging both main electrochemical processes. The subscripts \(u\) and \(s\) refer to unstable and stable states. Utilising cyclic voltammetry and aqueous solution theory Halpert and May [80] suggested that the nickel electrode reaction involved a two electron change and that the charge mechanism was consistent with a quasi-reversible reaction. The results followed the pattern of a two step reaction, that is, electrochemical followed by chemical. The combined reaction was suggested as:-

\[
\begin{align*}
\text{Ni(II)} & \rightleftharpoons \text{Ni(IV)} + 2e^- \text{ electrochemical} \quad (3.8) \\
\text{Ni(II)} + \text{Ni(IV)} & \rightleftharpoons 2\text{Ni(III)} \text{ chemical} \quad (3.9)
\end{align*}
\]

This would explain the wide range of oxidation states ranging from II to IV.
CHAPTER 4

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF SINTERED NICKEL AND SINTERED CADMIUM ELECTRODES

4.1 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF LARGE AREA SINTERED ELECTRODES

4.1.1 INTRODUCTION

Prior to this research impedance spectroscopy was employed by Hughes et al. [27] to investigate some 23Ah Ni-Cd cells with sintered electrodes which originally made up a 25V aircraft battery. The aim of the work was to assess the impedance technique as a possible tool for the evaluation of both the quality and residual capacity of the Ni-Cd cell for military applications. The study showed that the impedance data could not readily be matched to a simple analogue circuit, but found the best estimate of the state of charge could be obtained from the value of capacitive reactance at frequencies between 10Hz and 0.1Hz, the optimum was found to be 0.39Hz. However, impedance values measured at these frequencies were not reproducible from cell to cell or on repeated measurements on the same cell.

Inspection of the results showed impedance values of resistance and reactance which are consistently less than 3mΩ at all states of charge and over all the range of frequencies studied. A value of this magnitude is essential for a good quality cell and is indicative of high surface area of the active material. In addition the cell reveals a significant inductive component, which is typical of large capacity cells with numerous inter-electrode connections. Unfortunately not only do these factors tend to conceal the basic electrochemistry occurring at the electrodes, particularly at the higher frequencies where the inductive component imposes a large effect, it also
hinders any estimate of the contribution to the overall cell impedance from the individual nickel and cadmium electrodes. Also, cells with such low values of impedance are inherently difficult to measure using the a.c.impedance technique, since the value of the sense resistor used for measurement should be the same order of magnitude as the cell under test. This problem has been addressed and presented in a published article [6].

An impedance spectroscopy study was therefore carried out on single nickel and cadmium sintered electrodes extracted from the 23Ah Ni-Cd cell in order to elucidate the impedance contribution from each electrode. The reasoning behind this experimental regime was that once the isolated or de-convoluted response was established then the salient features could be re-combined to provide an interpretable whole. The overall objective is a route to state of charge prediction.

4.1.2 THE SINTERED ELECTRODE

The 23Ah Ni-Cd cell contains ten cadmium electrodes and nine nickel electrodes, it is common for this ratio of electrodes to be used to ensure that the cadmium electrodes are never completely discharged, since recharge is made much more difficult. Consequently the capacity of the cell is limited by the nickel electrode. Both the nickel and cadmium electrodes are made porous by the manufacturer to ensure a large surface area (210m²g⁻¹) available for intimate contact with the active material with a porosity greater than 80%. This engenders a low impedance, enables efficient current collection, good mechanical strength and makes the electrode especially suitable in high rate applications.

The electrode plaque is manufactured by sintering pure nickel powder onto a centrally located metallic mesh or perforated metal foil current collector. Pure nickel powder is prepared by passing carbon monoxide over finely divided nickel, nickel alloys or nickel ores at 200°C and 200 atmospheres. The resulting nickel carbonyl is
condensed and distilled to remove impurities. The nickel carbonyl is then decomposed into carbon monoxide and finely divided nickel powder. The apparent density, particle size and shape can be varied by controlling the reaction conditions.

The nickel powder is then sintered onto the chosen current collector. The current collector utilised in this study is a perforated steel foil, previously nickel plated. A lug for current take off is also welded to the foil, the foil is essential to prevent shrinkage during the sintering process. A graphite former is used to surround the grid with nickel powder which is then sintered at 900°C for about ten minutes, in an inert or reducing atmosphere.

The sintered plaque is then filled with active material by an impregnation process. This is achieved by soaking the plaque in a solution containing nickel nitrate (250g/l) and cobalt nitrate (12g/l) or cadmium nitrate (250g/l). The containing vessel is then evacuated to less than 40mmHg to ensure complete impregnation of the solution into the pores. After soaking, the nickel plaque is cathodically polarised and the cadmium plaque is anodically polarised in hot potassium hydroxide. The electrolysis reaction precipitates insoluble nickel hydroxide and cadmium hydroxide respectively within the pores of the plaque. The resulting electrodes are then washed in distilled water to remove nitrate ions, since these accelerate the self-discharge process on open circuit. This process is repeated, usually at least five times to introduce sufficient active material. For special applications where extra high rate cells are required the process would be repeated as many as twelve times. The resultant plates are then subjected to a formation process to generate the charged active materials nickel oxyhydroxide and cadmium.

4.1.3 EXPERIMENTAL

A 23Ah Ni-Cd cell was initially charged at the 0.1C rate for 16 hours to ensure the cell was fully charged. After resting for 2 hours the cell was then carefully
cut open to expose the electrodes. The individual electrodes were then removed and isolated from any separator material. A perspex (polymethylmethacrylate) box was procured which could accommodate three individual sintered nickel electrodes, these were arranged in the box in parallel formation, with a spacing of 5mm. The middle electrode was made the working electrode and the two outer electrodes were connected together to provide the counter electrode. The perspex box was then filled with 5.3M potassium hydroxide and the a.c. impedance measured in the two terminal mode. The experimental set up used to measure a.c. impedance is described in section 2.2. The same experimental procedure was used to determine the a.c. impedance of the cadmium electrodes.

4.1.4 RESULTS AND DISCUSSION

Figures 4.1 and 4.2 show the complex plane impedance plots for the sintered nickel and sintered cadmium electrodes respectively. It should be noted that the impedance plots do not represent the working electrode alone. Because the counter electrode area is only twice the area of the working electrode, there will be a significant impedance contribution from the counter electrode. However, since both working and counter electrodes are exactly the same material and are both at the same state of charge this is of no concern at this stage.

The complex plane plots for both nickel and cadmium show that both electrodes contribute impedance values of the same order of magnitude and the inductive component still imposes a very significant effect on the impedance spectrum. These results contradict the work of Reid [81], who determined the impedance of nickel electrodes of a 50Ah nickel-cadmium cell, using the metallic case as the reference electrode. It was claimed that the bulk of the impedance was usually due to the nickel electrode.
FIG 4.1 COMPLEX PLANE PLOT OF LARGE AREA SINTERED NICKEL ELECTRODE IN THE FULLY OXIDISED STATE
FIG 4.2 COMPLEX PLANE PLOT OF LARGE AREA SINTERED CADMIUM ELECTRODE IN THE FULLY REDUCED STATE
4.1.5 CONCLUSIONS

1. Sintered nickel and sintered cadmium electrodes make equal contributions to the overall cell impedance. Thus neither can be ignored when considering whole cell measurements.

2. Inductive effects are still very large for both electrodes and this may well conceal the true impedance response which describes the electrochemistry of nickel and cadmium.

4.2 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF 'MINI' SINTERED NICKEL ELECTRODES

4.2.1 INTRODUCTION

In order to establish the true impedance response which would describe the electrochemistry of the porous nickel electrode it was necessary to remove any impedance contribution from the counter electrode and also eliminate the masking effect of the inductive component.

4.2.2 EXPERIMENTAL

The necessary conditions described above were achieved by cutting a sintered nickel electrode to a geometric size of 1cm² (this size of electrode has been termed a "mini" electrode). A small tab at one corner was retained, from which the active material was removed to allow a nickel wire to be spot welded to the exposed steel perforated sheet current collector. The freshly cut edges and the nickel wire were stopped off with Lacomit (a proprietary lacquer stable in alkali).

The mini electrode was then disposed between two large area sintered cadmium electrodes and fully charged as described in experimental section 4.1.3. The cell container was filled with 5.3M potassium hydroxide. The cadmium electrodes were then removed and replaced with two large area sintered nickel electrodes which
were also in a fully charged condition. This arrangement is essential to ensure negligible impedance contribution from the counter electrode [82]. The a.c. impedance of the mini sintered nickel electrode was then determined using the 2-terminal technique described in section 2.2.

The a.c. impedance was determined at various states of charge, this was achieved by substituting the large area nickel electrodes with the large area cadmium electrodes. The mini sintered electrode was then discharged galvanostatically at the 1C rate to remove 10% of the residual capacity and then allowed to rest for one hour. The large area cadmium electrodes were then replaced by the large area nickel electrodes which had also been discharged by 10% and the a.c. impedance redetermined. This procedure was repeated, removing 10% of the capacity on each occasion until the electrode was fully discharged (i.e. 1V cut off). In addition the a.c. impedance was also determined at various levels of polarisation. This was achieved by again fully charging the electrode and then cathodically polarising the electrode in the potentiostatic mode. The impedance was then determined after the initial current had subsided.

After consideration of both the electrochemistry of nickel oxide and the impedance results a suitable electrical analogue was determined and the resultant impedance data were then computer matched using the modelling technique described in section 2.4.

4.2.3 RESULTS AND DISCUSSION

Figures 4.3 and 4.5 show the complex plane impedance plots over the frequency range 10kHz to 10mHz for the mini sintered nickel electrode when fully oxidised and fully reduced respectively. Figures 4.4 and 4.6 show the corresponding Randles plots, the solid line in both the complex plane and Randles plots represents the modelled behaviour generated from the electrical analogue in figure 4.7. Clearly
FIG 4.3 COMPLEX PLANE PLOT OF MINI SINTERED NICKEL ELECTRODE AT 100% STATE OF CHARGE
FIG 4.4  RANDES PLOT OF MINI SINTERED NICKEL ELECTRODE AT 100% STATE OF CHARGE

\[
\begin{align*}
R & \text{ vs. } \frac{1}{\omega^{1/2}}  \\
\text{Capacitive} & (\times) \\
\text{Resistive} & (+) 
\end{align*}
\]
FIG 4.5  
COMPLEX PLANE PLOT OF MINI SINTERED ELECTRODE  
AT 0% STATE OF CHARGE
FIG 4.6  RANDLE'S PLOT OF MINI SINTERED NICKEL ELECTRODE  
AT 0% STATE OF CHARGE
the problem of masking produced by the inductive component has been resolved over
the frequency range of interest. A significant change in impedance response can be
seen between the oxidised and reduced electrode. When fully reduced the electrode
reveals a flattened semi-circle at the higher frequencies. The semi-circle then relaxes at
lower frequencies to a dihedral which subtends an angle of 43°. The fully oxidised
electrode reveals a much reduced semi-circle at high frequencies and a dihedral of 35°
which increases to 50° at frequencies less than 100mHz.

Reported mechanisms for the nickel oxide electrode show the simplest process
for the overall exchange between Ni(II) and Ni(III) can be represented as:-

\[
\begin{align*}
\text{NiO} + \text{OH}^- & \rightarrow \text{NiOOH}^{\text{ads}} & 4.1 \\
\text{NiOOH}^{\text{ads}} & \rightleftharpoons \text{NiOOH} + e^- & 4.2
\end{align*}
\]

where the hydroxide ion is adsorbed and undergoes subsequent reaction with the NiO
to form the Ni(III) state.

The electrical analogue used to model this electrochemistry is shown in figure
4.7, where \( R_\Omega \) represents the ohmic resistance of the electrolyte, \( \Theta \) the charge transfer
resistance, \( \sigma \) the Warburg coefficient, \( C_L \) the double layer capacitance, \( C_A \) the
capacitance and \( R_A \) the resistance of the process 4.1 which precedes the charge
transfer. \( \gamma \) represents the porosity factor, operating on this part of the circuit.

As highlighted earlier battery companies manufacture cells with electrodes
which are porous, to ensure a large surface area for reaction and hence provide
optimum energy output. However, the porous nature of the electrodes makes
representation of the electrical analogue more complicated compared to the analogue
used to describe the processes at a planar electrode. Lenhart [83] has presented a
FIG. 4.7 ANALOGUE CIRCUIT FOR THE MINI SINTERED NICKEL ELECTRODE
model to describe the electrochemical behaviour of a planar nickel hydroxide electrode. Others [26,84] have used similar models for sintered nickel electrodes without accounting for porosity. As described in section 2.9 the planar electrode behaviour in the complex plane may be transformed into that corresponding to the porous electrode by square rooting the modulus of the impedance and halving the argument. These factors have been introduced into the electrical analogue (figure 4.7) to account for the porous nature of the sintered nickel electrode. The porosity factor is represented by $\gamma$, ($\gamma=1$ for a planar electrode and 0.5 in the case of a semi-infinitely porous electrode). The electrical analogue was tested using the numerical analysis described in section 2.8.

Figures 4.8 to 4.15 show the complex plane and Randles plots of the mini sintered nickel electrode at various states of charge. The modelled impedance data are represented by the solid line in each plot. The values of the computed electrical analogue component values are presented in table 4.1

4.2.4 A STATE OF CHARGE CORRELATION

The component values listed in table 4.1 were analysed for any parameter which might yield a correlation with residual capacity. The most useful correlation was found to be the product $\log(0\text{Cl})$. This product provides a value for the charge transfer resistance which is corrected for area. The general trend as the electrode is discharged is shown in figure 4.16

4.2.5 POLARISATION STUDIES

The potential dependence of the planar equivalent charge transfer resistance was determined for the nickel electrode by stepping the potential cathodically from the fully oxidised state and quickly determining the impedance, after the initial current had subsided, collecting only data which is attributable to charge transfer. This procedure was repeated for several cathodic potentials. The impedance results were
FIG 4.8  COMPLEX PLANE PLOT OF MINI SINTERED NICKEL ELECTRODE AT 80% STATE OF CHARGE
FIG 4.9  RANDLES PLOT OF MINI SINTERED NICKEL ELECTRODE
AT 80% STATE OF CHARGE

\[ R \& \frac{1}{\omega C} \quad (\Omega) \]

\[ \omega^{1/2} \quad (s^{1/2}) \]

+ Resistive

X Capacitive
FIG 4.10 COMPLEX PLANE PLOT OF MINI SINTERED NICKEL ELECTRODE AT 60% STATE OF CHARGE
FIG. 4.11  RANDLES PLOT OF MINI SINTERED NICKEL ELECTRODE AT 60% STATE OF CHARGE

\[ R \text{ & } \frac{1}{\mu C} \ (\Omega) \]

\[ \omega^{1/2} \ (s^{1/2}) \]

+ Resistive

× Capacitive
FIG 4.12  COMPLEX PLANE PLOT OF MINI SINTERED NICKEL ELECTRODE AT 40% STATE OF CHARGE
FIG 4.13 RANDLES PLOT OF MINI SINTERED NICKEL ELECTRODE AT 40% STATE OF CHARGE
FIG 4.14 COMPLEX PLANE PLOT OF MINI SINTERED NICKEL ELECTRODE AT 20% STATE OF CHARGE
FIG 4.15  RANDLES PLOT OF MINI SINTERED NICKEL ELECTRODE AT 20% STATE OF CHARGE

![Graph showing Randles plot for a mini sintered nickel electrode at 20% state of charge. The graph illustrates the relationship between R & 1/\omega C versus \omega^{-1/2} (s^{1/2}) for both resistive and capacitive regions.](image-url)
TABLE 4.1 Values of the circuit components for the sintered nickel electrode.

<table>
<thead>
<tr>
<th>Charge (%)</th>
<th>RΩ (Ohm)</th>
<th>θ (Ohm)</th>
<th>CL (Farad)</th>
<th>σ (s(^{-1/2}))</th>
<th>CA (Farad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.31</td>
<td>2.02e-5</td>
<td>3.86</td>
<td>2.54e-2</td>
<td>57.31</td>
</tr>
<tr>
<td>90</td>
<td>0.36</td>
<td>3.70e-5</td>
<td>3.13</td>
<td>2.32e-2</td>
<td>66.66</td>
</tr>
<tr>
<td>80</td>
<td>0.36</td>
<td>3.53e-5</td>
<td>4.83</td>
<td>3.59e-2</td>
<td>32.42</td>
</tr>
<tr>
<td>70</td>
<td>0.34</td>
<td>3.21e-5</td>
<td>0.29</td>
<td>3.07e-2</td>
<td>28.99</td>
</tr>
<tr>
<td>60</td>
<td>0.33</td>
<td>3.07e-5</td>
<td>5.41</td>
<td>3.53e-2</td>
<td>39.53</td>
</tr>
<tr>
<td>50</td>
<td>0.33</td>
<td>5.84e-5</td>
<td>4.46</td>
<td>4.32e-2</td>
<td>41.28</td>
</tr>
<tr>
<td>40</td>
<td>0.31</td>
<td>4.01e-4</td>
<td>4.86</td>
<td>4.40e-2</td>
<td>51.18</td>
</tr>
<tr>
<td>30</td>
<td>0.31</td>
<td>1.92e-4</td>
<td>5.46</td>
<td>2.64e-2</td>
<td>73.65</td>
</tr>
<tr>
<td>20</td>
<td>0.35</td>
<td>5.39e-4</td>
<td>6.37</td>
<td>2.26e-2</td>
<td>121.03</td>
</tr>
<tr>
<td>10</td>
<td>0.32</td>
<td>4.38e-4</td>
<td>0.25</td>
<td>2.75e-2</td>
<td>68.91</td>
</tr>
<tr>
<td>0</td>
<td>0.29</td>
<td>1.36e-2</td>
<td>6.2e-2</td>
<td>4.10e-2</td>
<td>48.50</td>
</tr>
</tbody>
</table>

The values of porosity and R_A were consistently 0.5 and 1MΩ respectively.
fitted using the electrical analogue shown in figure 4.7, to determine values of the charge transfer resistance at various levels of polarisation. Figure 4.17 shows the charge transfer data plotted as logθ versus potential. The Tafel plot shows a linear relationship with a slope of 36mVdecade⁻¹. For a simple electron transfer the Tafel slope should be 120mVdecade⁻¹. A slope of 36mVdecade⁻¹ therefore suggests a reaction involving three electrons. Tafel data obtained by Russian workers [85] have reported Tafel slopes of 40mVdecade⁻¹ in the high current region and 120mVdecade⁻¹ in the low current region. These values also varied with the number of cycles completed in a cyclic voltammetry experiment. This makes comparison with the data obtained here rather difficult. Examination of the literature in order to find a mechanism which implies a 40mVdecade⁻¹ slope was also unrewarding and a matter of some controversy. For example McArthur [86] suggested that the overall reaction involved a six electron change whilst Barnard [87] emphasises the importance of the precise nature of the co-existing phases. It is quite possible, in the face of this, that Tafel data may have limited significance. However, the quality of the Tafel data obtained indicates that this may not be entirely insignificant.

4.2.6 CONCLUSIONS

1. The use of mini sintered electrodes has eliminated the effects of inductance and revealed the true impedance response representative of the electrochemistry of the porous nickel electrode.

2. The parameters determined were to some degree successfully used to predict the state of charge of the electrode, using a corrected area (log(θCL)) plot versus state of charge.

3. The electrochemical behaviour of mini sintered nickel electrodes was successfully modelled using the electrical analogue technique.
Fig. 4.17 CATHODIC OVERPOTENTIAL VS. LOG$_{10}$ $\theta$

CATHODIC OVERPOTENTIAL / mV

LOG$_{10}$ $\theta$

40mV/decade
4. The porous nature of the electrode has been completely accounted for in the electrical analogue. Previous kinetic investigations have not done so and thereby uncertainty may arise from the oversimplifications introduced.

4.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF 'MINI' SINTERED CADMIUM ELECTRODES

4.3.1 INTRODUCTION

The electrochemical behaviour of cadmium electrodes in alkaline electrolytes has been reviewed by several authors including Milner and Thomas [60], Latham and Hampson [88], Armstrong et al. [89], Bamard [90] and Barton et al. [91].

The overall reaction at the cadmium electrode is generally recognised as:-

\[
\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 + 2\text{e}^-
\]

Cadmium hydroxide may exist in three phases i.e. \(\alpha\), \(\beta\) or \(\gamma\) both the \(\alpha\) and \(\beta\) phases having the Brucite structure. The unstable \(\alpha\) phase may have a greater degree of hydration than the \(\beta\) phase as well as a variable and increased interlayer spacing owing to the presence of water between the \(\text{OH}^-\) anion planes. These structures are analogous to those of \(\alpha\)-\(\text{Ni(OH)}_2\) and \(\beta\)-\(\text{Ni(OH)}_2\). \(\gamma\)-\(\text{Cd(OH)}_2\) has a entirely different structure and is believed to be monoclinic. There is some doubt as to whether the \(\gamma\) phase or one of the several secondary structures of the \(\beta\) phase is the 'active phase'. However, the reactions of the cadmium electrode are apparently less complicated than those at the nickel electrode.

4.3.2 EXPERIMENTAL

As described in section 4.4.2 the mini cadmium sintered electrode was prepared by first spot welding on a nickel wire contact and then disposing the
electrode between two large area nickel sintered electrodes in 5.3M potassium hydroxide. The cell was then charged at constant current until the cadmium electrode was fully reduced. The nickel electrodes were then replaced by two large area sintered cadmium electrodes which had also been previously fully reduced. The electrodes were then allowed to rest for one hour.

The a.c. impedance response was then determined in the 2-terminal mode as described in section 2.2. The mini electrode and the two large area electrodes were then discharged at constant current to remove 10% of their residual capacity and the a.c. impedance redetermined at the new state of charge. This procedure was repeated until the electrodes were fully discharged i.e. the condition where all the available cadmium was transformed to the oxidised (2+ state) form and further oxidation would result in evolution of oxygen.

4.3.3 RESULTS AND DISCUSSION

Figure 4.18 shows the complex plane plot of the fully charged mini sintered cadmium electrode. Figure 4.19 shows the same data in the high frequency domain. The dihedral from 10kHz to 100Hz leaves the real axis at 27° which increases to 54° at lower frequencies indicating a transition from porous to planar characteristics. At high frequencies when the reaction layer is thin the porous structure of the electrode is observed. At low frequencies when the reaction layer is thick only the superficial diffusing surface is evident.

Figures 4.20 and 4.21 show the complex plane plots of the electrode at 80% and 0% state of charge respectively. The two plots show that there is very little change in the a.c. impedance response over this range of states of charge and as a consequence the electrode process remains essentially similar throughout this region.

Two different mechanisms have been proposed for the oxidation of cadmium in alkali, a solid state growth mechanism [92,93] and a dissolution precipitation
FIG 4.18

COMPLEX PLANE PLOT OF A FULLY REDUCED
(100% STATE OF CHARGE) MINI SINTERED
CADMIUM ELECTRODE
FIG 4.19

COMPLEX PLANE PLOT OF A FULLY REDUCED MINI SINTERED CADMIUM ELECTRODE AT 100% STATE OF CHARGE IN THE HIGH FREQUENCY DOMAIN
FIG 4.20  COMPLEX PLANE PLOT OF A MINI SINTERED CADDIUM ELECTRODE AT 80% STATE OF CHARGE
FIG 4.21 COMPLEX PLANE PLOT OF A MINI SINTERED CADMIUM ELECTRODE AT 0% STATE OF CHARGE
mechanism [94-97] where soluble intermediates such as Cd(OH)$_3$ and Cd(OH)$_4^{2-}$ play a role in the charge-discharge reaction, the latter has been shown to be the predominant species in concentrations greater than 1M hydroxide solution. Of the reported investigations of the electrochemistry of cadmium using the a.c.impedance technique, [98-102] those of Armstrong and Edmundson [99,100] appear to be the most sophisticated. These authors have studied both planar and to a lesser extent porous cadmium electrodes and concluded that a simple Randles circuit representing charge-transfer and diffusion was sufficient for the interpretation of the impedance data at frequencies greater than 3Hz.

They suggested that their impedance results were indicative only of diffusion of the oxidised cadmium species Cd(OH)$_4^{2-}$ in the solution. Inspection of the complex plane plots figures 4.18 to 4.21 show that the dissolution process is very fast since there is no evidence of control by charge transfer at high frequencies and any phase formation is relaxed out. However, in distinction to Armstrong and Edmundson it was found necessary to modify the simple Randles circuit to account for a porous electrode of semi-infinite dimension and to include a component representing a film across the electrode surface. The new electrical analogue used to describe the electrochemistry of the porous cadmium electrode is shown in figure 4.22. $R_n$ represents the ohmic resistance of the electrolyte, $\Theta$ the charge transfer resistance, $\sigma$ the Warburg coefficient, $C_L$ the double layer capacitance, $C_x$ the capacitance and $R_x$ the resistance of the cadmium hydroxide film. $\gamma$ represents the porosity factor. During the data fitting procedure it was found necessary to include a small but finite value of charge transfer in order to complete the modelling process.

Oxide and hydroxide films are notoriously difficult to remove from porous structures. Thus it is possible that there exists a film on the fully charged electrode even after exhaustive cathodization and this may explain the difference between the
FIG. 4.22 ANALOGUE CIRCUIT FOR THE MINI SINTERED CADMIUM ELECTRODE
information presented here on porous electrodes and that presented on planar electrodes by earlier workers [99,100]. It is interesting to note that whilst it was not possible to detect a well defined charge transfer semi-circle by eye in the complex plane plots figures 4.18 to 4.21, it was necessary to include a small but finite value of charge transfer resistance in order to complete the modelling procedure. It has been possible to fit the data in the frequency domain down to 300mHz with a reasonable small divergence between the predicted behaviour and the experimental data. Figures 4.23 to 4.26 show the computer matched behaviour in the complex plane and the Randles representation. The analogue circuit components determined from this model are presented in table 4.2.

Some divergence between the data and the modelled behaviour was noted at frequencies below 300mHz. This is thought to be due to the intrusion of slow time dependent processes. The most likely process is electrocrystallization with a possible induction period for the nucleation process. At high frequencies such a process would be relaxed out, whilst at low frequencies when the process becomes increasingly able to follow the electric vector of the perturbating alternating current the process intrudes.

Armstrong and Edmundson [99] proposed that their data at high frequencies showed a skewed charge transfer semi-circle which has not been revealed in the data obtained here. However a degree of porosity would appear as an elongation of the semi-circle shape. A negligible charge-transfer semi-circle is in keeping with a very large surface area of electrode compared with the earlier work. It is clear that the charge transfer process exerts a control on the electrode reaction since it was necessary to include a small value in order to obtain a proper data match. The values shown in table 4.2 are too approximate for any conclusion regarding charge-transfer
FIG 4.23

COMPLEX PLANE PLOT OF A MINI SINTERED CADMIUM ELECTRODE AT 100% STATE OF CHARGE
(MODELLED BEHAVIOUR 10kHz to 0.3Hz)

\[ I \times 10C \text{ (Ω)} \]

\[ R \text{ (Ω)} \]
FIG 4.24
RANDLES PLOT OF A MINI SINTERED CADMIUM ELECTRODE AT 100% STATE OF CHARGE (MODELLED BEHAVIOUR 10kHz to 0.3Hz)
FIG 4.25  COMPLEX PLANE PLOT OF A MINI SINTERED CADMIUM ELECTRODE AT 0% STATE OF CHARGE (MODELLED BEHAVIOUR 10kHz to 0.3Hz)

![Complex Plane Plot](image)

- $\frac{1}{\omega C} (\Omega)$
- $R (\Omega)$

10kHz, 10Hz
FIG 4.26 Randles plot of a mini sintered cadmium electrode at 0% state of charge (modelled behaviour 10kHz to 0.3Hz)
TABLE 4.2 Values of the circuit components for the sintered cadmium electrode.

<table>
<thead>
<tr>
<th>Charge (%)</th>
<th>RΩ (Ohm)</th>
<th>θ (Ohm)</th>
<th>Cl (Farad)</th>
<th>σ (s⁻¹/²)</th>
<th>Cx (Farad)</th>
<th>Rx</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.5</td>
<td>1.0e⁻⁷</td>
<td>0.06</td>
<td>0.30</td>
<td>2.7</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>80</td>
<td>0.46</td>
<td>1.0e⁻⁵</td>
<td>0.20</td>
<td>0.08</td>
<td>2.3</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>60</td>
<td>0.42</td>
<td>1.0e⁻⁵</td>
<td>0.30</td>
<td>0.06</td>
<td>2.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>40</td>
<td>0.46</td>
<td>1.0e⁻⁵</td>
<td>0.13</td>
<td>0.12</td>
<td>3.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>20</td>
<td>0.41</td>
<td>1.0e⁻⁵</td>
<td>0.12</td>
<td>0.11</td>
<td>4.3</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>0.44</td>
<td>1.0e⁻⁵</td>
<td>0.13</td>
<td>0.08</td>
<td>3.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
to be drawn. The values of the analogue representation change only very slightly as the electrode is discharged

4.3.3 CONCLUSIONS

1. To a first approximation the Randles circuit modified for porosity and the presence of films fits the impedance data.

2. Slow processes relaxed out by the high frequencies complicate the impedance plots at frequencies lower than 300mHz.

3. It was considered that the electrochemistry of the porous cadmium electrode could be modelled to an accurate enough extent for its behaviour to be convoluted with the model developed for the mini sintered nickel electrode in section 4.2.3.

4.4 FINAL CONCLUSIONS

As discussed in section 4.1 one of the aims of this research was to be able to convolute the two electrical analogues developed for the sintered nickel and cadmium, so that the whole cell impedance could be represented. In addition to an increase in electrode area it was also necessary to account for the impedance contribution from the separator material. The results obtained for the sintered nickel and cadmium electrodes revealed that the impedance components were almost identical. However, formation of films of cadmium hydroxide on the negative electrode, may dominate the impedance spectrum of the whole Ni-Cd cell at low frequencies. At low states of charge and high frequencies, the charge transfer resistance of the nickel positive electrode dominates.

The electrical analogue circuits proposed for the sintered nickel and cadmium electrodes were to provide good correlation between the true and modelled data. However, the combination of the nickel and cadmium electrode models meant that ultimately fifteen different parameters had to be 'fitted'. Because of the large number
of circuit elements the matching procedure was fraught with difficulty and unfortunately no sensible match was achieved.

However, for the first time the a.c impedance technique has been used successfully to measure and subsequently model the electrochemical behaviour of porous nickel and cadmium electrodes.
CHAPTER 5

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF PLASTIC BONDED NICKEL ELECTRODES

5.1 INTRODUCTION

Because of the success achieved in the electrochemical impedance spectroscopy study of the sintered nickel electrode, it was considered opportune and appropriate to use the same technique to study the plastic bonded nickel electrode. This would allow the electrical analogue circuit developed for the sintered nickel electrode to be tested on an electrode whose fabrication technology was different but whose basic electrochemistry would remain unchanged.

Research and development work in the battery industry on plastic bonded nickel-cadmium cells for commercial applications is rapidly expanding and hopefully the results presented provide a contribution to the understanding of the mode of operation of such electrode structures.

In addition to the determination of the impedance response at different states of charge (at open circuit), the impedance was also determined at specific operating potentials.

5.2 EXPERIMENTAL

5.2.1 ELECTRODE FABRICATION

Plastic bonded electrodes do not contain an integral metallic substrate and hence rely on the addition of graphite which is essential to provide good electrical conductivity between the nickel current collector and the poorly conducting
discharged active material. According to Veres and Csath [103] the ideal properties which graphite should exhibit are low specific resistance, a high specific surface and be resistant to oxidation.

Plastic bonded nickel electrodes were fabricated by first dry mixing powders of nickel hydroxide (63.5%), cobalt hydroxide (1.5%) and Lonza 2.5μ graphite (30%). Propan-2-ol was then added to the mix in sufficient quantity to just wet the paste. Polytetrafluoroethylene P.T.F.E. as a suspension (I.C.I Fluon,60%w/w) was then added such that the overall P.T.F.E. content was 5%. The paste was then mixed for about five minutes, the actual time of mixing at this stage is critical since overmixing results in a stiff unusable paste. The final paste, which has dough like characteristics, was then rolled to the required thickness. During rolling the paste sheet was biaxially folded after each pass through the rollers. This process engenders cross orientation of the P.T.F.E. fibres, which extend as the paste is worked, see section 5.3.3. The resultant plastic bonded electrode was then air dried at 60°C for one hour. Although the active materials are now held together in an easy to handle form the electrodes mechanical strength is poor and consequently was supported on a nickel foil (60μ), which also provides a means of current collection.

5.2.2 THE ELECTROCHEMICAL CELL

A 1cm² plastic bonded nickel electrode was clamped onto a nickel foil using two slabs of perspex one of which was fitted with a window such that the electrode was readily exposed to the 7M potassium hydroxide electrolyte, as well as facing directly towards the luggin capillary. The current take off tag on the foil was manufactured so that it was long enough to enable the electrode assembly to be lowered into a standard three-limbed electrochemical cell. A large area nickel gauze was used as the counter electrode, the gauze was arranged so that it completely encircled the working electrode and all potential measurements were made against a
mercury-mercuric oxide reference electrode in 7M potassium hydroxide. The plastic bonded nickel electrode was initially formed by charging the electrode at the 0.1C rate for 14 hours and then subsequent discharge at the C rate to a cut-off potential of 100mV (vs Hg/HgO). The electrode was cycled in this mode until the maximum capacity had been established, usually after six cycles. The cycling procedure was then halted at top of charge and the electrode allowed to rest for one hour. The electrode was then discharged at the C rate and the voltage-time polarisation behaviour determined. The electrode was then recharged and allowed to rest for one hour.

After this rest period the a.c. impedance of the electrode was measured in the three terminal mode as described in section 2.2. The electrode was then discharged by 10% of its capacity at the 0.1C rate and allowed to rest for one hour before the a.c. impedance was redetermined. This procedure was repeated until the electrode was fully discharged, that is, to a potential limit of 0.0V versus Hg/HgO. Further a.c. impedance measurements were performed on the electrode to determine the response at various potentials. The plastic bonded electrode was again recharged and was then cathodically polarised to 400mV where the initial current was allowed to subside before the a.c. impedance measurement was made in the three terminal mode. This procedure was carried out at several cathodic potentials down to 100mV.

5.2.3 SCANNING ELECTRON MICROSCOPY

A morphological inspection of the plastic bonded nickel electrode was carried out in order to determine any surface changes on the electrode which may be attributable to its electrochemical behaviour. A 1cm² plastic bonded electrode was prepared and then formed up as described in sections 5.2.1 and 5.2.2 respectively. When fully charged the electrode was removed from the cell and thoroughly washed with distilled water. The excess water was removed with absorbent paper and the
electrode then placed in a desiccator containing silica gel. A new electrode was then prepared as described above. After formation this electrode was discharged at constant current until a potential of 450mV (vs Hg/HgO) was reached. At this potential discharge was halted and the electrode removed and washed and dried as above. This procedure was repeated starting with new electrodes and discharging the electrode to consecutive new lower potentials until a final potential of 100mV.

The dried samples were then coated with a thin film of gold to provide good conductivity to allow successful scanning electron microscopy of the surface.

5.3 RESULTS AND DISCUSSION

Figure 5.1 shows the voltage-time polarisation curve for both the 1cm² plastic bonded electrode and the 1cm² sintered electrode for comparison. The plastic bonded electrode discharge curve clearly reveals two potential plateaux. The first and main step is located in the potential range 350 to 250mV (vs Hg/HgO) and is the region which is utilised in alkaline power sources, where the active material nickel oxyhydroxide is reduced to nickel hydroxide. The second potential step occurs between -100 and -600mV (vs Hg/HgO), it can be seen that a substantial portion of the electrode capacity is discharged at this lower potential. The active material remaining in this lower potential window is known to behave as a semi-conductor [104]. Several hypotheses have been presented for the development of the second discharge step including, the reduction of dissolved or trapped oxygen, especially in the presence of graphite [63], the reduction of lower oxides [105], the reduction of oxygen to peroxide which participates in the reduction of nickel oxide [106] and more recently to differences in the ohmic contacts of the electroactive particles [107]. It is possible that the latter is more likely since it is necessary to design the cell such that allowance is made for volume changes during formation and that subsequently there
FIG 5.1 VOLTAGE - TIME POLARISATION CURVES FOR MINI PLASTIC BONDED AND SINTERED NICKEL ELECTRODES

- a sintered
- b plastic bonded
is sufficient compaction of the electrodes. This problem is discussed again in section 6.4.

Figures 5.2 and 5.3 shows the complex plane and Randles plot for a fully charged plastic bonded nickel oxide electrode, the resultant modelled behaviour is represented by the solid line. A well defined roughened charge transfer semi-circle can be seen which leaves the real axis at approximately 78°. This process then relaxes out in the lower frequency domain, around 80mHz, to a diffusional process with an angle of 22.5° to the real axis which is more typical of a semi-infinite porous electrode. A third process can then be observed at the lowest frequencies which is almost purely capacitive. These three distinct processes can also be clearly seen in the Randles plot. The $R$ and $1/\omega C$ data curves for the in-phase and out-of-phase components of the electrode impedance show behaviour indicative of charge-transfer at high frequency followed by diffusion and a cross-over of these curves at the lowest frequencies.

Figures 5.4 and 5.5 show the complex plane and Randles plots after removal of 13% of the electrode capacity. As can be seen the overall shape of the impedance locus is similar to the electrode when fully charged, however, the data indicate that the electrode appears to be more porous, since the charge-transfer semi-circle now leaves the real axis at 70° and the Warburg tail is now less than 22.5°. The angle that the third process now makes with the real axis has lowered by 10°. Figure 5.6 and 5.7 reveal the complex plane and Randles plots of a 75% state of charge nickel plastic bonded electrode. The porous nature of the charge-transfer semi-circle is still evident but the Warburg tail now exhibits more planar behaviour with an angle of 40°. The third process at the lowest frequencies has now been extinguished.
FIG 5.2 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 100% STATE OF CHARGE
FIG 5.3 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 100% STATE OF CHARGE

- Resistive
- Capacitive
FIG 5.4 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 87% STATE OF CHARGE
FIG 5.5 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 87% STATE OF CHARGE

![Graph showing Randles plot of mini plastic bonded nickel electrode at 87% state of charge with resistive and capacitive markers.](image-url)
FIG 5.6 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 75% STATE OF CHARGE
FIG. 5.7 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 75% STATE OF CHARGE
FIG 5.8 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 62% STATE OF CHARGE
FIG 5.9 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 62% STATE OF CHARGE

The diagram shows a Randles plot with the x-axis representing $\omega^{-1/2}$ (rad/s) and the y-axis representing $R$ or $1/C$ (in Ω). It includes two types of markers: + for resistive and × for capacitive behavior.
FIG 5.10 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 43% STATE OF CHARGE
FIG 5.11 RANDEL'S PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 43% STATE OF CHARGE
Fig. 5.12 Complex Plane Plot of Mini Plastic Bonded Nickel Electrode at 27% State of Charge
FIG 5.13 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 27% STATE OF CHARGE
FIG 5.14 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 15% STATE OF CHARGE
FIG 5.15 RANDEL'S PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 15% STATE OF CHARGE
FIG 5.16 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 0% STATE OF CHARGE
FIG 5.17 Randles Plot of Mini Plastic Bonded Nickel Electrode at 0% State of Charge
Inspection of figures 5.8 to 5.13 which show the corresponding complex plane and Randles plots of the electrode at 62%, 43% and 27% state of charge respectively, indicates that the porous nature of the charge-transfer semi-circle remains essentially constant over this range of states of charge, whilst the value of the impedance of the charge transfer gradually increases. The planar character of the Warburg diffusion gradually increases over this range up to 65\°.

At 15% state of charge the complex plane data in figure 5.14 still reveals similar porosity of the charge-transfer semi-circle at high frequencies, but at intermediate frequencies the semi-circle becomes elongated before relaxing out into the diffusion process, which has reversed character by behaving more porous. Figure 5.16 and 5.17 show the complex-plane and Randles plots when fully discharged. The data clearly reveal a completely new response. The magnitude of the impedance has increased five fold and the whole process seems to have become more controlled by the intermediate adsorption process which is clearly reflected by the overlap of the R and 1/\omega C lines in the Randles plot.

Comparison of the results obtained here for the plastic bonded electrode and those obtained for the sintered electrode show quite clear differences. For example the overall impedance values for the plastic bonded electrode are about 5\Omega rising to 50\Omega at the lowest state of charge, compared to about 1\Omega for the sintered electrode at all states of charge. In addition, the charge-transfer semi-circle and other processes are much more clearly revealed in the impedance data for the plastic bonded electrode. Also, a lower level of porosity has been identified for the plastic bonded electrode.

The reason for the greater clarity of data revealed for the plastic bonded electrode is probably due to the fact that the active area is much smaller than the sintered electrode. Although the geometric areas used in the experiments are the same the plastic bonded electrode contains graphite and P.T.F.E. which consequently
reduces the effective area of the active material. The sintered electrode contains no such additives and since the active material is supported in a porous nickel plaque this will also contribute to the overall available active area.

5.3.1 THE MODEL

Attempts were first made to fit the data using the electrical analogue developed for the sintered electrode with limited success. It was found necessary to refine the model by including a series network of a resistor and capacitor in parallel see figure 5.18. These new components were only required during the modelling procedure at the lowest frequencies where the data revealed a predominantly capacitive behaviour. This capacitive behaviour has been shown [108] to be due to the finite diffusion effects of the redox components in the nickel oxide phase. Table 5.1 shows the component values for the modelled behaviour of the nickel plastic bonded electrode at various states of charge.

5.3.2 STATE OF CHARGE CORRELATION

The modified electrical analogue used to model the behaviour of the plastic bonded electrode has provided some high quality fit with the measured data. However the circuit component values have not revealed any parameter which correlates with state of charge. Fortunately, inspection of the impedance data has indicated a good correlation of state of charge with the bulk resistance determined around 1Hz. The optimum frequency was found to be 0.6Hz. A plot of bulk resistance versus state of charge (25% to 100%) provided a correlation coefficient of 0.994 at this frequency.

5.3.2 POLARISATION STUDIES

The a.c. impedance responses of the plastic bonded electrode at various potentials are shown in the complex plane and Randles plots in figures 5.19 to 5.32. The plots show the data and the best computer generated fit (solid line) obtained using
Fig. 5.18 Analogue circuit for the mini plastic bonded nickel electrode

\[ R_\Omega \]

\[ C_L \]

\[ \gamma \]

\[ \Theta \]

\[ \sigma \]

\[ C_{\text{ads}} \]

\[ R_{\text{ads}} \]

\[ C_X \]

\[ R_X \]
TABLE 5.1 Values of the circuit components for the plastic bonded nickel electrode.

<table>
<thead>
<tr>
<th>Charge (%)</th>
<th>$R_{\Omega}$ (Ω)</th>
<th>$\theta$ (Ω)</th>
<th>$C_L$ (F)</th>
<th>$\sigma$ (s$^{-1/2}$)</th>
<th>$\text{Rads}$ (Ω)</th>
<th>$C_{ads}$ (F)</th>
<th>$C_x$ (F)</th>
<th>$R_x$ (Ω)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.15</td>
<td>3.4</td>
<td>4.52e-2</td>
<td>0.24</td>
<td>0.98</td>
<td>3.65</td>
<td>22</td>
<td>1e9</td>
<td>0.80</td>
</tr>
<tr>
<td>87</td>
<td>0.09</td>
<td>3.6</td>
<td>2.00e-2</td>
<td>0.37</td>
<td>0.66</td>
<td>2.58</td>
<td>26</td>
<td>1e9</td>
<td>0.74</td>
</tr>
<tr>
<td>75</td>
<td>0.1</td>
<td>2.9</td>
<td>3.34e-2</td>
<td>0.56</td>
<td>0.42</td>
<td>0.12</td>
<td>72</td>
<td>1e9</td>
<td>0.79</td>
</tr>
<tr>
<td>62</td>
<td>0.1</td>
<td>3.2</td>
<td>2.11e-3</td>
<td>0.52</td>
<td>0.30</td>
<td>8.9e-2</td>
<td>82</td>
<td>1e9</td>
<td>0.84</td>
</tr>
<tr>
<td>43</td>
<td>0.1</td>
<td>3.9</td>
<td>1.80e-3</td>
<td>0.50</td>
<td>0.37</td>
<td>9.5e-2</td>
<td>35</td>
<td>1e9</td>
<td>0.84</td>
</tr>
<tr>
<td>27</td>
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<td>4.7</td>
<td>1.65e-3</td>
<td>0.50</td>
<td>0.57</td>
<td>0.12</td>
<td>17</td>
<td>1e9</td>
<td>0.83</td>
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<tr>
<td>15</td>
<td>0.06</td>
<td>7.5</td>
<td>1.60e-3</td>
<td>1.50</td>
<td>2.18</td>
<td>5.5e-2</td>
<td>92</td>
<td>1e9</td>
<td>0.79</td>
</tr>
<tr>
<td>0</td>
<td>0.1</td>
<td>4.5</td>
<td>1.73e-3</td>
<td>20.4</td>
<td>152</td>
<td>4.4e-3</td>
<td>1e3</td>
<td>1e9</td>
<td>0.81</td>
</tr>
</tbody>
</table>
FIG 5.19 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 400mV
FIG 5.20 Randles plot of mini plastic bonded nickel electrode at 400mV.
FIG 5.21 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 350mV
FIG 5.22 RANKLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 350mV
FIG 5.23 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 300mV
FIG 5.24 Randles plot of Mini Plastic Bonded Nickel electrode at 300mV

- + Resistive
- × Capacitive
FIG 5.25 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 250mV
FIG 5.26 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 250mV

- Resistive
- Capacitive

$R \& \frac{1}{\omega C} (\Omega)$ vs $\omega^{-1/2} (s^{1/2})$
FIG 5.27 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 200mV
FIG 5.28 Randles plot of mini plastic bonded nickel electrode at 200mV.
FIG 5.29 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 150mV
FIG 5.30 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 150mV
FIG 5.31 COMPLEX PLANE PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 100mV
FIG 5.32 RANDLES PLOT OF MINI PLASTIC BONDED NICKEL ELECTRODE AT 100mV

- Resistive
- Capacitive

R & 1/ωC (Ω)

ω⁻¹/² (s⁻¹/²)
the same electrical analogue already described in figure 5.18. The complex plane plot and Randles plot at 400mV are shown in figures 5.19 and 5.20 respectively. The complex plane plot reveals that at the highest frequencies the impedance locus leaves the real axis at 45°, typical of a semi-infinitely porous electrode. At intermediate frequencies, up to , the locus returns to the real axis and forms a flattened semi-circle typical of the charge transfer semi-circle expected for a porous electrode. The locus then relaxes to a diffusion process which subtends an angle of 50°, more typical of the response expected for a planar electrode. The locus is then completed by an almost purely capacitive process from about 8 mHz. The Randles plot clearly reveals the three relaxation processes with the characteristic cross-over of the resistance and capacitance lines indicative of adsorbed species.

Figures 5.21 and 5.22 show the complex plane and Randles plots of the plastic bonded electrode polarised at 350mV. The complex plane plot shows a transition to apparently more planar behaviour, since at high frequencies the locus now leaves the real axis at 55°. The impedance locus up to 0.8 mHz clearly reveals two semi-circles which are flattened and merge into one another. The first semi-circle at high frequencies representing charge transfer resistance and the second the slower kinetics of the OH⁻ adsorption. The locus then relaxes to a diffusion process down to a frequency of 8 mHz with a tendency to return to the real axis.

The complex plane response at 300mV shows essentially the same response characteristics as the electrode when polarised at 350mV, with an overall small increase in the value of the impedance components. When cathodically polarised at 250mV the complex plane and Randles plots show significant changes in the impedance response. The most revealing changes are identified in the Randles plot. These changes may possibly suggest a change in the overall electrochemical reaction. This may well be justified if the galvanostatic discharge curve for the electrode is
TABLE 5.2 Values of the circuit components for the plastic bonded nickel electrode.

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>( R_\Omega ) (Ω)</th>
<th>( \theta ) (Ω)</th>
<th>( C_L ) (F)</th>
<th>( \sigma ) (s(^{-1/2}))</th>
<th>( R_{ads} ) (Ω)</th>
<th>( C_{ads} ) (F)</th>
<th>( C_x ) (F)</th>
<th>( R_x ) (Ω)</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.2</td>
<td>1.84</td>
<td>1.47e-2</td>
<td>0.38</td>
<td>1.05</td>
<td>12.5</td>
<td>54</td>
<td>75</td>
<td>0.6</td>
</tr>
<tr>
<td>350</td>
<td>0.22</td>
<td>1.11</td>
<td>1.48e-2</td>
<td>0.34</td>
<td>0.52</td>
<td>1.2e-2</td>
<td>63</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>300</td>
<td>0.22</td>
<td>1.74</td>
<td>1.13e-2</td>
<td>0.31</td>
<td>0.58</td>
<td>1.5e-2</td>
<td>144</td>
<td>0.27</td>
<td>0.6</td>
</tr>
<tr>
<td>250</td>
<td>0.1</td>
<td>10.5</td>
<td>7.40e-3</td>
<td>7.8</td>
<td>43.5</td>
<td>2.3e-3</td>
<td>1e9</td>
<td>1e9</td>
<td>0.6</td>
</tr>
<tr>
<td>200</td>
<td>0.21</td>
<td>3.12</td>
<td>7.70e-3</td>
<td>10</td>
<td>0.54</td>
<td>0.22</td>
<td>2e-2</td>
<td>20</td>
<td>0.6</td>
</tr>
<tr>
<td>150</td>
<td>0.11</td>
<td>5.5</td>
<td>5.81e-3</td>
<td>16.3</td>
<td>1e9</td>
<td>1e9</td>
<td>1.8e-2</td>
<td>115</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td>0.14</td>
<td>4.6</td>
<td>5.14e-3</td>
<td>14</td>
<td>1e9</td>
<td>1e9</td>
<td>1.9e-2</td>
<td>192</td>
<td>0.6</td>
</tr>
</tbody>
</table>
considered. Inspection of the discharge curve, figure 5.1 shows that at a potential of 250 mV the electrode is virtually reduced and as a consequence is likely to exhibit different electrochemical kinetics.

This change in the overall kinetics is again reflected in the complex plane and Randles plots of the electrode when polarised at 200 and 150 mV the value of the impedance has increased from approximately 1Ω to >25Ω. This increase can be attributed to an increase in concentration of non-conducting nickel hydroxide.

5.3.4 SCANNING ELECTRON MICROSCOPY

The resultant scanning electron micrographs did not reveal any specific trends in the morphology of the electrode which could be attributed to the state of charge of the electrode. However, plates 5.1 and 5.2 have been presented which show the morphology of the electrodes at 450 mV and 300 mV respectively, these have been selected since they clearly show the net like structure of P.T.F.E. fibrils which are formed during the biaxial rolling process described in section 5.2.1 and hold the active materials together.

5.4 CONCLUSION

1. Plastic bonded nickel electrodes readily display a second discharge plateau at potentials between -100 and -600 mV (vs Hg/HgO) which may be attributable to ohmic contact and that a substantial portion of the electrode capacity is available at these potentials.

2. The modified electrical analogue used to model the behaviour of the electrode has been extremely successful in matching the data. However, the resultant component values have not revealed any parameter suitable for use as a state of charge indicator.
PLATE 1 Scanning Electronmicrograph of a plastic bonded electrode at 350mV.

PLATE 2 Scanning Electronmicrograph of a plastic bonded electrode at 300mV.
3. The best indicator of residual capacity was obtained from the bulk resistance measurement at 0.6Hz. It was possible to make a good estimate of the residual capacity of the range 25% to 100% state of charge.

4. Scanning electron microscopy has shown the P.T.F.E. net like structure produced during the biaxial rolling process.
6.1 INTRODUCTION

In addition to the electrochemical impedance spectroscopy carried out on sintered and plastic bonded nickel electrodes the study was also extended to incorporate pocket nickel electrodes. This again would allow the original equivalent circuit developed for the sintered electrode to be compared on an electrode whose fabrication technology is inherently different from both the sintered and the plastic bonded electrodes.

Also, it had come to my attention that the nickel-cadmium pocket electrode system was apparently more susceptible to the 'memory effect' than other types of nickel-cadmium cell. Therefore it was hoped that electrochemical impedance spectroscopy may yield some insight into this phenomena.

The 'memory effect' can be revealed when the cell is subjected to a precise, highly repetitive depth of discharge. The effect shows itself in the voltage profile whilst discharging, as a premature output voltage drop. The effect can easily be removed by one complete deep discharge followed by a full charge.

6.2 ELECTRODE FABRICATION

The active material for the nickel pocket electrode consists of nickel and cobalt compounds mixed with graphite. The quality of the active material is of utmost
importance for the cell performance, and consequently, great efforts are made to establish proper and easily controlled manufacturing processes. A nickel sulphate solution is prepared to which is added cobalt sulphate in the ratio 100:1 w/w. This solution is then pumped into a hot sodium hydroxide solution. The hydroxide slurry is then filtered and washed with distilled water. The precipitate is then dried at 100°C which facilitates the subsequent washing process with distilled water on a suction filter to remove sulphate and sodium ions. The resultant hydroxide is then ground and mixed with graphite in order to obtain sufficient conductivity.

The active material is then encapsulated in a perforated metal pocket to provide support and a means of current collection. The pocket is manufactured from perforated cold rolled steel ribbon. The 'burr' formed by the perforation process are not removed but are turned to face the active material and provide greater contact area. The number of perforations determine the rateability of the electrode, i.e. high rate electrodes have a greater number of perforations than low rate. After perforation the steel ribbon is nickel plated, this prevents anodic oxidation during overcharge. The formation of ferrate ions in the electrolyte are considered to have deleterious effects on the active material.

The ribbon is then formed into a container-like shape by passing through a pair of ground rollers, into which is laid the active material as a loose powder. A second pair of rollers form the ribbon into a lid and the two halves are folded together in a special manner. The width of the pocket also determines the rateability of the electrode i.e. narrow for high rates and wide for low rate applications. The long, folded strips holding the active material are arranged to fit each other and are interleaved to form an electrode of suitable size. The complete electrode is provided with a frame and lug for current take-off.
6.3 EXPERIMENTAL

A mini 1cm² nickel pocket electrode was made from a large area positive electrode. This was achieved by removing a length (~15cm) of the perforated pocket strip (1cm wide) from the standard nickel plated steel frame. A 1cm² was then cut from the strip and the fold of one edge undone with care and into this was fitted a nickel wire (1mm diameter), this edge was then crimped onto the nickel wire and spot welded to provide electrical contact. Care was taken to 'stop off' any areas of mild steel exposed by cutting the pocket to size, using Lacomit. The resultant mini electrode was then placed in a three-limbed electrochemical cell containing 5.3M KOH, a Hg/HgO reference electrode and a large area nickel gauze as counter electrode. The electrode was then formed up and the voltage - time discharge profile determined as described in section 5.2. The impedance of the electrode was then determined at various states-of-charge as detailed in section 5.2.2. In addition the electrode was subsequently galvanostatically cycled between the potential limits of 350mV and 300mV in order to artificially induce the memory effect. The impedance was then determined.

6.4 RESULTS AND DISCUSSION

Figure 6.1 shows the voltage - time polarisation curve for the 1cm² pocket electrode. The discharge profiles for the 1cm² sintered nickel and 1cm² plastic bonded electrode are included for comparison. Clearly the pocket and plastic bonded electrodes behave similarly in that they both develop a second discharge plateau compared to the sintered electrode which yields only the normal discharge plateau. However, the sintered electrode has been shown to develop a second discharge plateau between -100 and -600 (vs Hg/HgO) after the electrode has been first discharged and then subsequently discharged at low rates (C/100) to remove the residual capacity [104]. One reason for the development of the second discharge step
FIG 6.1 VOLTAGE - TIME POLARISATION CURVES FOR MINI POCKET, PLASTIC BONDED AND SINTERED NICKEL ELECTRODES

a sintered
b plastic bonded
c pocket
has been attributed to the poor electronic contact through the graphite [107]. As described in section 5.2 and 6.2 both plastic bonded and pocket nickel electrodes rely on graphite to provide current collection from the active material to the current conductor. During charge and discharge the electrode undergoes expansion and contraction. These volume changes during the formation process are relied upon to ensure that the pocket is completely filled to optimise good contact to the inner walls of the pocket.

As described in section 5.3 it is important when fabricating cells containing plastic bonded electrodes that allowance should be made for expansion within the cell container, normally about 2% for volumetric changes which take place during formation. The structure of the sintered electrode is such that graphite is not needed since the active material directly contacts the porous nickel plaque. This ensures good electronic contact and negates the need for compaction. However, the sintered electrode is subject to the problem of dimensional changes during cycling, and is a source of cell failure due to mechanical fatigue of the plaque due to induced stress. Fortunately, several hundred cycles are obtainable before the effects of fatigue become apparent.

The need to provide some method of compaction to the pocket and plastic bonded electrodes, infers the likelihood of ohmic losses during the course of discharge. Inspection of the discharge profiles of the three types of electrode reveal a small but significant slope to the main discharge step for both the plastic and pocket electrodes, typical of ohmic losses.

Figures 6.2 and 6.3 show the corresponding Sluyters and Randles plots of the nickel pocket electrode when fully charged. The Sluyters plot shows that at approximately 10kHz the impedance locus leaves the real axis at about 52°, revealing the porous nature of the electrode, the locus then extends over four decades of
FIG 6.2

COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE AT 100% STATE OF CHARGE
FIG 6.3 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 100% STATE OF CHARGE
frequency producing an elongated semi-circle with an overall impedance of approximately 0.7\(\Omega\). This process then relaxes out at around 1Hz to a diffusional process over a short frequency range (1Hz to 0.01Hz), with an angle of 45° to the real axis which would normally be associated with a planar electrode response. This process relaxes further to a more purely capacitive response at lower frequencies. Evidence of those three processes are clearly revealed in the Randles plot.

Figures 6.4 and 6.5 show the complex plane and Randles plot at 84% state-of-charge. The complex plane plot shows a similar response to the fully charged electrode at high frequencies i.e. >1kHz, an elongated charge transfer semi-circle is again evident, but of smaller magnitude i.e. approximately 0.5\(\Omega\). Also, in the frequency range 10Hz to 1Hz the locus is elongated so that there is a gradual increase in resistance whilst the capacitive component is almost constant from the charge transfer process to the new diffusional process, which subtends an angle of about 50° before relaxing to the final process which becomes almost purely capacitive at the lowest frequencies.

Figures 6.6 and 6.7 show the complex plane and Randles plots of the nickel pocket electrode at 68% state-of-charge. The overall response is again similar, the semi-circle is increased by approximately 100m\(\Omega\) but the change from the charge transfer process to the diffusion process is now more rapid.

Figs. 6.8, 6.9, 6.10 and 6.11 show the complex plane and Randles plot at 53% and 37% state-of-charge respectively. The loci shows a similar response to the electrode at 68% state-of-charge with a slight increase in the magnitude of the charge transfer semi-circle. Figures 6.12 and 6.13 show the complex plane and Randles plots at 21% state-of-charge. The most distinctive change revealed in the complex plane plots is the tendency of the locus to return to the real axis at the lowest frequencies. This tendency is more evident in Figure 6.14 which is a complex plane
FIG 6.4 COMPLEX PLANE PLOT OF MINI NICKEL POCKET ELECTRODE AT 84% STATE OF CHARGE
FIG 6.5 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 84% STATE OF CHARGE

\[ R \text{\& } \ln(C) \text{ (Ω)} \]

\[ \omega^{-1/2} \text{ (S}^{1/2}) \]

- Resistive
- Capacitive
FIG 6.6  COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE
AT 68% STATE OF CHARGE
FIG 6.7 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 68% STATE OF CHARGE
FIG 6.8  COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE AT 53% STATE OF CHARGE
FIG 6.9 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 53% STATE OF CHARGE
FIG 6.10  COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE
AT 37% STATE OF CHARGE
FIG 6.11 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 37% STATE OF CHARGE

![Graph showing Randles plot with resistive and capacitive markers.](image-url)
FIG 6.12 COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE AT 21% STATE OF CHARGE
FIG 6.13 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 21% STATE OF CHARGE

+ Resistive
× Capacitive
FIG 6.14  COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE AT 5% STATE OF CHARGE
plot of the nickel pocket electrode a 5.2% state-of-charge, figure 6.15 shows the corresponding Randles plot. Figures 6.16 and 6.17 show the complex plane and Randles plot of the pocket electrode when fully discharged. The complex plane plot shows an impedance locus which is a magnitude larger than all other states-of-charge. The initial charge-transfer semi-circle relaxes to a flattened semi-circle at lower frequencies. At the lowest frequencies the impedance begins to return to the capacitive axis. It is possible at these low frequencies, where low integration times are used for data averaging and where the overall impedance of 20Ω is much greater than 0.1Ω sense resistor, that these data contain large errors.

The dissimilar nature revealed by the electrode at 0% state-of-charge, compared to all other state-of-charge, does perhaps suggest a different electrochemical process at this state-of-charge. Because of this anomaly identification of a model to satisfy the whole range including 0% becomes exceedingly difficult. The modelled behaviour shown by the solid line in Figures 6.1 to 6.17 was generated using the model shown in figure 6.18. It was necessary to again refine the model used for the plastic bonded nickel electrode to try to account for the inductive reactance exhibited by the pocket plate nickel electrode.

Comparison of the results obtained here for the pocket plate nickel electrodes and those obtained for the sintered and plastic bonded electrodes again shows clear differences from the sintered type electrode and similarities to the plastic bonded electrode. The magnitude of the impedance is of a similar order to the plastic bonded electrode and the overall impedance response clearly shows the charge transfer semi-circle and other processes. This behaviour is reflected in that for the plastic bonded electrode; here again the area of the active material is much reduced because of the addition of graphite. In addition the pocket plate nickel electrode uniquely reveals an
FIG 6.15 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 5% STATE OF CHARGE

![Randles Plot](image)

- + Resistive
- X Capacitive

\( R \) & \( \frac{1}{\omega C} \) (\( \Omega \))

\( \omega^{\frac{1}{2}} \) (s^{\frac{1}{2}})
FIG 6.16

COMPLEX PLANE PLOT OF MINI POCKET NICKEL ELECTRODE
AT 0% STATE OF CHARGE
FIG 6.17 RANDLES PLOT OF MINI POCKET NICKEL ELECTRODE AT 0% STATE OF CHARGE

- Resistive
- Capacitive

R & J/ωC (Ω)

ω^{-1/2} (S^{1/2})
FIG. 6.18 ANALOGUE CIRCUIT FOR THE MINI POCKET NICKEL ELECTRODE
inductive component which is probably due to the outer metallic nickel pocket containing the active material.

6.4.1 STATE OF CHARGE CORRELATION

Figure 6.19 shows the plots of bulk resistance versus state of charge at 0.6Hz, 6Hz and 60Hz. It can be clearly seen that at 6Hz a good straight line correlation exists and that the change in bulk resistance over the whole range of states of charge is readily measurable. At 0.6Hz it can be seen that at the higher states of charge the bulk resistance begins to increase, whereas at 60Hz the bulk resistance starts to decrease.

It is interesting to note that the change in bulk resistance between 80 and 100% state of charge at 60Hz is approximately the same as the change in the bulk resistance between 0 and 80% state of charge. This parameter may indicate a possible indicator of residual capacity at high states of charge, which are the most useful to know and has proved the most difficult to determine.

6.4.2 MEMORY EFFECT

Determination of the impedance spectrum of the electrode artificially induced with the memory effect revealed no difference in impedance compared to an electrode not suffering the effect.

6.5 CONCLUSION

1. Inductive contributions to the a.c.impedance response were found impossible to remove on pocket plate mini electrodes. It is thought that the metallic envelope is the main cause of the inductive component.

2. The electrical analogue used to model the characteristics of the pocket electrode was modified to account for inductive effects and the data fitted with some success at the higher states of charge.
FIG 6.19 STATE OF CHARGE VERSUS BULK RESISTANCE AT 60, 6 AND 0.6Hz.
TABLE 6.1 Values of the circuit components for the pocket nickel electrode.

<table>
<thead>
<tr>
<th>Charge (%)</th>
<th>$R_\Omega$ (Ω)</th>
<th>$\theta$ (Ω)</th>
<th>$C_L$ (F)</th>
<th>$\sigma$ (s^{-1/2})</th>
<th>$R_{ads}$ (Ω)</th>
<th>$C_{ads}$ (F)</th>
<th>$C_x$ (F)</th>
<th>$R_x$ (Ω)</th>
<th>IND (H)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.0e-2</td>
<td>0.25</td>
<td>7.50e-2</td>
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3. The bulk resistance at 6Hz was found to be the best indicator of residual capacity.

4. The computed circuit components revealed a reasonably good correlation between the charge transfer resistance and state of charge over the range 20 to 80%.

5. Bulk resistance measurements at 60Hz may provide a good indicator of residual capacity at high states of charge.

6. The electrochemical impedance technique did not reveal any marked changes in the impedance response of an electrode suffering the 'memory effect'.
CHAPTER 7

OVERALL CONCLUSIONS

Electrochemical impedance spectroscopy and the electrical analogue circuit method provide a powerful and useful technique for the determination of residual capacity in electrochemical power sources. Clearly the nickel-cadmium system is an especially difficult system to study compared with the lead-acid system in which there is an easily measurable change in electrolyte resistance. Also, some primary cells provide much easier analysis because one electrode of the cell can totally dominate the impedance spectrum.

However, this study has provided useful and new insight into some characteristics of sintered, plastic bonded and pocket nickel electrodes. The porous structure of these electrodes greatly complicate the interpretation of impedance data because of the effect they have on the measured phase angle. However, the porous nature of these electrodes has been accounted for within the electrical circuit analogues. In addition the experimental set-up and measurement should be carefully considered, especially on large area systems.

The results have shown that both nickel and cadmium electrodes make equal contributions to the cell impedance. Small area (mini) electrodes have been successfully modelled using a modified Randles equivalent circuit to account for porosity and adsorption effects. Convolution of sintered nickel and cadmium electrode analogues, to represent the whole cell proved unsuccessful. However, good state of charge correlations have been obtained for individual nickel sintered, plastic bonded and pocket electrodes.
The modelled data provided a low porosity factor for the plastic bonded electrode compared to the sintered and pocket electrode. To successfully model the pocket electrode it was necessary to incorporate an inductive circuit element to account for the metallic envelope which holds the active material.

The data reported in this thesis were used by the Department of Electrical Engineering at Loughborough University of Technology to define the design parameters for an electronic state of charge interrogation device suitable for use with the military specification nickel-cadmium batteries [109,110].

It is well known that any number of networks of resistors, capacitors and inductors can be constructed to fit the measured data. However, the simplest and most relevant electrical analogues have been deduced by consideration of both the electrochemistry occurring at the electrode and the porous nature of the electrode.

Electrochemical impedance spectroscopy has become an established technique for the study of electrochemical processes. However, as noted by Macdonald [111], "unfortunately, there is no 'easy' way of developing the skills and expertise necessary to properly interpret impedance data".
APPENDIX 1

The electrotechnology of the nickel positive electrode: A review of the recent literature.
REVIEW

THE ELECTROTECHNOLOGY OF THE NICKEL POSITIVE ELECTRODE: A REVIEW OF THE RECENT LITERATURE

R. T. BARTON, P. J. MITCHELL and N. A. HAMPSON

Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU (Gt. Britain)

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Summary

A review is presented of the very recent electrotechnology of the nickel positive electrode. The majority of the literature covered is from the 1980s and 61 references are noted.

1. Introduction

We present a review of the recent electrotechnology of the nickel positive electrode (61 references). The electrochemistry of nickel has previously been reviewed by Milner and Thomas [1], Falk and Salkind [2], Briggs [3], Bard [4], Oliva et al. [5] and more recently by Weininger [6]. This review highlights especially the literature from the period 1981 to 1985. The patent literature is excluded (since it is felt that much is conflicting and it is our intention to restrict ourselves to the uncontrovertible facts). We consequently deal selectively with fabrication techniques which may lead to electrodes with higher energy densities and lower manufacturing costs, the effect of additives, electrometric methods and the causes of electrode failure.

2. Fabrication

The recent aim of nickel electrode fabrication has been to find a substitute for sintered nickel plaque by using lighter structural and electrically conducting materials. So-called controlled microgeometry [7, 8] is a complete departure from the normal sintered plaque substrate. Extremely thin (4 μm thick) perforated nickel grids are coated with active material and then stacked so that the perforations register to form a continuous passage through the plate. The weight ratios of active mass to substrate is increased by a factor of 3.
Czech [9] and Hungarian [10] groups have studied the plastic-bonded nickel electrode originally developed for use in fuel cell technology. A network of polytetrafluoroethylene (PTFE) and Ni(OH)₂ incorporates acetylene black, graphite or carbonyl nickel to give it conductivity. The nature and quantity of these conductive components determine the electrode performance. The use of a carbon felt as a matrix for Ni(OH)₂ has been described by Appelt and Leczykiewicz [11]. Carbon fibres are an excellent substitute for the sintered nickel plaque because they are light, electrically conducting and have a large surface area. They may be used without further treatment or can be coated with pyrolytic graphite or nickel. In the latter case a thin layer (0.6 - 1.0 μm) of nickel is deposited and sintered to a compact structure and the porous structure is then impregnated electrochemically [12]. A lightweight organic non-woven felt has been developed [13], which is first chemically or physically plated; this is followed by nickel electrodeposition, and the felt is then pyrolysed and the nickel reheated. Faber [14] has designed a nickel electrode in which a nickel grid is covered by a polypropylene network onto which is pasted the active mass of Ni(OH)₂ and 30% graphite. A nickel fibre felt was also incorporated to seal the pasted grid; contact problems were encountered with the inner metal grid and hence an outer current collector was also required.

Japanese workers [15] have developed a foam type of nickel electrode in which the active paste (86% Ni(OH)₂, 10% nickel powder and 4% cobalt powder) is impregnated directly into the highly porous metal foam structure. A polyfluoro resin dispersion is added and the whole assembly is pressed and dried. Cells using the foam type of electrode have delivered 30% greater capacity than sintered plaque electrodes. A new electrochemical process has been perfected for the impregnation of nickel plaques with Ni(OH)₂ [16]. The process makes use of a.c. rather than d.c. and dilute solutions of KCl and KBr rather than KOH. Paszkiewicz [17, 18] has compared the various impregnation techniques and found that chemical impregnation produced electrodes with the highest capacity but which had a short cycle life, particularly when the plaque was produced from nickel powder of small particle size, which also produced higher capacities than plaque produced from large particle sizes.

3. Additives

Research efforts tend to have been concentrated on elements which have proved to be effective in bettering the performance of the Ni(OH)₂ electrode, especially cobalt and lithium. Cobalt is added to the active mass in the manufacture of most nickel electrodes; it remains as Co³⁺ throughout its cycle life. It has been confirmed [19] that β-NiOOH remains stable under conditions which in the absence of cobalt would give rise to γ-NiOOH. The presence of Co³⁺ in the layer lattice prevents the tight incorporation of K⁺ (γ-NiOOH), while the greater mobility of the K⁺ ions in β-NiOOH leads
to improved cycling behaviour. Cobalt has been shown [20] to reduce the oxidizing and reducing potentials of Ni(OH)$_2$ and to increase the overpotential of oxygen at the NiO electrode, thus improving utilization. Cobalt restrains the growth of crystal grains of active material in the charge-discharge process, thereby stabilizing the performance of the electrode.

Zimmerman [21] found that the addition of 10% Co(OH)$_2$ made the electrode less susceptible to the build-up of residual capacity, by allowing a lower oxidation state to be reached before the formation of an isolating boundary layer between the current collector and the uncharged active material. This layer caused the voltage to drop and resistive characteristics of the layer control electrode polarization. Continual discharge resulted in layer growth and a resultant decrease in voltage. Cobalt decreases the diffusion resistance of the active material; to utilize this property fully, cobalt should be put into the active material where it is most effective in delaying formation of high impedance layers at the current collector interface. Such electrodes [22] employ a cobalt gradient such that quite high concentrations exist at the current collector and the cobalt concentration decreases as the distance from the current collector increases.

Strain measurements [23] have indicated that cobalt additives act to relieve the internal electrode stresses induced by cycling and thereby control the rate of capacity degradation from physical changes in the active material.

Salkind [24] found that the addition of Co(OH)$_2$ to plastic-bonded nickel electrodes substantially eliminated the tendency to produce a second discharge step, sometimes referred to as the "graphite step". However, Klapste et al. [25] thought that the second discharge step was suppressed by the Teflon binder and/or cobalt, cerium or manganese hydroxide.

Oshitani et al. [26] have developed a nickel electrode with stable performance at various charge-discharge rates over a wide temperature range: to achieve this performance the electrode contained adequate amounts of Co(OH)$_2$ and Cd(OH)$_2$ in the active material which was also coated with a Cd(OH)$_2$-rich outer layer. Cadmium in the electrode prevented the formation of $\gamma$-NiOOH, whilst cadmium on the surface was thought to raise the oxygen evolution potential.

Further stabilization of the $\beta$-NiOOH phase is thought to occur by the addition of lithium by forming Li$_x$Co$_{1/3}$Ni$_{1-2x}$(OH)$_2$, hence inhibiting phase segregation [19].

Greaves and Thomas [27] found that the addition of LiOH to their PTFE-bonded Ni(OH)$_2$ electrodes caused marked effects in electrode performance because of the full discharge of small amounts of $\gamma$-NiOOH. LiOH stabilizes $\beta$-NiOOH with respect to $\gamma$-NiOOH since the $\beta$ phase could only be detected at high LiOH concentrations. However, elevated temperatures reduced electrode utilization on cycling and self-discharge of $\gamma$-NiOOH to $\beta$-Ni(OH)$_2$ was enhanced. Armstrong et al. [28] have found that lithium ions are preferentially taken up into the bulk of the $\alpha$- and $\beta$-Ni(OH)$_2$ electrodes in lithiated KOH solutions. Lithium addition was found to increase the maximum charging potential without significantly changing the efficiency of the process.
Ferric compounds precipitated on the hydroxide surface of the nickel electrodes rather than inserted in their structure have been found [29] to increase the charging efficiency of the nickel electrode. Addition of Zn(OH)\textsubscript{2} has been shown [30] to exhibit excellent dimensional stability with good utilization efficiency, comparable with cobalt; however, problems were encountered with dendritic growth.

4. Electrometric measurements

The reversible potentials for various Ni(OH)\textsubscript{2}-NiOOH couples have been determined [31] over a range of KOH concentrations. The results were interpreted using the concept of coexisting phases [32, 33]. Both the β phase and the α-γ phase system showed a dependence of reversible potential with KOH and H\textsubscript{2}O activity. The α-γ phase couple showed the largest dependence because of the incorporation of K\textsuperscript{+} ions and H\textsubscript{2}O in the interlayer structure of the active material. A range of so-called “activated” and “deactivated” couples for both the α-Ni(OH)\textsubscript{2}-γ-NiOOH and the β-Ni(OH)\textsubscript{2}-β-NiOOH systems was identified and differences in formal potential were related to crystal structure [34]. The reversible potentials of the above couples were also determined in LiOH, NaOH, RbOH and CsOH [35]; the results showed close similarity to those found for KOH.

In a voltammetric study of electrodes containing β-Ni(OH)\textsubscript{2} Barnard and Randell [36] found that by restricting the anodic limit and the charge applied to β-Ni(OH)\textsubscript{2} the oxidized phases also remained within the β-phase system. At low average oxidation states (2.1 - 2.2) a single broad cathodic peak appeared at about 400 mV, ascribed to the reduction of coexisting phase $V_\beta ([0.9\text{NiOOH}·0.1\text{Ni(OH)}\textsubscript{2}]0.21\text{H}_2\text{O}·0.03\text{KOH})$ to phase $U_\beta ([0.25\text{NiOOH}·0.75\text{Ni(OH)}\textsubscript{2}]0.25\text{H}_2\text{O})$. When the average oxidation state was increased progressively to 2.7 the reduction process was found to shift to more cathodic potentials in the range 350 - 300 mV.

In more detailed studies [37, 38] the voltammetric behaviour was examined of electrodes which were previously charged to give the γ phase, $V_\gamma ([0.833\text{NiO}_2·0.166\text{Ni(OH)}\textsubscript{2}]0.35\text{H}_2\text{O}·0.33\text{KOH}$ or $0.33\text{NiO}_2·0.67\text{H}_2\text{O}$), and then discharged. It was found that subsequent oxidation-reduction cycles probably involved a complex mixture of coexisting phases of the general types $U_\gamma$, $V_\gamma$, and $V_\beta$ ($V_\gamma$, $0.33\text{NiO}_2·0.67\text{H}_2\text{O}$; $U_\gamma$, $0.125\text{NiO}_2·0.875\text{Ni(OH)}\textsubscript{2}]0.87\text{H}_2\text{O}$). The β-phase couple β-Ni(OH)\textsubscript{2}-β-NiOOH has been used [39] to oxidize α-Ni(OH)\textsubscript{2} to the γ phase, thus demonstrating the greater stability of the latter in 7 mol cm\textsuperscript{-3} KOH.

Several investigations by Burke and Twomey [40 - 43] using cyclic voltammetry have revealed the presence of both anhydrous and hydrous components within nickel oxide films. Cyclic voltammetry experiments by Visscher and Barendrecht [44] on α- and β-Ni(OH)\textsubscript{2} have shown the anodic oxidation peak for β-Ni(OH)\textsubscript{2} to be about 70 mV higher than for α-Ni(OH)\textsubscript{2}. 
A potentiodynamic investigation [45] of the Ni(OH)$_2$–NiOOH redox couple at the inner layer of the complex interface indicated that the water content of the inner film is probably lower than that of the bulk, the nickel(III) species probably approaching the oxygen atom octahedral coordination corresponding to $\gamma_1$NiOOH. The potentiodynamic characteristics of the model interface M–Ni(OH)$_2$ (where M = Pt or vitreous carbon) have been investigated [46] to determine the influence of the Ni(OH)$_2$ layer thickness on the kinetics of the electro-oxidation reaction. For thin layers it appeared that the reaction was controlled by a complex surface reaction mechanism. Conversely, for thick films a clear mass transport control was observed.

Study of the discharge process by the potential step technique [47] showed little variation in diffusion coefficients with aging at room temperature, but higher values were found for $\beta$-Ni(OH)$_2$ in the temperature range 25–75 °C. Galvanostatic discharge curves obtained on plane nickel hydroxide electrodes [48] were found to fit the Peukert equation $i = \text{constant}$. The diffusion coefficients of the moving species were found to be of the order of $10^{-5}$–$10^{-2}$ cm s$^{-1}$. Microcracks which appeared in the active mass during cycling were thought to account for the high values of the diffusion coefficients.

General models applicable to the electrocrystallization of nickel have been analysed and the relevant current–time transients for the initial stages of deposition derived [49]. Theoretical equations were derived for the models and fitted to the deposition transients [50]; the formation of one or more monolayers was shown to be followed by three-dimensional nucleation and growth of the bulk phase. Synchronized death and rebirth processes were also detected.

Transmission electron microscopy examinations [51] of cross-sectioned nickel electrodeposits grown on oriented substrates show that their structure results from a competition between an epitaxial growth process and a non-epitaxial growth initiated by a substrate-independent nucleation. This independent nucleation is a necessary step prior to the progressive development of a definite fibre texture in thicker deposits. Both processes were investigated separately on either single crystals or amorphous carbon, by means of a correlation between structural examinations and transient analysis. It was found that, for an amorphous substrate, multitwinned particles with roughly hemi-spherical shape were generated by independent nucleation. Models were presented which accounted for the experimental current–time transients. The situation was found to be more complex when the substrate was a low index plane of a single crystal in which several competitive growth processes were contributing to the whole current.

The impedance technique has been used by Russian workers [52] to study the effect of the additives NH$_4^+$, S$^{2-}$ and antimony(III) on the polycrystalline nickel electrode. Generally, all were found to depress the capacitance and to reduce the dispersion at potentials between $-1.25$ and $-0.35$ V. The impedance was essentially unaffected at potentials where
nickel was in the passive state. The effects of barium, cadmium, cobalt, lithium, manganese and zinc additives on the impedance of porous nickel electrodes were studied by Zimmerman and Effa [53]. The resistance to proton diffusion in the charged electrode was decreased by lithium, cobalt and manganese. The charge transfer resistance was decreased by cobalt and lithium. The electronic resistance of the discharge-active material was reduced significantly by manganese and cobalt and to a lesser extent by lithium.

Barton et al. [54] have investigated the sintered nickel electrode using the impedance technique. The electrode impedance was modelled using a Randles circuit. To account for adsorption an additional resistor and capacitor in parallel were included, which were in series with the charge transfer resistance and the Warburg component. Porosity of the electrode was also accounted for, producing an excellent fit over six decades of frequency. The aim of the work was to isolate a parameter on which to base measurements of the state-of-charge of nickel–cadmium cells.

Admittance measurements of NiO films were reported [55] as functions of frequency, potential and film thickness. The oxidized film was found to have a large capacitance proportional to thickness. The reduced film showed a much smaller capacitance which decreased rapidly with potential and which was independent of thickness at large cathodic potentials. During the transition between oxidation states, a transient conductance was seen which was attributed to phase boundary motion within film grains.

Madou and McKubre [56] have confirmed that the reduced film exhibits a smaller capacitance than the oxidized film. A study of the photo-effects [56] showed that, depending on the potential, an n-type (β-NiOOH) or p-type (NiO) semiconducting oxide can be present giving rise respectively to anodic or cathodic photocurrents under illumination. Investigation of the internal resistance of plastic-bonded high rate electrodes [57] showed that the internal resistance was dependent on external pressure and changes in it were described by a hysteresis curve. Deterioration of the electrode examined during a high rate cycle life test was considered a cause of the increase in the ohmic part of the impedance, while the non-ohmic part was almost unchanged.

5. Failure

The mechanical characteristics of the nickel plaque electrode have been investigated [58]. It was found that plaque fatigue, sensitivity and hardness directly affect electrode performance. The harder the plaque is then the greater the shedding of active material, and harder plaques are subject to greater strains. Mechanical stresses existing in the plaque were estimated [59] by comparing the deterioration of the electrode during cycling with nickel fatigue data. The results indicated that at least 30% of the plaque is subject to work hardening prior to failure by fatigue. 10% of the plaque
is stressed at substantially higher levels than the remainder and fails within 200 discharge cycles.

The loss of capacity of sintered nickel electrodes on cycling was measured and correlated in statistical studies with the physical properties of the electrode before and after cycling [60]. Cycle life is highly correlated with sintering temperature, with porosity and with bond strength of the unimpregnated plaque. Cycle life increases with sinter temperature and bond strength but decreases with increasing porosity. Increasing the sinter temperature by 100 °C from 850 to 950 °C gave an approximate 30% increase in cycle life. Cycle life was also found to be increased by electrochemical rather than chemical impregnation. Destructive examination of the electrodes after failure revealed an increase in electrode thickness (typical of corrosion of the nickel structure during cycling) and the formation of discrete blisters on the outer surface of the electrode. Fritts [61] has investigated the cause of blistering of the electrode and concluded that macropores in the electrode were the source. The macropores may be the result of defects in the sinter or may develop during normal cycling by localized fatigue of the sinter. Loading levels, gas venting paths within the sinter, the degree of overcharge, the impregnation process and the number of cycles were all shown to influence the formation of blisters.

6. Final remarks

It is clear from the great activity in this field that the nickel oxide electrode offers potential for future development. Modification and improvements to electrode format are developing continually so that specific power and energy improvements are emerging which keep the system in the forefront of industrial interest.

The reaction mechanisms at the electrode are now reasonably well explained in as much as this is possible within the framework of a solid state process involving oxide formation at a metal surface followed by valence transitions between oxidation states. Microscopic mechanistic shortcomings in the theory are clearly avoidable if a macromolecular concept is assumed such as has been done in recent impedance experiments.

References

APPENDIX 2

Cadmium: A review of the recent literature.
CADMIUM — A REVIEW OF THE RECENT LITERATURE

R. T. BARTON*, S. J. LAWSON, P. J. MITCHELL and N. A. HAMPSON

Department of Chemistry, University of Technology, Loughborough, Leicestershire, LE11 3TU (U.K.)

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Summary

Recent electrotechnological aspects of the cadmium electrode have been reviewed. Forty-four references are included and the electrode characteristics in the alkaline battery systems are highlighted.

Introduction

The electrochemical behaviour of the cadmium electrode has previously been reviewed by Milner and Thomas [1], Hampson and Latham [2], Armstrong et al. [3] and more recently by Barnard [4], as well as in Falk and Salkind's [5] excellent monograph on alkaline battery systems. The established processes of impregnation in sintered plaque electrodes have also been recently reviewed [6]. Research work connected with the electrochemistry of cadmium has been scarce in recent years, but there have been a number of papers dealing with alkaline cadmium battery systems: this review presents the electrochemical aspects of the cadmium electrode used in such alkaline battery systems published since the last review [4]. Electrometric methods, the effect of additives, morphological aspects and porosity of the cadmium electrode are the main headings under which the published work has appeared, and these form our major review headings.

Electrometric methods

A cyclic voltammetric study [7] on planar cadmium in various concentrations of potassium hydroxide achieved good agreement with the previously reported work of Barnard et al. [8], showing the sharp anodic oxidation peak, and the development of a shoulder on the main peak becoming more pronounced at high sweep speeds, >200 mV s⁻¹ before the electrode passivated. The usual single reduction peak was also observed.

*Author to whom correspondence should be addressed.

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square root dependence for the peak currents was obtained and the peak potentials varied linearly with sweep rate at high speeds. Potentiostatic work in the anodic region revealed a Tafel relation, slopes of $4/7 \text{RT}/F$ in 0.5 M KOH and $3/4 \text{RT}/F$ for all other concentrations were found. A very complex, multistep electrode process was proposed, involving the formation of CdO and Cd(OH)$_2$ films.

A galvanostatic study [9] was used to confirm the mechanism in identical experimental conditions. A further galvanostatic study [10] of the reduction of oxide films formed on cadmium led to a proposed mechanism derived from the electrochemical parameters obtained at various current densities.

Bumstein [11] analysed the transient electrochemical behaviour of freshly generated cadmium surfaces produced by scratching the metal with a diamond stylus whilst immersed in various concentrations of potassium hydroxide. The anodic reaction rate of the metal surface was found to follow Tafel's law with a slope of 63 mV/decade and a reaction order of 1.1. The equilibrium parameters were defined by $E_0 = 18 \text{mV} \text{ (N.H.E.)}$ and $i_0 = 2 \text{mA cm}^{-2}$. These results were interpreted as showing the simultaneous loss of two electrons per cadmium atom in a single reaction step. No evidence of any Cd(I) species was found. The rate determining step was thought to be one of the following:

$$\text{Cd} \text{H}_2\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{CdO}^+ + \text{H}_2\text{O} + 2e$$
$$\text{Cd} \text{H}_2\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{Cd(OH)}_2 + \text{H}^+ + 2e$$
$$\text{Cd} \text{H}_2\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{CdO} + \text{H}_3\text{O}^+ + 2e$$

Lobanova et al. [12] used the technique of chronopotentiometry and impedance to study the anodic oxidation of cadmium in KOH. At low current densities the process was found to be controlled by a homogeneous chemical reaction (i.e., formation of the cadmiate ions) following a transition step, but at higher currents the controlling factor became the diffusion rate of the cadmiate ions.

Barton et al. [13] also used the impedance technique to study the sintered cadmium electrode in alkali. Measurements were made on 1 cm$^2$ mini-electrodes over the frequency range 10 kHz - 300 mHz. It was shown that the electrode behaviour conforms to that of a porous film electrode under charge transfer and diffusion control. A Randles circuit, modified for porosity and the presence of films, was found to match the data over the specified range of frequency. In the lower frequency domain the electrode behaviour becomes more complicated due to slow processes which are effectively masked out at the higher frequencies.

L'vova et al. [14] studied the effect of the structure of Cd(OH)$_2$ on its chemical dissolution in alkali using pressed pellets of Cd(OH)$_2$ as disc electrodes and Cd metal as a ring electrode. The rotating ring disc measurements were used to determine the chemical dissolution rate of $\beta$- and $\gamma$-polymorphs of cadmium hydroxide. The results were compared with the
dissolution of CdO. The rate of dissolution was found to increase on passing from the \( \beta \)- to the \( \gamma \)- phase, owing to an increase in electrochemical activity. Polarisation curves were presented for the reduction on a rotating ring disc.

Additives

Addition of polyvinyl alcohol (PVA) to the cadmium pocket electrode helps to prevent crystal growth and, hence, safeguard capacity. Munshi et al. [15] measured the impedance of such electrodes over the active and passive regions at different PVA concentrations in KOH electrolyte. The addition of PVA markedly increased the double layer capacity of the electrode and decreased the solution resistance. The impedance data were interpreted using an equivalent circuit containing two double layer capacitors in series, together with a resistance proportional to the conductivity of the electrolyte.

Polyethylene oxides and their derivatives have been used [16] to improve the structure of cathodic metal deposits and to hinder the growth of dendrites, which has led to improved characteristics and service life. The compounds act as surfactants, with a high surface activity.

Sathyanarayana [17] incorporated an alkali-stable colloidal surfactant (ethyl cellulose) into the cadmium electrode during fabrication such that both crystal growth and cadmium hydroxide migration were suppressed. The doped electrode was capable of \( 96 \pm 2\% \) capacity utilization even at the end of fifty deep discharge cycles. The beneficial effects of ethyl cellulose were lost, however, when subjected to severe overdischarge. Excessively thick coatings of the ethyl cellulose reduced capacity due to the large ohmic resistance of the film.

Mrha and co-workers [18] studied the rate of oxygen recombination on plastic (poly(tetrafluoroethylene)) bonded Cd electrodes for use in nickel–cadmium cells. A comparison of results obtained with pocket-type and plastic bonded cadmium electrodes showed that oxygen was reduced on metallic conductors of the electrodes which were covered with a thin electrolyte layer, are easily accessible to oxygen, and are short-circuited by the electroactive Cd/Cd\(^{2+}\) material. The latter has a sufficiently negative potential and electronic conductance to allow the electro-reduction of \( O_2 \) to take place.

Various additions have been made to the plastic bonded cadmium electrode to enhance the rate of oxygen recombination. The inclusion of a metal screen [19] of optimum geometry allowed ideal conditions for the existence of a uniform electrolyte film covering the total screen surface. The oxygen recombination rate was also increased if an Ag-plated rather than a steel or nickel screen was used.

The rate of oxygen recombination on plastic bonded cadmium electrodes in sealed Ni–Cd cells can be controlled by the use of a catalytic mix of active carbon, carbon black and poly(tetrafluoroethylene) [20]. A rate of oxygen recombination was claimed which surpassed that obtained on
commercial pocket type electrodes. Further increase in the rate of oxygen recombination has been achieved \[21\] by addition of Ni(OH)\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4} and carbon black to the plastic bonded cadmium electrode.

Munshi \textit{et al.} \[22\] investigated the dissolution of iron from the additive α-Fe\textsubscript{2}O\textsubscript{3} in the negative cadmium pocket electrode. Iron poisoning of the positive electrode is a common failure mode in flooded Ni-Cd cells. The investigation revealed some dissolution of the α-Fe\textsubscript{2}O\textsubscript{3}, though the amount was found to be much lower than the amount dissolved from the perforated mild steel ribbons used to enclose the active material.

Al-Mosawi \textit{et al.} \[23\] studied the hydrogen evolution reaction on porous cadmium pocket electrodes containing iron oxide and graphite, under commercially relevant conditions in lithiated potassium hydroxide. Their results showed how the relatively slow reaction on cadmium was influenced by the electrode structure, mixed expander, and powder lubricant, and, hence, suggested that these additional materials promote the hydrogen reaction, possibly by a synergistic mechanism.

Reshetov \textit{et al.} \[24\] investigated the formation mechanism of the intermetallic compound Ni\textsubscript{5}Cd\textsubscript{21} which occurs when a charged cadmium electrode containing Ni(OH)\textsubscript{2} is stored in alkaline solution. Formation of this compound causes capacity loss. The kinetics of accumulation of the compound were studied as a function of temperature and quantity of Ni(OH)\textsubscript{2} introduced. The kinetic curve exhibited a two-step form, thus indicating that the intermetallic compound could be formed during storage of cadmium electrodes according to two parallel mechanisms, both involving Ni\textsuperscript{0} and Ni\textsuperscript{2+}.

Morphology

Popkov and co-workers \[25 - 28\] studied the surface morphology of cadmium deposits obtained with periodic current under different solution stirring conditions at pH 5. At a stationary electrode, spongy deposits were formed, whilst at a rotation speed of 25 Hz only compact, fine, crystalline deposits with spiral forms were obtained. This change in morphology was attributed to the effect of the d.c. and periodic currents on the concentrations of species of intermediate valency. The spongy deposits were eliminated, however, when the ionic strength of the solution was increased by the addition of neutral salts such as aluminium sulphate.

In a kinetic investigation \[29\] of the growth of cadmium dendrites on planar cadmium and nickel electrodes, approximately 30 μm long dendrites were found after 6 days at overpotentials of −300 mV (Hg/HgO) in 10 M KOH and a Cd(II) concentration of 2.8 × 10\textsuperscript{-4} M. When small quantities of Cd(OH)\textsubscript{2} were placed in suspension the growth time was reduced.

Barnard \textit{et al.} also studied the growth of cadmium dendrites in both alkaline \[30\] and acidic media \[31\]. In potassium hydroxide, 2D fern dendrites were observed at an overpotential of −150 mV, needle-like dendrites at −200 mV and large, ‘filled in’ fern dendrites at −300 mV. At higher over-
potentials crystalline aggregate dendrites were observed. Under the well defined condition of a rotating disc electrode only small ferns were seen over a wide range of overpotentials.

In another study of dendrite growth in acidic media [31] the morphology and induction time were found to be concentration or overpotential dependent. Barnard's theoretical treatment [32] was in good agreement with the earlier work of Diggle et al. [33]. The total current–time behaviour for the alkaline system can be predicted using the exponential limiting form of the equations with the assumption that the dendrites approximate to rectangular rods and follow first order progressive initiation law. The very different behaviour in acidic media was predicted from the linear limiting form of the equations, with the assumption that the dendrites approximate to cylindrical rods and follow an instantaneous law.

Popov and co-workers [34] studied the morphology of cadmium deposits obtained on foreign substrates at high overpotentials in acidic media. Their short communication confirmed the earlier work of Barnard [31, 32]. Kazarinov and co-workers [35] showed how the structural characteristics (crystal lattice period, unit size, specific surface area, and structural water content) of \( \beta \)-modifications of \( \text{Cd(OH)}_2 \) affected the cathodic reduction behaviour in alkaline media. A relationship was found between the particle size of the \( \text{Cd(OH)}_2 \), the rate of chemical dissolution, and the electrochemical activity.

Fritts and Dueber [36] used time lapse microphotography to study the surface morphology of cadmium. The technique revealed numerous migration regions growing during the life of a single cell. The dominant transport mechanism of the active material was hydrodynamic in nature and was due to molar volume changes occurring in the electrode. Migration was found to occur \textit{en masse} with the migration region charging and discharging with the electrode. Scanning electron microscopy was used to inspect individual migration regions; these were shown to consist of both crystalline and amorphous forms of Cd. The amorphous material contained metallic Cd which allowed for an electrical connection to the negative electrode. Growth of the migration regions occurs through a precipitation–dissolution mechanism of the active material until a short circuit developed between the two electrodes.

Mrha et al. [37] investigated the anomalous behaviour of deeply discharged, sealed Ni–Cd cells. After polarity reversal the cell voltage resides in the range \(-60\) to \(-260\) mV, and the situation can sometimes persist for an unlimited time without any increase in overpressure in the cell. A necessary condition for the appearance of this discharge voltage level was found to be a capacity reserve of the cadmium electrode, and the presence of cadmium in the separator as a result of migration from the negative electrode. The cadmium particles form bridges across the separator leading eventually to a short circuit and consequent cell failure.

Marek and co-workers [38] studied the temperature behaviour of plastic bonded cadmium electrodes in sealed Ni–Cd cells. A decrease in capacity was
found for temperatures below room temperature. At elevated temperatures, large crystals of active material were formed accompanied by a decrease in specific surface area.

Fiala et al. [39] studied the experimental conditions for the formation of cadmium bridges to protect sealed Ni-Cd cells from cell voltage reversal. They found that a common polyamide separator, used as the electrolyte carrier, could also function as a carrier for the Cd/Cd$^{2+}$ system, the deposition method being the same as that in the preparation of sintered cadmium electrodes. The separator was found to be suitable if cycled at least once in excess alkali prior to sealing and, if the cell capacity is limited by the positive electrode, the explosion hazard of the sealed cell can be eliminated. Cadmium bridges formed in the separator under these conditions prevent gas formation on either electrode, their properties depending on the quality of the separator and its loading with cadmium.

**Pores**

Palanisamy and co-workers [40] reported the electrochemical aspects of the cadmium impregnation process where they employed electroanalytical methods to investigate the cathodic deposition, on a nickel plaque, of cadmium hydroxide from cadmium nitrate solution. Two different deposition products were generated depending on the potential. At potentials positive of $-0.6$ V a grey, non-crystalline cadmium hydroxide was produced and at potentials negative of $-0.8$ V a black precursor to cadmium hydroxide was deposited. The black material was thought to be a cadmium complex of a nitrate reaction product. Although both compounds readily converted to crystalline, hexagonal cadmium hydroxide, the grey cadmium hydroxide deposited with minimal concurrent gas evolution and achieved high cadmium hydroxide loadings in the pores of the nickel plaque.

Pensenson [41] used the theory of transient liquid and gas filtration to describe electrolyte displacement by gas in sealed Ni-Cd battery separators. The author has modified this theory to describe electrolyte displacement from the pores of the cadmium electrode, taking into account that the displacing oxygen is reduced at the cadmium (beneath an electrolyte film) electrode occurring under diffusion control.

Novak and Grachev [42, 43] showed that the effective electrolyte resistance in the pores of the cadmium electrodes increased several-fold during discharge. Results obtained in measurements of effective electrolyte resistance in the pores were compared with results for the total porosity of the electrode. The change in effective resistance of the electrolyte in the pores was found to be caused by the change in structure of the pores during charge and discharge. The technique of contact standard porosimetry has been used to study the size distribution of pore volumes in cadmium electrodes [44]. The pore size of the active material was found to be 0.04 $\mu$m and the intervals between particles of active material were about 1 $\mu$m.
A specific surface area of 14-15 m² g⁻¹ for a fully charged electrode was quoted, whilst the B.E.T. method on the same electrode was 3.5 m² g⁻¹. The reason suggested for this difference was the blocking of large pores by fine particles in porous materials with complex shaped pores.

Final remarks

Research on the cadmium electrode has been limited in recent years, although work on the morphology of the electrode, particularly on the formation of cadmium bridges, seems on-going. Recent advances in lithium primary battery systems has highlighted the relatively poor energy density characteristics of the traditional alkaline battery systems incorporating cadmium. This inadequacy has been solved to some extent by the introduction of plastic bonded electrodes which have stimulated new interest in this area.

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References

APPENDIX 3

Presented below is a list of the articles and technical papers published during the course of this research.


REFERENCES:

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