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STUDIES OF THE ELECTROCHEMISTRY OF LEAD DIOXIDE

by

JAMES PETER CARR, B.TECH.

A Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology.

June 1972

Supervision: N.A. HAMPSON, PhD.
Department of Chemistry,
R. TAYLOR, PhD.
Joseph Lucas Limited

(c) by James Peter Carr
The work described in this thesis has not been submitted, in full or in part, to this or any other Institution for a higher degree.
To my Parents.
ACKNOWLEDGEMENT

I wish to express my thanks to my Supervisors, Dr. N.A. Hampson and Dr. R. Taylor, for the advice, help and encouragement given to me throughout this work.

My thanks are also expressed to my fellow research students for their help and friendship; to Professor R.F. Phillips for providing the facilities to carry out this work; to members of the technical staff of the Chemistry Department for their assistance and to the Science Research Council and Joseph Lucas Limited for the provision of a research grant.
SUMMARY

Differential capacitance studies at $\alpha$ and $\beta$-PbO$_2$ electrodes in a number of ultra pure aqueous electrolyte solutions established that, in general, the electrode interphase is complicated by adsorption. In KNO$_3$ solutions, however, the PbO$_2$ electrode is relatively uncomplicated by adsorption and, after allowing for surface roughness effects, behaves as predicted by the Gouy-Chapman theory. The pzc', estimated from the measurements in KNO$_3$ solutions, occurs at 1.07 ± 0.01V for $\alpha$-PbO$_2$ and 1.15 ± 0.01V for $\beta$-PbO$_2$.

The kinetics of the exchange reaction at $\alpha$ and $\beta$-PbO$_2$ in alkaline, perchlorate and sulphate solutions has been investigated using the galvanostatic and faradaic impedance techniques. The overpotential - current density data was interpreted in terms of two rate controlling charge transfer mechanisms. At potentials not too distant from the equilibrium potential, the charge transfer process involves a simultaneous two electron transfer whereas at higher overpotentials two consecutive single electron transfers are involved. The impedance measurements are interpreted in terms of a simultaneous two electron transfer but the overall exchange reaction rate is considerably greater than that estimated from the galvanostatic measurements. An explanation of the enhanced reaction rate is given involving apparent lattice activation by application of repetitive potential stimuli. Measurements obtained from both techniques confirm that the exchange reaction involves adsorbed intermediates at the electrode.

Linear sweep voltammetric studies in NaOH and H$_2$SO$_4$ solutions indicate that the Pb(IV)/Pb(II) reaction in both electrolytes involves diffusion processes in solution.
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A  electrode area

$C_L$  total double layer capacitance

$C_{\text{diff.}}$  diffuse layer capacitance

$C_{\text{comp}}$  compact layer capacitance

$C_d$  capacitive component of faradaic impedance due to diffusion in solution

$C_r$  equivalent capacitive component of faradaic impedance

$C_{\text{ps}}$  adsorption capacitance

$C_{\text{xs}}$  experimental capacitive component in measured series combination

$C_0$  concentration of oxidised species at the electrode

$C_R$  concentration of reduced species at the electrode

$C^s$  bulk concentration of electrolyte

$D_i$  diffusion coefficient of species i

$E_Z$  potential of zero charge

$E_r$  rational potential

$E$  potential

$E^o$  standard potential

$\Delta G^o$  standard free energy of adsorption

$\Delta H$  enthalpy of activation for charge transfer

$I$  faradaic current in potential sweep measurements

$R$  gas constant

$R_E$  resistance of electrolytic system

$R_D$  resistance component of faradaic impedance due to charge transfer

$R_d$  resistive component of faradaic impedance due to diffusion in solution

$R_r$  equivalent resistive component of faradaic impedance

$R_{\text{xs}}$  experimental resistive component in measured series combination
\( T \)  
Temperature

\( W \)  
Warburg impedance

\( a \)  
Activity of species i

\( b \)  
Constant in eq. 2.11

\( i_i \)  
Faradaic current density

\( i_0 \)  
Exchange current density

\( i_{oa} \)  
Apparent exchange current density

\( i_A \)  
Anodic current density

\( i_C \)  
Cathodic current density

\( k \)  
Rate constant

\( k^0 \)  
Standard rate constant

\( q_D \)  
Charge on diffuse layer

\( q_n \)  
Charge on electrode

\( q_l \)  
Specifically adsorbed charge

\( v \)  
Potential sweep rate

\( z \)  
Number of electrons involved in electrode reaction

\( a \)  
Charge transfer coefficient

\( \beta \)  
Adsorption coefficient

\( \eta_D \)  
Charge transfer overpotential

\( \eta_\Omega \)  
Ohmic overpotential

\( \eta_d \)  
Overpotential due to diffusion in solution

\( \mu \)  
Chemical potential of species i

\( \theta \)  
Surface coverage by adsorbed species

\( \sigma \)  
Warburg coefficient

\( \Gamma_A \)  
Surface concentration of adsorbed species

\( \Gamma_{AM} \)  
Maximum surface concentration of adsorbed species
\( \omega \)  angular frequency
\( \psi_u \)  potential drop across the inner layer
\( \psi_1 \)  potential at adsorption plane
\( \tau \)  transport number of an ion in the double layer
\( \epsilon_{2-s} \)  dielectric constant of diffuse layer
CHAPTER 1

INTRODUCTION

The study of the electrochemical behaviour of solid metals is of fundamental importance in the understanding of electrochemical energy conversion devices. In recent years relaxation techniques, successfully developed using amalgam electrodes, have been applied to the study of solid metal electrodes. It is desirable to extend electrochemical studies to oxide electrodes since these are the cathodic counterparts of metals and form important electrodes in certain energy storage systems. Although many oxides are non-conducting and difficult to study electrochemically a class of oxides exists which possess a certain degree of electronic conduction. Of these lead dioxide, which forms the positive active material of the lead-acid cell, has pronounced metallic characteristics and is amenable for electrochemical study.

Due to its importance in the lead-acid cell a considerable amount of work has been reported concerning the lead dioxide electrode. In general investigations have involved long time polarization and equilibrium studies and the use of relaxation methods has been fairly limited. Recent work has emphasized several unresolved problems:

(i) The behaviour of lead dioxide is complicated by the existence of more than one polymorphic form and results indicate significant activity differences between the forms.
(ii) It is fairly well established that the lead dioxide/aqueous solution interphase is complicated by adsorption of species from solution however the exact mechanism of the adsorption and its effect on the electrode kinetics are as yet unresolved.
(iii) Exchange current densities observed for the lead dioxide (Pb(IV)/Pb(II)) exchange reaction in aqueous solution is small (in acid solution Jones reports values of \( \sim 10^{-1} \text{ mA cm}^{-2} \)). In general, other electrode systems used in energy conversion

(1)
devices have shown large exchange current densities (e.g. Pb/Pb(II) \( \sim 10 - 10^3 \text{ mA cm}^{-2} \)).

It was decided to study the electrochemical behaviour of lead dioxide in a number of aqueous solutions using relaxation techniques and obtain further information concerning the above problems.

The Lead Dioxide Electrode

A full review of the lead dioxide electrode is given in Appendix 1. In this review attention is given to the reported work more relevant to the present studies.

There are at least three different crystallographic forms of lead dioxide, orthorhombic (\( \alpha \)) \(^3,5\) and pseudo-tetragonal (\( \delta \)) \(^6\) and tetragonal (\( \beta \)) \(^7\). As yet little is known of the \( \delta \) form and most of the reported work has been concerned with the \( \alpha \) and \( \beta \) forms. \( \alpha \)-Lead dioxide has the orthorhombic structure of columbite and \( \beta \)-lead dioxide the rutile structure. It was first shown by Pauling and Sturdivant \(^8\) that a close relationship exists between the two lattices. In both cases the Pb(IV) ion is at the centre of a distorted octahedron. The essential difference in structure is in the way that the octahedra are packed. In \( \beta \)-lead dioxide neighbouring octahedra share opposite edges, which results in the formation of linear chains of octahedra. In \( \alpha \)-lead dioxide neighbouring octahedra share non-opposing edges in such a way that zig-zag chains are formed. In both cases each chain is connected with the next one by shared corners.

It is fairly well established that lead dioxide is a non-stoichiometric compound. Several attempts to prepare stoichiometric lead dioxide have been unsuccessful. The non-stoichiometric compositions have been determined by a number of workers \(^10-12\) as PbO 1.83 - 1.98 and PbO 1.95 - 2.0 for \( \alpha \) and \( \beta \)-lead dioxide respectively.
Lead dioxide has a high electrical conductivity, comparable with that of some metals. This property is important in its use in the lead-acid cell. Kittel and Thomas carried out Hall effect measurements on electrodeposited samples and concluded that the observed conduction was due to electron mobility and was closer to the conductivity of metals than semi-conductors. Electron densities of \(10^{20} - 10^{21}\) cm\(^{-3}\) were reported with ionic mobilities of \(10^{3}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). It was assumed that the free electrons were due to an effective deficiency of oxygen. According to Thomas, the temperature coefficient of the resistance is positive in the temperature range \(-100^\circ C\) to \(100^\circ C\) and the sign of the thermoelectric power negative. Later work by Mindt showed that films of both \(\alpha\) and \(\beta\)-lead dioxide show low resistivities (\(\alpha\): \(10^{-3}\) \(\Omega\)-cm, \(\beta\): \(10^{-4}\) \(\Omega\)-cm) and electron densities of \(10^{21}\) cm\(^{-3}\). Mindt suggested that the free electrons were due to either the non-stoichiometry or to the inclusion of hydrogen ions in the oxide lattice.

Nuclear magnetic resonance studies have shown relative shifts of 0.48 for the \(\alpha\)-form and 0.63 for the \(\beta\)-polymorph with respect to \(207\) Pb. Piette and Weaver concluded that the chemical shift was a qualitative measure of the conductivity and was due to conduction of electrons.

The above evidence indicates that \(\alpha\)-lead dioxide is a better conductor than \(\beta\)-lead dioxide.

Thermodynamically both polymorphs are very similar. Table 1.1 summarizes some of the more important thermodynamic functions.

Surface area determinations have not conclusively shown whether \(\alpha\) or \(\beta\)-lead dioxide has the greatest surface area but most of the work reports a greater surface area for \(\beta\)-PbO\(_2\).

The lower oxides of lead are of interest since they are possible products of the reduction of lead dioxide. Two polymorphs of the next lower oxide, PbO, have been
Table 1.1.

Some thermodynamic properties of lead dioxide.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha{\text{-PbO}}_2 )</th>
<th>( \beta{\text{-PbO}}_2 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode potential, ( E ), in 4.4 mol ( \text{L}^-1 )</strong></td>
<td>1.708 V</td>
<td>1.715 V</td>
<td>20</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4, 25\degree\text{C}, \text{vs} \text{NHE} )</td>
<td>1.697 V</td>
<td>1.687 V</td>
<td>22, 23</td>
</tr>
<tr>
<td><strong>Standard potential, ( E_0 )</strong></td>
<td>1.691 V</td>
<td>1.682 V</td>
<td>24</td>
</tr>
<tr>
<td><strong>Temperature coefficient of potential in</strong></td>
<td>(-0.36,\text{mV})/(\degree\text{C}^-1)</td>
<td>(-0.20,\text{mV})/(\degree\text{C}^-1)</td>
<td>25</td>
</tr>
<tr>
<td>( 4.62,\text{mol},\text{L}^-1,\text{H}_2\text{SO}_4 )</td>
<td>218 kJ</td>
<td>220 kJ</td>
<td>25</td>
</tr>
<tr>
<td><strong>Standard free energy of formation, ( \Delta G^0 ), per mol.</strong></td>
<td>-265 kJ</td>
<td>-261 kJ</td>
<td>24</td>
</tr>
<tr>
<td><strong>Standard heat of formation, ( \Delta H^0 ), per mol.</strong></td>
<td>-76.44</td>
<td>J/(\degree\text{C}^-1)</td>
<td>24</td>
</tr>
<tr>
<td><strong>Molar heat capacity</strong></td>
<td>(-64,\text{J/}\degree\text{C}^-1)</td>
<td>(64,\text{J/}\degree\text{C}^-1)</td>
<td>24</td>
</tr>
<tr>
<td><strong>Free energy of reaction, ( \Delta G_R ), in ( \text{H}_2\text{SO}_4 )</strong></td>
<td>(-333.5)</td>
<td>(-343.5)</td>
<td>24</td>
</tr>
<tr>
<td>per mol.</td>
<td>kJ</td>
<td>kJ</td>
<td>24</td>
</tr>
<tr>
<td><strong>Heat of reaction in ( \text{H}_2\text{SO}_4 ), ( \Delta H_R )</strong></td>
<td>(-354)</td>
<td>(-343.5)</td>
<td>24</td>
</tr>
<tr>
<td>per mol.</td>
<td>kJ</td>
<td>kJ</td>
<td>24</td>
</tr>
<tr>
<td><strong>Entropy of reaction in ( \text{H}_2\text{SO}_4 ) per mol</strong></td>
<td>(-69.6)</td>
<td>(-38.6)</td>
<td>24</td>
</tr>
</tbody>
</table>

reported in the literature, tetragonal and orthorhombic. Olin has shown, from a potentiometric study of the hydrolysis of Pb(II) in perchlorate electrolytes, that there is good evidence for a Pb(OH)\(^+\) complex. Pb(OH)\(_2\) also exists and is stable in electrolytes of high pH. Very little is known of Pb(IV) hydroxy complexes and the existence of Pb(IV) ions in solution is uncertain.

With the development of the lead acid battery by Plante in 1859 considerable attention has been focused on the lead dioxide/\( \text{H}_2\text{SO}_4 \) system. The generally accepted theory for the reactions taking place in the cell can be conveniently expressed as:

\[(4)\]
\[
PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O \quad (1.1)
\]

or:

\[
PbO_2 + 4H^+ + SO_4^{2-} + 2e = PbSO_4 + 2H_2O \quad (1.2)
\]

The picture is complicated by the participation of two electrons in the overall reaction and the involvement of two solid phases, PbO₂ and PbSO₄. It is also difficult to formulate a mechanistically satisfactory picture of the dynamic equilibrium between lead dioxide and Pb(II) ions in solution because trivalent lead is relatively unknown and tetravalent lead has not been detected in solution. Consequently the exchange mechanism and reaction steps involved in the overall reaction are not well established.

The discharge properties and discharge mechanism of the \( \beta \)-lead dioxide electrode in \( H_2SO_4 \) solutions have been studied by a number of workers. As yet there is some uncertainty concerning the exact mechanism. Studies of the discharge mechanism of \( \alpha \)-lead dioxide are few. Mark suggested that the discharge mechanism in dilute \( H_2SO_4 \) (< 0.1 mol \( L^{-1} \)) may be different for the two polymorphs; PbSO₄ formed on discharge of \( \alpha \)-lead dioxide remains on the undischarged electrode as an adherent film but on \( \beta \)-lead dioxide as widely dispersed nuclei.

The formation of lead dioxide by the anodic oxidation of lead or PbSO₄ has been investigated by a number of workers. Feitknecht and Gauman showed that the passivation of lead in \( H_2SO_4 \) resulted in the formation of \( \beta \)-lead dioxide by the oxidation of plumbous ions:

\[
Pb(II) + 2OH^- = \beta-PbO_2 + 2H^+ \quad (1.3)
\]

However, Sparhbier found that the reactions occurring during the formation of \( \beta \)-lead dioxide could be summarized as:

\[
H_2O = H^+ + OH_{ads} + e \quad (1.4)
\]

\[
Pb(II) + H_2O = Pb(OH)^{++} + H^+ + e \quad (1.5)
\]
At present it is generally accepted that the passivation mechanism includes the \( \text{OH}^- \) ion discharge, adsorption of the hydroxyl radical at the electrode surface and immediate oxidation of the \( \text{Pb(OH)}_2 \) formed to give one or both polymorphs of lead dioxide.

The possibility of the participation of the plumbic ion in the exchange reaction has been suggested\(^{32,41}\), but Bone et al.\(^{42}\) showed that plumbic ions were not involved in the oxidation process and that the total exchange between plumbous ions in the solution and lead dioxide is very rapid.

The deposition of \( \alpha \)-lead dioxide was investigated by Fleischmann and Liler\(^{43}\) who suggested the mechanism:

\[
\begin{align*}
\text{OH}^- - e &= \text{OH}_{ads} \quad (1.6) \\
\text{Pb}(\text{II}) + \text{OH}_{ads} + \text{OH}^- - e &= \text{Pb(OH)}_2^{++} \quad (1.7) \\
\text{Pb(OH)}_2^{++} &= \text{PbO}_2 + 2\text{H}^+ \quad (1.8)
\end{align*}
\]

where reactions 1.7 and 1.8 are the rate determining steps.

The lead dioxide/\( \text{Pb(II)} \) exchange reaction in acid perchlorate electrolyte solutions was investigated by Jones et al.\(^{1,44-47}\). For the \( \alpha \)-polymorph the exchange was shown to be complicated by an \( \alpha/\beta \) interconversion process. At potentials close to the equilibrium potential, the exchange reaction involved the transfer of two electrons, simultaneously, but at potentials more removed from the equilibrium two consecutive single electron transfers. The presence of \( \text{H}^+ \) adsorption was inferred from the abnormal experimental charge transfer coefficients observed.

The mechanism of oxygen evolution on lead dioxide electrodes has attracted considerable attention since the charging of the lead-acid cell occurs at appreciable overpotentials. The published data\(^{20,21,48-55}\) is in agreement with a Tafel slope of ~ 0.12 – 0.14V per decade of current for \( \beta \)-lead dioxide and ~ 0.05 – 0.07 V for
impedance studies of the lead dioxide electrode have been relatively few\textsuperscript{56-60}. Kabanov\textsuperscript{56,57} from differential capacitance studies, reports the potential of zero charge at 1.78 V in H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4} (0.01 mol l\textsuperscript{-1}) solutions, shifting to more negative potentials with decreasing acid concentration. Hardness measurements\textsuperscript{61} were in agreement with this value for the pzc. Surface modification has been inferred from both capacitance\textsuperscript{55,56} and hardness measurements\textsuperscript{61}. An equation to explain such a modification was proposed\textsuperscript{55}:

\[ S_{\text{true}} = S_{\text{limit}} + (a + bt) \tau^{0.5} \]  

(1.9)

where \( a \) and \( b \) are constants, \( \tau \) is the time of electrode/electrolyte contact and \( t \) the temperature. From these results it was also suggested that adsorption of SO\textsubscript{2}\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-} and H\textsubscript{2}SO\textsubscript{4} occurs at the electrode.

Kokarev et al\textsuperscript{59} has proposed several equivalent electrical circuits to represent the electrical double layer at the lead dioxide/aqueous electrolyte interphase, however, these experiments were performed in the oxygen evolution region. They concluded that the overall equivalent circuit included impedance terms due to the capacitance of the double layer, diffusion, adsorption and the resistance of the electrochemical reaction.
2.1. The Electrode-Electrolyte Interphase

Electrochemical processes take place within a thin surface layer at the interphase between an electrode and a solution. Thus, in order to understand the mechanism of electrochemical processes, it is essential that the structure of the electrode/electrolyte interphase is described.

At a metal/solution interphase a region exists where the electric field strength differs from zero and an electrical double layer is formed. The formation of an electrical double layer at a metal/solution interphase is a general phenomenon and consists of two layers of electric charge of opposite sign and equal magnitude separated by a distance of the order of Angstrom units. The existence of an electrochemical double layer depends on an inhomogeneity in the system and is always closely associated with a phase boundary. The two layers of charge may be situated one in each phase, separated by the phase boundary, in which case there is a net charge in each phase. Alternatively, the two layers may be situated within one phase but close to the interphase. It is also possible that the two types of double layer may co-exist.

In general, metal/solution interphases can be theoretically divided into:

(a) ideally polarizable,

(b) non-polarizable.

An ideally polarizable interphase can be defined as a system for which potential excursions from equilibrium do not cause passage of charge or faradaic reactions across the interphase. In the case of non-polarizable electrodes either the presence of a potential determining ion in either or both phases causes concentration changes at the electrode for potential excursions according to the Nernst equation, or, faradaic reactions cause
passage of charge across the interphase.

The earliest model of the electrical double layer at an electrode/electrolyte interphase was proposed by Helmholtz \(^{62}\) in which the interphase was considered to consist of two layers of equal and opposite charge, one layer situated on the electrode and the other on the solution side of the interphase, approximating to a parallel plate condenser. From thermodynamic considerations such a system is not stable and moreover, values of the differential capacitance, calculated using this model did not agree with experimental results.

Gouy \(^{63}\) and Chapman \(^{64}\) independently modified the above model by considering the thermal motion of the ions in the electrolyte and developed the concept of the diffuse layer rather than the compact layer of Helmholtz. Their calculation was very similar to the ionic atmosphere theory of Debye and Hückel; \(^{65}\) the solution side of the double layer effectively acts as an ionic atmosphere of the electrode. The theoretical predictions of this theory fitted with experimental results at low electrolyte concentrations and potentials close to the electrocapillary maximum.

Both the above theories assume:

(i) a continuous incompressible ideal medium,

(ii) non-polarizable point charges,

(iii) no specific adsorption.

By considering ions to have a finite distance of approach to the electrode and taking into account specific adsorption of ions, a closer agreement of theory with experimental results is obtained. Stern \(^{66}\) was the first to suggest the concept of a plane of closest approach for ions and considered the electrical double layer to consist of two parts, a compact layer and a diffuse layer extending into the solution. Grahame \(^{67}\) improved the Stern model by considering specific adsorption of ions and represented the double layer as:-
Fig 2.1 Possible structure of a metal electrolyte interface (Bockris et al., 1963)

Inner Helmholtz plane

Outer Helmholtz plane

Metal plane

Solvated cations

Specifically adsorbed anions

Normal water structure

Primary water layer

Secondary water layer

Metal
(a) the inner Helmholtz plane which is governed by the plane of closest approach of the solvent dipoles and specifically adsorbed ions.

(b) the outer Helmholtz plane which is determined by the plane of closest approach of the solvated cations.

Fig. 2.1 shows, schematically, a model of the electrode/electrolyte interphase. Using a similar model Grahame showed that the total double layer capacitance is represented by:

$$\frac{1}{C_L} = \frac{1}{C_{\text{diff}}} + \frac{1}{C_{\text{comp}}}$$  \hspace{1cm} (2.1)

where \(C_L\) is the double layer capacitance, \(C_{\text{diff}}\) the capacitance of the diffuse layer and \(C_{\text{comp}}\) the capacitance of the compact layer. A relationship for the diffuse layer capacitance is given by:

$$C_{\text{diff}} = \left( \frac{2F}{9} \frac{\epsilon_2 - 5}{2\pi RT} \right) \left[ \cosh \left( \frac{\Pi}{2RT} \frac{\epsilon_2 - 5}{\epsilon_2} C_S q_n \right) \right]$$  \hspace{1cm} (2.2)

where \(\epsilon_2\) is the dielectric constant in the diffuse layer, \(C_S\) the bulk concentration of the electrolyte and \(q_n\) the charge on the electrode. This expression predicts that as \(q_n\) passes through zero the diffuse layer capacitance goes through a characteristic minimum (since \(\cosh 0 = 1\) and \(\cosh y > 1\) for all other values of \(y\) near \(y = 0\)). Also, \(C_{\text{diff}}\) decreases with decreasing bulk concentration of electrolyte near the potential of zero charge, \(E_z\). Thus for electrolyte solutions of sufficiently low concentration, the measured capacitance vs potential curves approximate to the diffuse layer capacitance curves.

Other workers have proposed further corrections to the above double layer theory which mainly concern (1) the finite size of the ions in the diffuse layer, (2) dielectric saturation, (3) polarisation of the components of the system, (4) the association of an electrode with counter ions on the electrode surface.
iation effect, and (5) the self atmosphere effect. More recently Barlow and Macdonald and Levine and Bell have considered the discreteness of charge effect on the double layer but as yet this has only been interpreted for the diffuse layer.

The importance of the pzc has been discussed by Frumkin. As was shown in equation 2.2., the value of the pzc can be obtained from the differential capacitance-bias potential curves for low electrolyte concentrations, and plays an important role in determining the extent of adsorption at an electrode (determines charge on the electrode). The charge on the electrode is determined by the quantity \( E - E_z \) which is termed the rational potential, \( E_{\text{rat}} \). At positive \( E_{\text{rat}} \), adsorption of negative ions is favoured while at negative \( E_{\text{rat}} \), positive ions are attracted to the electrode. When \( E_{\text{rat}} \) is small adsorption of neutral ions or molecules competes favourably with ionic adsorption. Thus a knowledge of the pzc is an important precursor to the study of the kinetics of an electrode reaction.

2.2. Adsorption at Electrode

Many electrode reactions and coupled chemical reactions take place via adsorbed species on the electrode surface. The adsorbed species may be the starting material, an intermediate, the product, the electrolyte, the solvent or other species such as hydroxyl or hydrogen radicals. The presence of adsorption can be detected in a number of ways:

(i) Fractional orders of reaction with respect to a particular electroactive species.

(ii) In cyclic voltammetric studies, a plot of peak current vs \( v \) is linear for the reduction or oxidation of adsorbed species (cf. diffusion controlled reaction where peak current vs \( \sqrt{v} \) is linear).

(iii) The measured current-time transients, for potentiostatic measurements, show higher currents than calculated theoretically.
(iv) Rapid changes in the differential capacitance with concentration of a particular species.

In studies of the kinetics of a heterogeneous process involving adsorbed species it is necessary to replace the bulk electrolyte concentration terms by surface concentration. This necessitates the use of adsorption isotherms which relate the concentration of adsorbed species at the electrode, $I_A$ with the bulk concentration, $a$. In non-electrochemical adsorption, the isotherm is a function only of the bulk concentration but in electrochemical adsorption an additional electrical variable is present, which determines the state of the system.

Adsorption isotherms are based on molecular models and the model that is normally used assumes that the adsorbed species forms a monomolecular layer immediately adjacent to the electrode surface. The equilibrium between the adsorbed layer and the bulk solution can be conveniently considered as a partition between two phases, the bulk solution and the surface phase however, in determining which isotherm fits the experimental data a definition of activity must be made. Since equilibrium prevails across the whole system, the chemical potential of the adsorbate, $\mu_A$, must be uniform. Thus one may write:

$$\mu_A^{\text{soln.}} = \mu_A^{\text{ads.}} \quad (2.3)$$

where $\mu_A^{\text{ads.}}$ and $\mu_A^{\text{soln.}}$ are the standard chemical potentials of adsorbate in the adsorbed state and in the solution respectively.

If the configuration entropy of the adsorbed ions is expressed in terms of $R \ln \theta$ assuming ideal behaviour of the adsorbed film, equation 2.3. becomes:

$$\mu_A^{\text{ads.}} + RT \ln \frac{q')_{\max}}{q'} + z F K \psi_u + Z_A F \psi_o = \mu_A^{\text{soln.}} + RT \ln \alpha_A \quad (2.4)$$

(12)
where \( K \psi_u = \psi_i \left| q' \right| \) is the amount of charge specifically adsorbed, \( \psi_u \) is the potential drop across the inner layer and \( \psi_i \) is the potential at the adsorption plane (assumed to be a fraction of the total potential drop across the inner region). It is possible that equation 2.4. is incorrect due to the non-ideality of the adsorbed film and because the micropotential at the adsorption plane changes radically with dilution due to changes in the imaging forces in the diffuse layer. Also equation 2.3. may not be the correct thermodynamic description of the adsorption equilibrium. The uncertainty introduced by changes in the micropotential at the adsorption plane cannot be removed except by exposing this effect through the isotherm parameters. The equilibrium to which equation 2.3. refers is:

\[
A(aq) \rightleftharpoons A(ads)
\]

(2.5)

where \( A \) is the adsorbed species. If equation 2.5. is correct, the concentration variable in the adsorption isotherm can be equated to the mean activity of the salt, \( a_+ \).

If the adsorbed species is charged then in order to keep the interface electroneutral the adsorption of an anion must be accompanied by the corresponding adsorption of a cation and vice versa, and the correct concentration variable is thus \( \ln a_+^2 \), instead of \( \ln a_+ \). At constant electrode charge the inclusion of one Faraday of anions in the inner layer results in corresponding changes in the diffuse layer. For each Faraday of \( X^- \) ion adsorbed, \( \tau_+ \) Faradays of \( Y^+ \) are absorbed, and \( \tau_- \) Faradays of anions in the diffuse layer are desorbed, where \( \tau \) is the transport number of the anion and cation respectively in the double layer, and is defined in this case by 81, 82:

\[
\tau_+ = \frac{dq_{D+}}{d(q_n + q')} = \left( \frac{q_{D+}}{q'} \right) q_n
\]

(2.6)
where \( q_D \) is the charge on the diffuse layer and \( q_n \) is the charge on the electrode.

The adsorption of one Faraday of anions in the inner layer is then accompanied by the disappearance of \( \tau_+ \) equivalent of salt from the solution, and the equilibrium to be considered is:

\[
\tau_+ Y X_{(aq)} \rightleftharpoons \tau_+ Y X_{(ads)}
\]

(2.7)

and implies that the adsorbed species is the ion pair \( XY \).

In recent work, Horanyi et al.\(^8^3,8^4\) investigated the adsorption phenomena on platinized platinum electrodes, and suggested that the adsorption of \( \text{Cd}^{2+} \) ions from sulphate and perchlorate solutions was accompanied by the adsorption of anions (in this case \( \text{ClO}_4^- \), and \( \text{HSO}_4^- \)). Thus Schiffrin\(^7^8\) suggests that the correct term in the adsorption isotherm should be \( \tau_+ \log a_{\text{aq}}^2 \).

A number of isotherms have been used to describe adsorption of ions and molecules at electrodes, each characterised by certain assumptions and each applicable to certain experimental systems. Table 2.1. lists several possible equations of state for adsorption and the corresponding adsorption isotherms. The isotherm corresponding to each equation of state gives the form of the activity of the adsorbed species in the bulk electrolyte, \( a_A \), as a function of the surface concentration \( \Gamma_A \), or alternatively, the surface pressure \( p \). \( \Gamma_{AM} \) represents the maximum surface concentration of the adsorbed species and \( \theta = \frac{\Gamma_A}{\Gamma_{AM}} \).

To deduce the nature of the particle - particle interactions in an adsorbed layer it is necessary to compare experimental adsorption with that predicted by the above isotherms. These isotherms are based on the assumption of constant electrical state. There seems to be little question that the electrical variable which should be held constant is the electric field operative in the adsorbed layer. Parsons\(^5^3\) has suggested that measurements at constant charge are appropriate pointing out that such

(14)
<table>
<thead>
<tr>
<th>NAME</th>
<th>EQUATION OF STATE</th>
<th>Surface Pressure Form</th>
<th>ISOTHERM</th>
<th>Surface Concentration Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry's law</td>
<td>$p = RT \Gamma_A$</td>
<td>$\beta_a^b = p$</td>
<td>$\beta_a^b = RT \Gamma_A$</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$p = xRT \Gamma_A$</td>
<td>$\beta_a^b = p^x$</td>
<td>$\beta_a^b = (xRT \Gamma_A)^x$</td>
<td></td>
</tr>
<tr>
<td>Volmer\textsuperscript{86}</td>
<td>$p = \frac{RT \Gamma_A}{(1 - b \Gamma_A)}$</td>
<td>$\beta_a^b = \frac{p e^{bp/RT}}{e^{b \Gamma_A}}$</td>
<td>$\beta_a^b = \frac{RT \Gamma_A}{(1 - b \Gamma_A)} \exp \left[ \frac{-b \Gamma_A}{(1 - b \Gamma_A)} \right]$</td>
<td></td>
</tr>
<tr>
<td>van der Waals</td>
<td>$p = \frac{RT \Gamma_A}{(1 - b \Gamma_A)} + g(\Gamma_A)^2$</td>
<td>$\beta_a^b = \frac{RT \Gamma_A}{(1 - b \Gamma_A)} \exp \left[ \frac{-b \Gamma_A}{(1 - b \Gamma_A)} \right] \exp \left[ \frac{2g \Gamma_A}{RT} \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Virial</td>
<td>$p = RT \Gamma_A + g(\Gamma_A)^2$</td>
<td>$\beta_a^b = \frac{RT}{2g} \left[ \left( \frac{1}{\Gamma_T^2} + \frac{b}{RT} \right) \right. - 1 \left. \right]$</td>
<td>$\beta_a^b = \Gamma_A \exp \left( \frac{2g \Gamma_A}{RT} \right)$</td>
<td></td>
</tr>
<tr>
<td>Langmuir\textsuperscript{85}</td>
<td>$p = -RT \Gamma_A \ln \left( 1 - \frac{\Gamma_A}{\Gamma_{AM}} \right)$</td>
<td>$\beta_a^b = e^{p/(RT \Gamma_A)} - 1$</td>
<td>$\beta_a^b = \frac{\Gamma_A}{\Gamma_{AM} - \Gamma_A} = \theta$</td>
<td></td>
</tr>
<tr>
<td>Logarithmic</td>
<td>$p = g(\Gamma_A)^2$</td>
<td>$\beta_a^b = \exp \left( \frac{b \Gamma_A}{RT} \right)$</td>
<td>$\beta_a^b = \exp \left( \frac{2g \Gamma_A}{RT} \right)$</td>
<td></td>
</tr>
<tr>
<td>Temkin\textsuperscript{88}</td>
<td>$p = -RT \Gamma_A \left( 1 - \frac{\Gamma_A}{\Gamma_{AM}} \right)$</td>
<td>$\beta_a^b = \exp \left( \frac{b \Gamma_A}{RT} \right)$</td>
<td>$\beta_a^b = \exp \left( \frac{2g \Gamma_A}{RT} \right)$</td>
<td></td>
</tr>
<tr>
<td>Frumkin\textsuperscript{87}</td>
<td>$p = -RT \Gamma_A \left( 1 - \frac{\Gamma_A}{\Gamma_{AM}} \right)$</td>
<td>$\beta_a^b = \exp \left( \frac{b \Gamma_A}{RT} \right)$</td>
<td>$\beta_a^b = \exp \left( \frac{2g \Gamma_A}{RT} \right)$</td>
<td></td>
</tr>
<tr>
<td>&quot;Square root&quot;</td>
<td>$\frac{1}{\Gamma_A} = \frac{RT}{p} + \left( \frac{\Gamma_A}{\Gamma_{AM}} \right)^2$</td>
<td>$\beta_a^b = p \exp \left( \frac{b \Gamma_A}{RT} \right)$</td>
<td>$\beta_a^b = \frac{\theta}{1 - \theta}$</td>
<td></td>
</tr>
<tr>
<td>Modified</td>
<td>$p = RT \frac{\Gamma_A}{(1 - b \Gamma_A)^2} + g(\Gamma_A)^2$</td>
<td></td>
<td>$\beta_a^b = \frac{\theta}{1 - \theta}$</td>
<td></td>
</tr>
<tr>
<td>Helfand, Frisch, and Lebowitz\textsuperscript{89}</td>
<td>$\frac{1}{\Gamma_A} = \frac{RT}{p} + \left( \frac{\Gamma_A}{\Gamma_{AM}} \right)^2$</td>
<td></td>
<td>$\beta_a^b = \frac{\theta}{1 - \theta}$</td>
<td></td>
</tr>
</tbody>
</table>

a state corresponds to the case of non-electrochemical adsorption since in such systems
the value of charge density is always zero. Damaskin, on the other hand, has preferred to hold the potential of the electrode constant.

The question of which of the two electrical variables, $q_n$ or $E$, should be held constant to keep the electrical state of the adsorption layer constant is not completely resolved. At the present stage it would appear that the constant charge isotherm provides a more convenient starting point for interpretation of adsorption since under such conditions the electrode-particle interaction should be approximately constant so that the interaction parameters derived from the isotherm are a true reflection of the particle-particle interaction.

In assigning a particular isotherm to experimental data several methods are available. Gileadi and Conway pointed out that the dependence of $\theta$ on the potential was not very sensitive to the type of isotherm applied to the system. The dependence of the adsorption pseudocapacitance, $C_{ps}$, on the potential was found to be very sensitive to the exact form of the isotherm. More recently, Parsons showed that a plot of $\theta$ vs \log ($\beta a_A$) was not very sensitive to the isotherm employed, but some distinction between isotherms could be observed from plots of $\frac{d \theta}{\log (\beta a_A)}$ vs \log ($\beta a_A$) and that a suitable technique for obtaining values of $\theta$ is from capacitance-bulk concentration curves at constant charge.

2.3. Charge Transfer Kinetics

For a simple electrode process the rate determining step can be identified with the overall reaction:

$$O + ze = R \quad (2.15)$$

The free energy barrier for such a reaction has been fully discussed by Vetter.
Delahay\textsuperscript{93}. For such a process occurring at an electrode, the current - overpotential relationship was derived by Erdez-Gruz and Volmer\textsuperscript{94}:

\[ i = i_0 \left[ \exp \left( \frac{-zF}{RT} \eta_D \right) - \exp \left( \frac{(1-\alpha)zF}{RT} \eta_D \right) \right] \]  

(2.16)

where \( i_0 \) is the exchange current and depends on the concentration of the reactants and products as:

\[ i_0 = zFk_0 \cdot (C_0)^{1-\alpha} \cdot (C_R)^\alpha \]  

(2.17)

\( \eta_D \) is the charge transfer overpotential, \( \alpha \) is the charge transfer coefficient, \( k_0 \) the heterogeneous rate constant, \( C_0 \) and \( C_R \) the concentrations of O and R respectively and \( z, R, T, F \) have their usual significance.

Equation 2.16 was verified by Horiuti and Polanyi\textsuperscript{95} using a quantum mechanical treatment. Marcus\textsuperscript{96} has shown that the charge transfer coefficient is a function of several terms which are dependent on potential, however, if the effects due to the double layer are small and the potential is not too far removed from the equilibrium potential (+250mV) \( \alpha \) becomes independent of potential.

Double layer effects can be reduced by carrying out the experiments in the presence of an excess concentration of supporting electrolyte.

For low overpotentials \( (\eta_D < 7 \text{ mV}) \) the current - overpotential curve reduces to a linear relationship which on differentiation gives:

\[ -\left( \frac{di}{d\eta_D} \right)_{\eta_D \to 0} = \frac{zF}{RT} \cdot i_0 \]  

(2.18)

Since the above current density - overpotential quotient is constant, its reciprocal, termed the polarisation resistance, is directly analogous to a simple electronic resis-
tance and can be treated as such. Thus the charge transfer resistance, \( R_D \), is given by:

\[
R_D = \frac{RT}{zF} \cdot \frac{1}{T_0}
\]  

From equation 2.17

\[
\ln i_0 = \ln zFk_0 + (1-\alpha) \ln C_0 + \alpha \ln C_R
\]  

and hence maintaining one of the components, \( C_0 \) or \( R \), constant whilst varying the other will lead to a linear plot of \( \ln i_0 \) versus \( \ln C \) from the slope of which \( \alpha \) may be extracted.

Thus:

\[
\left( \frac{8\ln i_0}{8\ln C_R} \right)_{C_0, \mu, T} = \alpha
\]  

\[
\left( \frac{8\ln i_0}{8\ln C_0} \right)_{C_R, \mu, T} = (1-\alpha)
\]

At higher overpotentials (\( \eta_D > 50 \text{ mV} \)) the rate of the reaction opposed by the overpotential is reduced to negligible proportions and the second term in equation 2.16 can be ignored, hence for cathodic overpotentials:

\[
i = i_0 \exp \left( -\frac{\alpha zF}{RT} \eta_D \right)
\]  

and

\[
\ln i = \ln i_0 - \frac{\alpha zF}{RT} \eta_D
\]
Rearranging equation 2.24 gives:

\[ \eta_{D} = \frac{RT}{a z F} \ln i - \frac{RT}{a z F} \ln 1 \] (2.15)

i.e. \[ \eta_{D} = a - b \log_{10} i \] (2.26)

Equation 2.25 is termed the Tafel equation. For a cathodic process:

\[ a = 2.303 \frac{RT}{a z F} \log_{10} i_{o} \] (2.27)

\[ b = 2.303 \frac{RT}{a z F} \] (2.28)

For an anodic process - (1 - a) replaces a

The possibility that the exchange reaction mechanism may change as the over-potential increases also exists. Gerischer and Mehl and Bockris found that the deposition of Ag from AgClO₄ is controlled by surface diffusion at or near the reaction equilibrium potential but that at high overpotentials charge transfer becomes rate determining.

At solid metal electrodes several factors favour such a process change as over-potentials increase:

(a) the fraction of the active growth sites may increase with increasing potential resulting in a decrease in the effective distance through which adspecies have to migrate; the rate of surface diffusion increases and thus decreases the tendency for rate control by surface diffusion.

(b) at high cathodic overpotentials the rate of the anodic process decreases and the time spent on the surface, after charge transfer, by a reduced species and the probability of that species reaching an atomic step and being incorporated at a growth site increases. The result of this is to increase the rate constant for surface diffusion which ceases to be rate controlling.
The participation of adspecies in the rate controlling step can be precluded if the \( \eta_D - i \) data obeys the charge transfer equations over the whole potential range.

There also exists possible changes in charge transfer mechanism with increasing overpotential. The probability of electrons exchanging in pairs has attracted considerable attention. Conway and Bockris showed that the heat of activation for a simultaneous two electron transfer exceeds 400 kJ mol\(^{-1}\), resulting in an exceedingly small rate constant. It seems more probable that charge transfer reactions occur as two consecutive single electron transfers over the whole potential region but with the time interval and activation energy difference between the electron transfers becoming greater as the overpotential increases. Consequently, due to limitations in the experimental procedure, it may only be possible to distinguish between the two charge transfer steps at high overpotentials.

The theory for consecutive electron transfer reactions is well established and has been verified experimentally. The reaction mechanism for a two electron transfer between O and R involving two consecutive single electron transfer steps and an intermediate S can be represented as follows:

\[
\begin{align*}
(a) & \quad O + e & = S \\
(b) & \quad S + e & = R
\end{align*}
\]

Each step has its own characteristic apparent exchange current (\( i_{oa} \) and \( i_{ob} \)) and transfer coefficient (\( \alpha_a \) and \( \alpha_b \)). The exchange currents can be defined in terms of concentration of electroactive species and corresponding standard rate constants, \( k^o \):

\[
\begin{align*}
i_{oa} &= F k^o_a C_o^{1-\alpha_a} C_s^{\alpha_a} \\
i_{ob} &= F k^o_b C_s^{1-\alpha_b} C_R^{\alpha_b}
\end{align*}
\]
By writing for each step a charge transfer equation (equation 2.16) and eliminating terms connected with the concentration of the intermediate species, Vetter\textsuperscript{92} obtained the expression:

\[
\frac{1}{2} = \frac{\exp(-\left(\alpha_a + \alpha_b\right)\frac{F\eta_D}{RT} - \exp(2 - \alpha_a - \alpha_b)\frac{F\eta_D}{RT})}{\frac{1}{i_{oa}}\exp(1-\alpha_a)\frac{F\eta_D}{RT} + \frac{1}{i_{ob}}\exp(-\alpha_b)\frac{F\eta_D}{RT}}
\]

(2.33)

At high overpotentials this equation gives plots of $\eta_D$ vs ln $i$ (Tafel plots) having a slope of $-\left(\frac{\alpha}{F/RT}\right)$ and $\left((1-\alpha)\frac{F}{RT}\right)$ for the cathodic and anodic branches respectively. The corresponding rectilinear parts of these curves intercept the $\eta_D = 0$ axis at $2i_{oa}$ and $2i_{ob}$. Current - overpotential characteristics corresponding to equation 2.33 have been computed by Hurd\textsuperscript{102} for a number of $i_{oa}/i_{ob}$ ratios. It was confirmed that the curves passes through the origin ($\eta_D = 0$, $i = 0$) with the slope predicted by:

\[
-\left(\frac{\partial \eta_D}{\partial i}\right)_{\eta_D = 0} = \frac{RT}{F} \frac{1}{i_{oa}} + \frac{1}{i_{ob}}
\]

(2.34)

which can be obtained by differentiating equation 2.33 with respect to $i$ and setting $\eta_D = 0$. Vetter and Thiemke\textsuperscript{104} calculated $i_{oa}$ and $i_{ob}$ for the Tl(III)/Tl(I) reaction from the intercepts of the cathodic and anodic branches of the Tafel curves and showed that the slope calculated from equation 2.34 agreed with that observed at $\eta_D = 0$. This evidence confirmed the view that the Tl(III)/Tl(I) exchange involves two consecutive one electron transfer steps within the potential range investigated.

For the case of a two electron transfer involving consecutive single electron steps in which one step is slow and rate determining, Lovrecek\textsuperscript{105} has shown that the slopes of the cathodic and anodic branches of the linear - logarithmic regions are given by:

(20)
\[
\frac{\partial \ln i_c}{\partial \eta_D} = -\frac{F}{R T} \left( n_c - 1 + a_i \right) \tag{2.35}
\]

and

\[
\frac{\partial \ln i_A}{\partial \eta_D} = \frac{F}{R T} \left( n_A - a_i \right) \tag{2.36}
\]

where \( n_c \) (and \( n_A \)) is the ordinal number of the slowest step in a multistep cathodic (or anodic) reaction, and \( a_i \) is \( a_a \) or \( a_b \) (equation 2.29 and 2.30). For the two step mechanism, if \( n_c = 1 \) then \( a_i = a_a \) and if \( n_c = 2 \), \( a_i = a_b \). Similarly when \( n_A = 1 \), \( a_i = a_b \) and when \( n_A = 2 \), \( a_i = a_a \). Equation 2.35 and 2.36 are derived more fully in appendix 2.

Expressions equivalent to equation 2.35 and 2.36 can be obtained from equation 2.33 by putting either \( i_{oa} \) or \( i_{ob} \) respectively equal to infinity. This has the effect of ensuring that the other reaction, for which \( i_o \) is finite, controls the reaction (e.g. considering equation 2.29 and 2.30 for \( i_{oa} = \infty \), \( i_{ob} \) is finite and reaction 2.30 controls). Four values (two cathodic and two anodic) are obtained corresponding to \( n_c = 1 \) or 2, and \( n_A = 1 \) or 2 using the appropriate value of the transfer coefficient in each case.

Determination of the reaction order by observing the dependence of the rate of reaction on the concentration of the reaction components is well established. This method has not been applied to studies of electrode reactions to any great extent, with the exception of the work by Vetter, Gerischer, and their collaborators, who have used the method exclusively to elucidate electrochemical reactions at mercury and amalgam electrodes. The basis of this method is that at sufficiently high cathodic overpotentials the cathodic current flowing at a fixed potential is a function of the concentration of those electroactive species directly involved in the cathodic reaction.
versely, at high anodic overpotentials the anodic current is a function of the concentration of reduced species. For comparison of these reaction rates (current densities), potentials must be referred to some standard and in this work the reference potential chosen is that corresponding to arbitrarily selected solutions of fixed composition.

The above reasoning is only applicable if either the anodic or cathodic exchange reactions can be suppressed by application of high overpotentials. In some cases such overpotential measurements are not feasible but reaction orders may still be deduced from the dependence of the exchange current on the concentration ion using equations of the type equation 2.31 and 2.32.

2.4. Faradaic Impedance

The theory of faradaic impedance was developed by Randles\textsuperscript{106}, Gerischer\textsuperscript{107} and Grahame\textsuperscript{108} and first used by Dolin and Ershler\textsuperscript{109} for the determination of the rate of ionization of hydrogen at platinum electrodes.

The basis of the method is to represent the ac impedance of the electrode as a model impedance network. The components of the network may or may not exist independently of the network, e.g. frequency dependent resistors and capacitors and negative resistance\textsuperscript{110}. The electrode is subjected to a low amplitude (7 mV peak to peak) sinusoidal voltage and, for the general reaction equation 2.15 when controlled by charge transfer and diffusion in solution, Randles\textsuperscript{106} proposed the equivalent circuit shown in figure 2.2., where $R_E$ is the electrolyte ohmic resistance, $C_L$ the double layer capacitance which varies with the dc voltage depending on the concentration and nature of the electrolyte. $R_D$ is the charge transfer resistance and is related to the exchange current density by equation 2.19. The Warburg impedance, $W$, (due to diffusion or mass transfer) in the abbreviated form, can be represented by:

$$W = a \omega^{-\frac{1}{2}} (1-j)$$

(2.37)

(22)
Fig 2.2 Electrical analogue of the electrode interphase for the case of charge transfer and diffusion control.

\[ \begin{align*}
R_e & \\
C_\alpha & \\
R_p &
\end{align*} \]

Fig 2.3 Theoretical impedance curves for the case of charge transfer and diffusion control.
where $\sigma$ is the Warburg coefficient, $\omega$ the angular frequency and $j = \sqrt{-1}$. The Warburg coefficient can be expressed as:

$$\sigma = \frac{RT}{z^2F^2\sqrt{2}} \sum \left[ \frac{1}{C_i \sqrt{D_i}} \right]$$  \hspace{1cm} (2.38)

where $C_i$ is the surface concentration of the $i$th species and $D_i$ is the diffusion coefficient.

The faradaic impedance due to the electrode reaction is itself a combination of capacitance and resistance terms corresponding to various reaction steps. For a reaction consisting of only charge transfer and diffusion processes, it has been shown that:

$$R = \frac{RT}{z^2F^2AC} \left[ \sqrt{\frac{2}{\omega D} + \frac{1}{k_c}} \right]$$  \hspace{1cm} (2.39)

$$C_r = \frac{z^2F^2AC}{RT} \left[ \frac{\sqrt{D^2}}{\sqrt{2}\omega} \frac{1}{\sqrt{z^2}} \right]$$  \hspace{1cm} (2.40)

where $A$ is the electrode area, $R_r$ and $1/\omega C_r$ are the equivalent resistance and reactance respectively, and $C$ and $D$ the geometric means of the concentrations and diffusion coefficient respectively. Thus a plot of $R_r$ and $1/\omega C_r$ versus $\omega^{-1}$ should be linear; the latter passing through the origin whilst the $R_r$ line intercepts the $R$ axis for $\omega = 0$ at:

$$R = \frac{1}{\omega C} = \frac{RT}{z^2FAC} \cdot \frac{1}{k_c}$$  \hspace{1cm} (2.41)

Laitenen and Randles have shown how the impedance due to the faradaic reaction ($C_r$ and $R_r$) can be obtained by successive series to parallel and parallel to series circuit transformations (appendix 3). The elucidation of these parallel-series transformations (23).
ations requires known values of the double layer capacitance and the electrolyte resistance. In general these parameters are not known for solid metals or oxide electrodes and the circuit transformations are performed with the use of a computer program using selected values of $C_L$ and $R_E$ until the requisite parallel plots of $R_f$ and $1/\omega C_r$ are obtained.

2.5. **Linear Sweep Voltammetry (L.S.V.)**

The principle of L.S.V. is the application of a potential, varying linearly with time, on the working electrode. As the potential increases the substance reacting at the electrode is progressively removed in the vicinity of the electrode causing current limitations. As this limitation becomes more severe, the current potential curve develops a maximum the magnitude of which is proportional to the concentration of the species controlling the current flow at the electrode.

In discussing this technique it is necessary to distinguish between single sweep and multi-sweep methods. In single sweep methods the current - potential profile is recorded once and the system then allowed to return to its original state. In multi-sweep methods the current - potential profile is continuously recorded. In the latter method, boundary value problems and the concentration distribution of the reacting species may vary markedly from those of the former case.

For the reversible formation of an insoluble substance by a cathodic reaction Berzins and Delahay $^{112}$, assuming linear diffusion, applied the general theory of Randles $^{113}$ and Sevcik $^{114}$ and obtained the relationship:

$$I = -\left[\frac{2}{\pi \lambda}\right] \left[\frac{x^{3/2}}{R^2} \frac{1}{\lambda^{3/2}}\right] A \cdot D^{1/2} \cdot C \cdot x^{1/2} \cdot \Phi (\lambda)$$  \hspace{1cm} (2.42)

where

$$\Phi = \exp \left(-\lambda^2\right) \int_0^\lambda \exp (p^2) \, dp$$  \hspace{1cm} (2.43)
\[ \lambda = \left( \frac{zFvT}{RT} \right)^{\frac{1}{2}} = -\left[ \frac{zF (E-E_f)}{RT} \right]^{\frac{1}{2}} \]  (2.44)

\( I \) is the peak current density, \( v \) the potential sweep rate, \( E \) the potential of the system at a particular point in time, \( E_i \) the initial potential of the potential sweep, \( C \) the species bulk concentration and \( D \) the diffusion coefficient. When \( \theta(\lambda) \) passes through a maximum the current density, \( I \), shows a maximum, \( I_m \), which at \( 25^\circ C \) is given by: \( 112,115 \)

\[ I_m = 3.67 \times 10^5 \cdot z \cdot D^{\frac{1}{2}} \cdot C \cdot v^{\frac{1}{2}} \]  (2.45)

Similar equations can be deduced for the anodic reaction. The theory assumes reversibility of the system and that the activity of the insoluble product is unity. Hence equation 2.45 only holds for solid electrode metal ion systems where only diffusion overpotential is present. Quantitatively, use of equation 2.45 is complicated by uncertainties concerning the true concentration of the reacting species at the electrode and the diffusion coefficient of the species controlling the current flow.

For the reversible formation of a soluble product at the electrode the peak current is given by: \( 112,115 \)

\[ I_m = 0.452 \frac{z^2}{R^2} \cdot A \cdot D^{\frac{1}{2}} \cdot C \cdot v^{\frac{1}{2}} \]  (2.46)

or at \( 25^\circ C \): \( 115 \)

\[ I_m = 2.72 \times 10^5 \cdot z^2 \cdot A \cdot D^{\frac{1}{2}} \cdot C \cdot v^{\frac{1}{2}} \]  (2.47)

For totally irreversible electrode processes Delahay \( 116 \), using a method developed by Wagner \( 117 \), obtained the expression for the peak current: \( 25 \)
\[ I_m = \frac{1}{2} z \cdot F \cdot A \cdot \beta^2 \cdot D^{\frac{1}{2}} \cdot C \cdot x \cdot (\beta t) \tag{2.48} \]

where \( x (\beta t) \) is a variable function and

\[ \beta = \frac{\alpha z F \cdot v}{RT} \]

At 25°C:

\[ I_m = 3.01 \times 10^{-5} \cdot z \cdot (\alpha z_a)^{\frac{1}{2}} \cdot A \cdot D^{\frac{1}{2}} \cdot C \cdot v^{\frac{1}{2}} \tag{2.49} \]

where \( z_a \) is the number of electrons involved in the rate determining step.

The expressions for \( I_m \) of a reversible and irreversible process differ in that the peak current for an irreversible process is proportional to the product \( z \cdot (\alpha z_a)^{\frac{1}{2}} \) instead of \( z^{\frac{3}{2}} \) as in the case of a reversible process. Since \( \alpha \) is smaller than unity and \( z_a \) is generally smaller than \( z \), peak currents for irreversible processes are smaller than the values one would expect in the case of reversibility.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Electrolytes Solution

All electrolyte solutions were prepared from A.R. grade chemicals and water twice distilled from deionised stock. Analysis of solutions, (appendix 3), was carried out before and after experimental runs. All glassware was thoroughly cleaned by standing in a mixture of concentrated nitric and sulphuric acid (50:50) for one week to remove impurities, then thoroughly washed in bidistilled water, soaked in bidistilled water for 24 hrs and finally dried in an oven at 120°C. At all times care was taken to handle surfaces that would be in contact with electrolyte solutions with clean paper tissues.

Continuous purification of the electrolyte solutions over specially prepared activated charcoal (appendix 3) using a nitrogen pump (white spot N₂ passed over heated copper to complete deoxygenation and humidified by passage through a water trap) was employed. The electrolyte purity was judged by the stability of the ac impedance of a sitting mercury drop. In general, at least 5 weeks circulation was considered necessary to achieve a satisfactory level of purity.

3.2. Test Electrodes

PbO₂ electrodes were prepared by electrodeposition of a layer of the required polymorph onto an etched (50:50 concentrated nitric:sulphuric acid mixture) platinum mount. The electrode mount was the cross section of a platinum rod (geometric area $4.9 \times 10^{-2} \text{ cm}^2$) sealed into a lead free (lead glasses deteriorate in perchlorate solutions) soda glass sleeve. The end of the mount was cut square, polished with emery paper and diamond powder until microscopic examination of the platinum-glass seal
showed no microcracks and the platinum surface no scratches.

α-PbO$_2$ was deposited by electroperoxidation of alkaline sodium plumbite solution 119 (2 mol $1^{-1}$ NaOH saturated with PbO) at 0.8 mA cm$^{-2}$ and 25°C using a lead cathode and the platinum mount as the anode. β-PbO$_2$ was deposited by electroperoxidation of lead perchlorate solution 120 (2.25 mol $1^{-1}$) at a rate of 1 mA cm$^{-2}$ and 25°C. Comparative x-ray diffraction measurements, using a Phillips diffractometer (type P.W. 1051), were made in order to establish the freedom of each deposit from the unrequired polymorph.

3.3. Electrolytic Cells

All cells were made from borosilicate glass and cell fittings were lubrication free ground glass joints. The cell used for impedance studies is shown in figure 3.1. The counter electrode was of large area platinum gauze and the reference electrode a saturated calomel electrode (wick type). The test electrode was as described above. The cell used in the galvanostatic studies is shown in figure 3.2. The test, counter, and reference electrodes were of identical material with the counter electrode having a geometric area of ~2 cm$^2$. For the L.S.V. studies the cell is shown in figure 3.3. The test and counter electrodes were of identical material and the reference electrode was a saturated calomel electrode (wick type).

3.4. Electrical Circuits

The electrical circuit used in the impedance studies is shown in figure 3.4. A modified Schering-bridge 121,122 was used to match the interphase as a series combination of resistance and capacitance. For zero out of balance current:

$$\frac{Z_1}{Z_{cell}} = \frac{Z_2}{Z_4}$$  \hspace{1cm} (3.1)
Fig. 3.1.

Cell for faradaic impedance studies

A - Reference electrode compartment
B - Test electrode compartment
C - Counter electrode compartment
D - Purification limb
E - Glass frits
Cell used for galvanostatic studies

A - Purification limb
B - Glass frit
Fig. 3.3.

Cell used for linear sweep voltammetry studies

A - Test electrode compartment
B - Reference electrode compartment
C - Counter electrode compartment
D - Luggin capillary
Fig 3.4 Electrical circuit for impedance measurements

\[ C_{xs} = \frac{C_4 R_3}{R_1} \quad : \quad R_{xs} = \frac{R_4 C_2}{C_4} \]
The a.c. was applied to the bridge by an audio frequency generator (Advance type H1) via a screened 65:1 isolating transformer (Radio Spares 'Hygrade' mike transformer). The amplitude of the a.c. was \( \sim 5 \text{ mV peak to peak} \). The out of balance signal was passed via a filter (Muirhead, type D-925-B), set to reject 50 Hz, to a tuned amplifier (General Radio type 1232A). The amplifier was continuously tunable in the frequency range 20 - 20 000 Hz. The dial accuracy was 3\% and the meter sensitivity 1 V F.S.D.

The bridge was polarized symmetrically and during all experiments the test electrode was connected to earth in order to avoid screening difficulties. Ac and dc were separated by a 40 Hz choke. Potential measurements were made using an electrometer (Keithly type 610B), the input impedance of which was effectively infinite (\( > 10^{12} \)).

Before any measurements were made the frequency response of the bridge was tested by measuring the impedance of a high stability resistance and a standard capacitance in series over a range of frequencies. The discrepancies between bridge readings and known values are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>30-500 Hz</th>
<th>500-1000 Hz</th>
<th>1-5k Hz</th>
<th>5-10k Hz</th>
<th>10-20k Hz</th>
<th>20k Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error ( % )</td>
<td>+ 1\°</td>
<td>+ 1</td>
<td>+ 2</td>
<td>+ 5</td>
<td>+ 9</td>
<td>( &gt; + 10 )</td>
</tr>
</tbody>
</table>

The bridge had a satisfactory response over the frequency range 30 Hz - 10 k Hz.

For galvanostatic measurements the circuit was as shown in Figure 3.5. The square wave current pulse was obtained from a pulse generator, (Solartron type g.O.1377) the output of which was of continuously variable amplitude to a maximum of 40 mA into 2500 \( \Omega \). It was necessary to introduce a load resistance into the circuit in order to reduce the output since microelectrodes were used. The current amplitude was calculated by measuring the potential developed across a standard resistance in the pulse circuit by an oscilloscope (Hewlett Packard type 130C). The potential response of the test
Fig 3.5. Electrical circuit for galvanostic technique.

C - Counter electrode
W - Working electrode
R - Reference electrode
S - Standard resistance
L - Load resistance
PG - Pulse generator
CRO - Cathode ray oscilloscope
electrode to the current pulse was measured between the test electrode and reference electrode by an oscilloscope fitted with a camera (Hewlett Packard type 1963). To minimize iR drop the electrolyte solution was kept at 3 mol $1^{-1}$ uni-univalent ionic strength with a carrier electrolyte. The rise time of the current pulse was $\sim 0.5\mu s$ and potential measurements could be made to an accuracy of $\pm 0.01\,mV$ in the range up to $2\,mV$, and $\pm 0.05\,mV$ in the range up to $10\,mV$. Current measurements were accurate to $\pm 3\%$.

L.S.V. studies were carried out using a linear sweep generator in conjunction with a potentiostat (Chemical Electronics Limited). The resulting current-potential curves were recorded by an X/Y recorder (Bryant Instruments). There was no parasitic interaction between the potentiostat and the chart recorder. Each experimental potential sweep was repeated several times and the average peak current and potential recorded. Reproducibility was $\pm 10\%$. 

(30)
CHAPTER 4

THE ELECTROCHEMICAL BEHAVIOUR OF PbO₂ IN NITRATE ELECTROLYTES

4.1. The Electrical Double Layer

Preparation of test electrodes and the experimental procedure were as described in Chapter 3.

Experimental Results

Figure 4.1. shows typical faradaic current - bias potential curves for HNO₃ solutions indicating experimental polarizable regions of \( \sim 1.47 - 1.97 \, \text{V} \) for \( \alpha-\text{PbO}_2 \) and \( \sim 1.47 - 2.03 \, \text{V} \) for \( \beta-\text{PbO}_2 \). Neither polymorph was ideally polarizable, the experimental polarizable limits being governed by oxygen evolution at the positive extremity and lattice dissolution at the negative limit. The potential of zero faradaic current flow was \( \sim 1.63 \, \text{V} \) for \( \alpha-\text{PbO}_2 \) and \( \sim 1.67 \, \text{V} \) for \( \beta-\text{PbO}_2 \).

Figures 4.2. and 4.3. show differential capacitance - bias potential curves for \( \alpha-\text{PbO}_2 \) and \( \beta-\text{PbO}_2 \) respectively. For potentials within the polarizable region stable impedance readings were obtained within 5 hrs of electrode/electrolyte contact time for \( \alpha-\text{PbO}_2 \) and 4 hrs for \( \beta-\text{PbO}_2 \). Hysteresis of the impedance measurements was small for potential excursions within the polarizable region. Potential excursions outside these limits caused serious irreversible changes at the electrode and impedance readings never returned to their original values. Replicate impedance measurements indicated a 10% variation about a mean.

Figures 4.4. and 4.5. show typical frequency dispersion of the capacitance curves which amounted to \( \sim 30\% \) for a frequency change 120 Hz - 500 Hz.

Figure 4.6. shows typical faradaic current - bias potential curves for KNO₃ solutions indicating experimental polarizable regions of \( \sim 0.65 - 2.00 \, \text{V} \) for \( \alpha-\text{PbO}_2 \).

(31)
Fig 4.1. Faradaic current-bias potential curves for 

$\text{PbO}_2$ in $\text{HNO}_3$ electrolyte.
Fig 4.2 Differential capacitance-bias potential curves for \( \alpha - \text{PbO}_2 \) in HNO\(_3\) electrolyte.
Fig 4.3 Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in HNO$_3$ electrolyte.
Fig 4.4 Typical frequency dispersion of differential capacitance-bias potential curves for $\alpha$-PbO$_2$ in HNO$_3$ electrolyte.

![Graph showing typical frequency dispersion of differential capacitance-bias potential curves for $\alpha$-PbO$_2$ in HNO$_3$ electrolyte.](image-url)
Fig 4.5 Typical frequency dispersion of differential capacitance-bias potential curves for $\beta$-PbO$_2$ in HNO$_3$ electrolyte.
Fig 4.6 Faradaic current - bias potential curve for PbO$_2$ in aqueous KNO$_3$ electrolyte
and ~ 0.65 - 1.95 V for β-PbO₂. Ideal polarizability was never observed; the extent of non-polarizability was similar to that observed for some solid metal electrodes (e.g., Cu). The potential of zero faradaic current flow was 1.12 V for α-PbO₂ and 1.17 V for β-PbO₂. Potential excursions outside the experimental polarizable region were subject to hysteresis of the impedance measurements, particularly at the positive limit where oxygen evolution eventually occurred.

Figures 4.7 and 4.8 show differential capacitance - bias potential curves for α and β-PbO₂ respectively. Stable impedance measurements were obtained after 1 hr. electrode/electrolyte contact time. Readings taken at very short contact times showed a certain amount of variation but once stability had been reached the system remained stable for at least 24 hrs. Replicate impedance measurements showed a 7% variation about a mean.

Figures 4.9 and 4.10 show typical frequency dispersion of the capacitance curves which amounted to ~ 15 - 20% for a frequency change 120 Hz - 500 Hz.

Discussion of Differential Capacitance Results

The capacitance values obtained in HNO₃ solutions were significantly larger than those observed in KNO₃ solutions. The shape of the capacitance curves for HNO₃ solutions, particularly the absence of a clearly defined minimum developing with dilution, suggests that adsorption complicates the electrode. In KNO₃ the differential capacitance curves for β-PbO₂ were much flatter than the corresponding curves for α-PbO₂. For α-PbO₂ a well-defined 'hump' in the capacitance curve is observed at ~ 1.5 V which progressed into a distinct minimum at 1.06 ± 0.01 V with electrolyte dilution. The curves resemble, in shape, those for Hg in NaF solutions. For β-PbO₂ the capacitance minimum was less well defined at 1.15 ± 0.01 V. The potential of the capacitance minimum was independent of dilution for both polymorphs.

In both HNO₃ and KNO₃ solutions the frequency dispersion of the differential
Fig 4.7 Differential capacitance-bias potential curve for $\alpha$-PbO$_2$ in KNO$_3$ electrolyte
Fig. 4.8 Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in KNO$_3$ electrolyte
Fig 4.9 Typical frequency dispersion of differential capacitance-bias potential curves for α-PbO₂ in KNO₃ electrolyte.

Electrolyte 0.307 mol l⁻¹

- 120 Hz
- 500 Hz
- 1000 Hz
- 10 KHz
capacitance seemed to be an inherent property of both α- and β-PbO₂ electrodes and is of considerable significance. Since PbO₂ electrodes are nowhere ideally polarizable it follows that the impedance measurements are made with a.c. imposed on d.c. which in itself can give rise to a frequency dispersion. The extent of the faradaic current flow is, however, too small to fully account for the observed dispersion and other possible causes must be considered. In the case of solid metal electrode systems, several models have been proposed in an attempt to explain frequency dispersion. Armstrong et al.¹²³ suggested that for solid copper electrodes a pseudo-capacitance, associated with an adsorption/desorption process at the electrode, was the cause of a certain amount of the observed dispersion. McMullen and Hackerman¹²⁵ suggested that it was caused by the presence of small amounts of impurities on the electrode surface; the stringent purification procedure employed in the present experiments would minimize such effects. Bockris and Conway¹²⁶ proposed that, due to strong adsorption forces, the water molecules in the inner Helmholtz layer are unable to follow the applied electrical field resulting in a frequency dispersion of capacitance. Frumkin¹²⁷ associated frequency dispersion with irregularities and cracks in the electrode surface creating paths of different resistance for different areas of the electrode which have different time constants resulting in a frequency dispersion of the capacitance. Ramaley and Enke¹²⁸ and Tsa and Jofa¹²⁹ proposed a similar model to that of Frumkin¹²⁷ suggesting that different areas of the electrode have slightly different capacitances such that the electrode analogue becomes a parallel network of series resistance-capacitance units. Dolin¹³⁰ suggests that high surface heterogeneity would cause limited adsorption of H⁺ and OH⁻ on different areas giving rise to a frequency dependent capacitance. For the present measurements it is not considered that defects in the electrode construction are a major cause of dispersion since microscopic examination of the electrode indicated no crevicing.
It seems most probable that for PbO₂ electrodes the frequency dispersion may be associated with surface roughness in the sense of De Levie. The electrochemical response of a "rough" electrode differs from that of an ideally "smooth" one due to the finite solution resistance and/or finite diffusion resistance, both of which favour the flow of current to protruding parts of the electrode in preference to recessed parts. Such effects lead to a frequency dispersion of the capacitance. There is ample evidence to show that the electrodeposition of PbO₂ produces a surface of considerable roughness and such effects would readily account for the magnitude of the dispersion.

The time stability of the impedance data for both α and β-PbO₂ in KNO₃ solutions indicated little or no development of the electrode surface with electrode/electrolyte contact time. In this respect the system differed from the behaviour in HNO₃ solutions where an initial increase in the capacitance with time indicated some surface modification as observed by Kabanov.

For KNO₃ solutions the capacitance curves, figures 4.7 and 4.8, can be integrated to give the surface charge on the electrode as a function of the electrode potential since, from the definition of the differential capacitance:

$$q = \int_{E_z}^{E} C \cdot dE + \text{const.} \quad (4.1)$$

where $E$ is an arbitrary potential and $E_z$ the pzc. The integration supposes that the value of the surface charge is accurately known at a particular potential so that the constant of integration can be ascertained. In the present case this constant cannot be fixed by separate experiment; it is assumed that the potential of the capacitance minimum in the most dilute solutions represents the pzc and since $q > 0$ for $E > E_z$, the capacitance curves were integrated from this point, i.e. from 1.06 V for α-PbO₂ and 1.15 V for β-PbO₂. The results of such an integration are shown in figures 4.11 and 4.12, for α- and β-PbO₂ respectively. Comparison of these curves with similar curves for Hg
Fig 4.11. Charge-rational potential curves for $\alpha$-PbO$_2$ in KNO$_3$ electrolyte.
Figure 4.12: Charge-rational potential curves for $\beta$-PbO$_2$ in KNO$_3$ electrolyte.

**ELECTROLYTE CONC.**
- 0.307 mol$^{-1}$
- 0.115 mol$^{-1}$
- 0.0179 mol$^{-1}$
- 0.0121 mol$^{-1}$
- 0.00435 mol$^{-1}$

Charge($q$) / $\mu$C cm$^{-2}$

$(E - E_*) / V$
in non-interacting electrolytes\textsuperscript{124} show that if a roughness factor of 5-10 is assumed for the \( \text{PbO}_2 \) electrode surfaces then the form of the curves is similar.

The effect of concentration changes on the differential capacitance follows from the Gibbs adsorption isotherm which for solutions of simple electrolytes at constant temperature and pressure can be expressed as:

\[
- d\gamma = q \frac{dE_\pm}{F} + \Gamma_\pm \frac{d\mu}{F} \tag{4.2.}
\]

where \( \gamma \) is the interfacial tension, \( q \) the surface charge, \( \mu \) the chemical potential of the electrolyte, \( \Gamma_\pm \) the surface excess of the anion or cation and \( E_\pm \) is the potential of the electrode in combination with a reference electrode reversible to the cation \( (E_+) \) or anion \( (E_-) \).

Since equation 4.2. is a complete differential it follows that:

\[
\left( \frac{\delta E_+/\delta \mu}{\Gamma_+} \right)_q = - \left( \frac{\delta \Gamma_+/\delta q}{\Gamma_+} \right)_\mu \tag{4.3}
\]

It is convenient to write equation 4.3. in terms of the charge in the solution due to anions and cations, \( q_\pm \), and since:

\[
\Gamma_\pm = \left( \frac{q_\pm}{z_\pm F} \right) \tag{4.4}
\]

and

\[
d\mu = RT \, \delta \ln a_s \tag{4.5}
\]

where \( a_s \) is the activity of the electrolyte, it follows that:

\[
\left( \frac{\delta E_+/\delta \ln a_s}{\Gamma_+} \right)_q = \frac{RT}{z_+ F} \left( \frac{\partial q_+/\partial q}{a_s} \right) \tag{4.6}
\]

in which \( a_s \) is equated to \( a_+ \) for a binary electrolyte. The potential, \( E_R' \), of a cell in
which the test electrode is combined with a reference electrode of constant electrolyte activity and constant junction potential, can be written as:

\[ E_R = E_+ \pm \frac{RT}{2F} \ln a_+ \pm \text{const.} \quad (4.7) \]

Combining equation 4.5. and 4.7. for the condition when \( q = 0 \) and for a 1:1 electrolyte:

\[ \left( \frac{\partial E_R}{\partial \ln a^2} \right)_q = \pm \frac{RT}{F} \left[ \left( \frac{\partial a_+}{\partial q} \right)_{a_+} + \frac{1}{2} \right] \quad (4.8) \]

In the absence of specific adsorption limiting values of \( \left( \frac{\partial a_+}{\partial q} \right)_{a_+} \) and \( \left( \frac{\partial a_-}{\partial q} \right)_{a_-} \) follow from the Gouy-Chapman theory \(^{63,64}\):

<table>
<thead>
<tr>
<th>Charge</th>
<th>( \left( \frac{\partial a_+}{\partial q} \right)<em>{a</em>+} )</th>
<th>( \left( \frac{\partial a_-}{\partial q} \right)<em>{a</em>-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>High positive charge</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>Zero charge</td>
<td>-1/2</td>
<td>-1/2</td>
</tr>
<tr>
<td>High negative charge</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Values of \( \left( \frac{\partial E_R}{\partial \ln a^2} \right)_q \) at high positive, zero and high negative charge are then 1, 0 and -1 respectively.

Figures 4.13. and 4.14. show plots of potential, referred to \( E_z \), as a function of activity at constant charge, and verify that the above limiting values of 

\[ \left( \frac{\partial E_R - RT}{F \ln a^2} \right)_q \]

obtain (approximately) for the present experimental results. Some divergence from the behaviour observed in the case of mercury and expected from the Gouy-Chapman theory \(^{63,64}\) is apparent. In particular the magnitude of charge corresponding to particular slopes of the \( E_R \) - log \( a \) lines are much less than the presently measured surface charge densities.

(36)
Fig 4.13. Rational potential as a function of activity at constant charge for $\alpha$-PbO$_2$ in KNO$_3$ electrolyte.
Fig. 4.14. Rational potential as a function of activity at constant charge for $\beta$-PbO$_2$ in KNO$_3$ electrolyte.

Charge ($q$) expressed as $\mu$C cm$^{-2}$.
This apparently arises since the Gouy-Chapman treatment was for a smooth uniform electrode whereas the PbO₂ electrode is fairly "rough". At the higher electrode charge densities the magnitudes of the slopes increase. Delahay¹³² has pointed out that even for the Hg electrode at high charge densities, deviations occur due to defects in the Gouy-Chapman theory and because the contribution of the diffuse layer is relatively minor at higher charges. The symmetry of the family of curves, figures 4.13. and 4.14, and the satisfactory slopes of the E-log a lines at potentials not too far removed from the proposed $E_Z$ support the choice of the pzc.

For the case of HNO₃ solutions it is evident from the form of the capacitance curves, figures 4.2. and 4.3., that adsorption from solution occurs for potentials within the experimental polarizable region. It can be concluded from the results for KNO₃ solutions that the adsorption of the NO₃⁻ is unlikely, however, the presence of the H⁺ ion obviously influences the adsorption process. For HNO₃ solutions the direct adsorption of the H⁺ ion is unlikely because of the positive rational potential of the experimental polarizable region; adsorption of HNO₃ molecules is a possibility. The adsorption of molecules in preference to ions has been observed by other workers for some similar systems, as discussed in Chapter 2.2. Consequently it is proposed that for PbO₂ electrodes in HNO₃ solutions adsorption of HNO₃ molecules occurs at the electrode surface.

### 4.2. The Exchange Reaction

The galvanostatic experimental procedure was as described in Chapter 3. Measurements were only made at low overpotentials ($\eta_D < 7$ mV) in order to study the PbO₂/Pb(II) exchange reaction at potentials close to the equilibrium potential of the system. Electrolytes were maintained at 3 mol $1^{-1}$ equivalent univalent salt concentration with added KNO₃. Experiments were commenced after 15 min. electrode/electrolyte
contact time. Results were reproducible to ± 5%. The ohmic overpotential was generally < 5% of $\eta_D$. Two series of experiments were performed. In one series $[\text{Pb(II)}]$ was varied at constant $[\text{H}^+]$ and in the second series $[\text{H}^+]$ varied at constant $[\text{Pb(II)}]$.

**Experimental Results**

Figure 4.15. shows a typical overpotential - time transient for $\alpha$-PbO$_2$ in nitrate electrolyte solutions. The transient shows an initial steep rise, due to the double layer charging process, followed by a steadily increasing linear region from which $\eta_D$ results by extrapolation to zero time. Figures 4.16. and 4.17. show typical faradaic current - overpotential data for $\alpha$ and $\beta$-PbO$_2$ respectively, in electrolytes of varying $[\text{Pb(II)}]$ and constant $[\text{H}^+]$. Complementary curves for electrolytes of varying $[\text{H}^+]$ at constant $[\text{Pb(II)}]$ were also obtained and were of similar form to those shown in figures 4.16. and 4.17. The exchange current density for both anodic and cathodic processes, calculated from the slope of the $i - \eta_D$ curves at the origin using equation 2.18., were identical. Figures 4.18. and 4.19. show the variation of the exchange current with $[\text{Pb(II)}]$ for $\alpha$ and $\beta$-PbO$_2$ respectively and figures 4.20 and 4.21. complementary plots for $[\text{H}^+]$.

Figures 4.22. and 4.23. show the effect of temperature on the exchange current, in the form of Arrhenius plots.

**Discussion of Galvanostatic Results**

The magnitude of the exchange current, $i_o \approx 10^{-1}$ mA cm$^{-2}$, confirms that the reaction is slow and therefore concentration polarization is relatively small during the time of each experimental pulse (70 ms). Linear extrapolation of the $\eta - t$ curves to zero time, in order to separate $\eta_D$, is therefore justified. In the work of Jones et al. a reaction mechanism for the PbO$_2$/Pb(II) exchange, in acid solution,
Fig. 4.15. Typical overpotential-time transient for PbO₂ in nitrate electrolyte

ELECTROLYTE: 3 mol\textsuperscript{-1} K\textsuperscript{+} (with added KNO₃)

\[
\begin{align*}
\text{[Pb(II)]} & \quad 0.031 \text{ mol}\textsuperscript{-1} \\
\text{[H\textsuperscript{+}]} & \quad 0.41 \text{ mol}\textsuperscript{-1}
\end{align*}
\]

CATHODIC PULSE CURRENT 0.05 mA cm\textsuperscript{-2}
ELECTRODE/ELECTROLYTE CONTACT TIME 20 mins
ELECTRODE AREA 4.9 x 10\textsuperscript{-3} cm\textsuperscript{2}
Fig 4.16. Faradaic current-overpotential curves for α-PbO₂ in nitrate electrolyte.

ELECTROLYTE: 0.41 mol⁻¹ Pb(II) 3 mol⁻¹ NO₃⁻ (WITH KNO₃)
- 0.052 mol⁻¹ Pb(II)
- 0.0079 mol⁻¹ Pb(II)
- 0.0055 mol⁻¹ Pb(II)
- 0.0013 mol⁻¹ Pb(II)
Fig 4.17. Faradaic current-overpotential curves for $\beta$PbO$_2$ in nitrate electrolyte

\[
\eta, \text{ mV} \quad \text{vs} \quad E
\]

ELECTROLYTE: 0.41 mol$^{-1}$ H$^+$

3 mol$^{-1}$NO$_3^-$ (WITH KNO$_3$)

- 0.052 mol$^{-1}$ Pb(II)
- 0.013 mol$^{-1}$ Pb(II)
- 0.0055 mol$^{-1}$ Pb(II)
- 0.0013 mol$^{-1}$ Pb(II)
Fig 4.18. Variation of exchange current with $[\text{Pb(II)}]$ for $\alpha$-PbO$_2$ in nitrate electrolyte

**ELECTROLYTE:** 0.41 mol$^{-1}$ H$^+$

3 mol$^{-1}$ NO$_3^-$ (WITH KNO$_3$)

Slope = $\frac{\delta \log_{10} I_o}{\delta \log_{10} [\text{Pb(II)}]} = 0.49$
Fig 4.19. Variation of exchange current with [Pb(II)] for β-PbO in nitrate electrolyte

Electrolyte: 0.41 mol/l H+ 3 mol/l NO₃⁻ (with KNO₃)

Slope = \frac{\delta \log j}{\delta \log [Pb(II)]} = 0.34
Fig 4.20 Variation of exchange current on $[H^+]$ for $\alpha$-PbO$_2$ in nitrate electrolyte

Electrolyte: 0.031 mol$^{-1}$ Pb(II)$^+$
3 mol$^{-1}$ NO$_3^-$ (WITH KNO$_3$)

Slope = $\frac{\delta \log i_e}{\delta \log [H^+] = 0.11}$

$\log_{10}(i_e/\text{mA cm}^{-2})$

$\log_{10}([H^+]/\text{moll}^{-1})$
Fig 4.21 Variation of exchange current with $[H^+]$
for $\beta$-PbO$_2$ in nitrate electrolyte

ELECTROLYTE: 0.031 mol$^{-1}$ Pb(II)
3 mol$^{-1}$ NO$_3^-$ (WITH KNO$_3$)

Slope $= \frac{\delta \log i}{\delta \log [H^+]} = 0.54$
Fig 4.22. Variation of exchange current with temperature for $\alpha$-PbO$_2$ in nitrate electrolyte.

Electrolyte:
- 0.031 mol l$^{-1}$ Pb(II)
- 0.17 mol l$^{-1}$ H$^+$
- 3 mol l$^{-1}$ NO$_3^-$ (WITH KNO$_3$)
Fig 4.23. Variation of exchange current with temperature for $\beta$-PbO$_2$ in nitrate electrolyte.

**ELECTROLYTE:**
- 0.031 mol$\cdot$l$^{-1}$ Pb(II)
- 0.17 mol$\cdot$l$^{-1}$ H$^+$
- 3 mol$\cdot$l$^{-1}$ NO$_3^-$ (WITH KN$O_3$)
was proposed. At low overpotentials, the exchange proceeds via a two step mechanism:

\[ \text{PbO}_2 + 2H^+ + 2e = \text{Pb(OH)}_2 \quad (4.9) \]

\[ \text{Pb(OH)}_2 + 2H^+ = \text{Pb(II)} + 2H_2O \quad (4.10) \]

where reaction 4.9 may occur as two consecutive single electron transfer steps. Using this mechanism to describe the present exchange process and applying the rate equation, equation 2.19, to reaction 4.9., assuming [PbO\textsubscript{2}] and [H\textsubscript{2}O] constant, gives:

\[ i_0 = zFk_4 [H^+]^{2(1-\alpha)} [\text{Pb(OH)}_2]^\alpha \quad (4.11) \]

Incorporating reaction 4.10:

\[ i_0 = zFk_4^1 [H^+]^{2(1-\alpha)} - 2\alpha \quad [\text{Pb(II)}]^\alpha \quad (4.12) \]

where \( k_4 \) is a constant.

Hence:

\[ \frac{8 \log_{10} i_0}{\alpha \log_{10} [H^+]} [\text{Pb(II)}], \mu, T \]

\[ \frac{8 \log_{10} i_0}{\alpha \log_{10} [\text{Pb(II)}]} [H^+], \mu, T \]

Table 4.1. summarizes the experimental exchange current dependencies on the concentration of electroactive species. Substituting these values into equation 4.13. and 4.14. for \( \beta \)-PbO\textsubscript{2} gives a value for the apparent charge transfer coefficient, \( \alpha \), of 0.35. Similarly, for \( \alpha \)-PbO\textsubscript{2}, the experimental exchange current dependencies shown

(39)
in Table 4.1. indicate a value of 0.5 for the apparent charge transfer coefficient.

**Table 4.1.**
Exchange current dependencies on concentration of electroactive species. Electrolyte total equivalent uni-univalent salt concentration 3 mol \(1^{-1}\) (with added KNO\(_3\)).

<table>
<thead>
<tr>
<th></th>
<th>(\beta)-PbO(_2)</th>
<th>(\alpha)-PbO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{\partial \log_{10} i_0}{\partial \log_{10} [H^+] [Pb(II)]}, \mu, T)</td>
<td>0.54</td>
<td>0.1</td>
</tr>
<tr>
<td>(\frac{\partial \log_{10} i_0}{\partial \log_{10} [Pb(II)]}, \mu, T)</td>
<td>0.35</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Consideration of the experimental charge transfer coefficient does not conclusively show that adsorption of solution species at the electrode is absent, although the value of 0.5 obtained in the case of \(\alpha\)-PbO\(_2\) does suggest a simple symmetrical electron transfer process. The possibility of adsorption must not be neglected; previous work \(^{25,45-47,134-135}\) has shown that the PbO\(_2\) electrode is generally complicated by adsorption of solution species. In general, reported adsorption has involved the H\(^+\) ion but, at the present experimental potentials (positive rational potentials), direct adsorption of H\(^+\) ions is unlikely. There still exists the possibility that H\(^+\) ions may be involved in an adsorbed Pb(II) complex.

In later work, chapter 5-7, adsorption of neutral Pb(II) species at the PbO\(_2\) electrode is suggested. In order to test the present results for similar adsorption it was decided to attempt to fit the present data into the calculations used for the perchlorate system data (since the present acidic electrolytes are more in common with the perchlorate solutions).
A sequence of reactions that may describe the electrode process is:

\[
PbO_2 + 2H^+ + 2e = Pb(OH)_2_{ads} \tag{4.15}
\]

\[
Pb(OH)_2_{ads} = Pb(OH)_2_{aq} \tag{4.16}
\]

\[
Pb(OH)_2_{aq} + 2H^+ = Pb(II) + 2H_2O \tag{4.17}
\]

By applying a Freundlich type isotherm of the form:

\[
\theta = \beta C_A^{P_4} \tag{4.18}
\]

to describe the possible adsorption (reaction 4.15), and incorporating this into equation 4.11 gives:

\[
I_o = zFk_{11}^{11} [H^+]^2 (1 - \alpha) - 2\alpha P_4 [Pb(II)]^{\alpha P_4} \tag{4.19}
\]

where \( k_{11}^{11} = k_4^1 \beta \)

From equation 4.19:

\[
\left( \frac{\partial\log_{10} I_o}{\partial\log_{10} [Pb(II)]} \right)_{[H^+], \mu, T} = \alpha P_4 \tag{4.20}
\]

\[
\left( \frac{\partial\log_{10} I_o}{\partial\log_{10} [H^+]} \right)_{[Pb(II)], \mu, T} = 2(1 - \alpha) - 2\alpha P_4 \tag{4.21}
\]

Substituting the values of Table 4.1, into equations 4.20 and 4.21, for \( \beta-PbO_2 \):

\[
\alpha P_4 = 0.35 \quad \text{and} \quad 2(1 - \alpha) - 2\alpha P_4 = 0.54 \tag{4.22}
\]
Thus $\alpha = 0.35$ and $\beta_4$ approaches unity indicating that little or no adsorption of the Pb(II) species occur at the electrode. Similar reasoning for $\alpha$-$\text{PbO}_2$ indicates values of $\alpha = 0.46$ and $\beta_4$ approaches unity. Hence $\alpha$-$\text{PbO}_2$ behaves in a similar manner to $\beta$-$\text{PbO}_2$ and adsorption of the Pb(II) species is absent.

Temperature Dependence of Exchange Current

The magnitude of the enthalpy of activation the Arrhenius plots, figures 4.22. and 4.23, is 27.7 kJ mol$^{-1}$ for $\beta$-$\text{PbO}_2$ and 35.6 kJ mol$^{-1}$ for $\alpha$-$\text{PbO}_2$. Both of these values approximate to the activation enthalpies obtained for other charge transfer reactions however such values are of only limited significance because of an unknown thermal junction potential.

Conclusions

It is clear from the differential capacitance measurements, that both $\alpha$- and $\beta$-$\text{PbO}_2$ electrodes in aqueous KNO$_3$ solutions behave very much like Hg electrodes in non-interacting electrolytes$^{124}$, provided that surface roughness effects are taken into account. Serious divergencies from "Hg like" behaviour occur in the non ideal polarizability, the magnitude of the frequency dispersion of the capacitance and the divergence from linearity of the $E_R - \log \alpha_+$ curves at constant charge.

In the case of HNO$_3$ solutions the differential capacitance curves indicated the presence of adsorption at the electrodes and it is suggested that this adsorption may involve the HNO$_3$ molecule.

The galvanostatic measurements indicate that the PbO$_2$/Pb(II) exchange reaction is slow and that adsorption of neutral Pb(II) species at the electrodes does not occur.
CHAPTER 5

THE ELECTROCHEMICAL BEHAVIOUR OF PbO₂ IN ALKALINE ELECTROLYTES

Thermodynamically α-PbO₂ is the more stable polymorph in alkaline solutions. Interest in the behaviour of PbO₂ in alkali exists since, in the interior of the positive plates of lead–acid cells during their manufacture, basic conditions prevail and recent work has established the existence of α-PbO₂ in positive plates. Other investigations also have shown that α-PbO₂ is the main constituent of the anodic corrosion product of lead.

Investigations of the reactions of PbO₂ in alkali and their influence in the lead–acid cell are limited. Chartier and co-workers studied the reduction of α and β-PbO₂ in alkali and, for β-PbO₂ it was suggested that the electrode reaction involves two steps:

(a) a solution reaction:

\[ \beta\text{-PbO}_2 + H_2O + 2e^- = HPbO_2^- + OH^- \] (5.1)

(b) a solid phase reaction:

\[ \beta\text{-PbO}_2 + H_2O + 2e^- = PbO + 2 OH^- \] (5.2)

A mechanism for the electrode reaction at the α-PbO₂ electrode was not proposed.

5.1. The Electrical Double Layer

The preparation of test electrodes and experimental technique were as described in Chapter 3.
Results

Figure 5.1 shows typical faradaic current - bias potential curves for α and β-PbO₂ in NaOH solutions. The electrodes were nowhere ideally polarizable. The experimental polarizable region, extending from ~ 0.5 - 1.3 V for α-PbO₂ and ~ 0.5 - 1.35 V for β-PbO₂, is limited by oxygen evolution at the positive extremity and lattice dissolution at the negative extreme. A small difference in the potential of zero faradaic current flow occurred, ~ 0.66V for α-PbO₂ and ~ 0.75V for β-PbO₂.

Figures 5.2 and 5.3 show a series of differential capacitance-bias potential curves for α- and β-PbO₂ respectively. Stable impedance measurements were obtained within 2 hrs. of electrode/electrolyte contact time for α-PbO₂, however, for β-PbO₂ ~ 10 hrs. contact were required. Once stability had been achieved the α-PbO₂ electrode remained stable for potentials within the polarizable region for at least 24 hrs. without significant change; the β-PbO₂ electrode was stable for only a relatively short period (~ 5 hrs.). Replicate electrode impedance measurements showed a 5% variation about a mean for both polymorphs. Hysteresis of the capacitance measurements for potential excursions within the experimental polarizable region was negligible, but when the potentials were forced outside these limits serious irreversible changes occurred at the electrode and it was found impossible to return to the original condition.

Figures 5.4 and 5.5 show typical frequency dispersion of the capacitance curves. The extent of the dispersion, which was similar for both polymorphs, amounts to ~ 10% for a frequency change 1 kHz - 500 Hz.

Discussion of the Differential Capacitance Results

The capacitance magnitudes observed for NaOH solutions were significantly greater than those for KNO₃ solutions but smaller than the capacitance values recorded in HNO₃ solutions. In general, the capacitance curves for α-PbO₂ were flatter than the corres-
Fig. 5.1  Faradaic current-bias potential curves for PbO$_2$ in NaOH electrolyte

ELECTROLYTE: 0.1 mol/l NaClO$_4$

- O - $\beta$-PbO$_2$
- • - $\alpha$-PbO$_2$

Faradaic current/mA cm$^{-2}$

E (NHE)/V

0.6  1.0  1.4
Fig. 5.2. Differential capacitance - bias potential curves for α-PbO₂ in NaOH electrolyte.
Fig. 5.3. Differential capacitance - bias potential curves for $\beta$-PbO$_2$ in NaOH electrolyte
Fig. 5.4. Typical frequency dispersion of differential capacitance–bias potential curves for $\alpha$-PbO\textsubscript{2} in NaOH electrolyte.
Fig. 5.5. Typical frequency dispersion of differential capacitance bias potential curves for $\beta$-PbO$_2$ in NaOH electrolyte.
ponding curves for \( \beta \)-PbO\(_2\). The minimum in the capacitance curves, obtained at 1.15 V for \( \beta \)-PbO\(_2\), corresponds to the potential of the estimated pzc in nitrate solutions, however, the rather broad minimum in the present case indicates that the electrode/electrolyte interphase is probably complicated by adsorption (e.g. OH\(^-\) ions). In the case of \( \alpha \)-PbO\(_2\), the flatter capacitance curves and the absence of a clearly defined minimum indicates that the electrode appears to be more complicated by adsorption than for the \( \beta \)-PbO\(_2\) electrode. Consideration of the species present in the solution suggests that the adsorbed species is the OH\(^-\) ion. That adsorption appears to be greatest at the \( \alpha \)-PbO\(_2\) electrode does not seem unreasonable since it has been suggested that the electrodeposition of \( \beta \)-PbO\(_2\) depends on the adsorption of H\(^+\) ions,\(^{20,134}\) then the deposition of \( \alpha \)-PbO\(_2\) may well depend on the adsorption of OH\(^-\) ions at the electrode.

The lower capacitance values observed for both polymorphs in NaOH solutions, compared with those of acid solution, indicates that the adsorption pseudocapacitance associated with the OH\(^-\) ion is less than that of the H\(^+\) ion. Alternatively, in NaOH solutions the PbO\(_2\) electrode may be covered by a film of the lower oxide.

5.2. The Exchange Reaction

The galvanostatic experimental procedure was as described in Chapter 3. Measurements were commenced after 15 min. electrode/electrolyte contact time. Overpotential - current density data were obtained corresponding to electrolytes based on 3 mol\(^{-1}\) equivalent uni-univalent salt concentration, maintained with added KNO\(_3\). Two series of experiments were performed; in the first [Pb(II)] was varied and [OH\(^-\)] kept constant and in the second [OH\(^-\)] varied at constant [Pb(II)].
Experimental Results

The differential capacitance results indicated that in Pb(II) free solutions $\beta$-PbO$_2$ electrodes exhibit a certain degree of stability. In Pb(II) containing solutions $\beta$-PbO$_2$ electrodes progressively deteriorated, mechanical strength and adhesion were affected, the deposit tended to disintegrate and it was not possible to obtain reliable faradaic current-overpotential data. In all the experimental electrolyte solutions $\alpha$-PbO$_2$ electrodes were stable and reproducible overpotential-faradaic current data were obtained.

Figure 5.6. shows a typical overpotential-time transient for $\alpha$-PbO$_2$. Such transients were characterized by an initial steep rise in overpotential, corresponding to the double layer charging process, followed by a steadily increasing region, due to concentration overpotential effects (extrapolation of which allowed $\eta_D$ values to be obtained). Figure 5.7. shows typical faradaic current-overpotential data corresponding to measurements at low overpotentials for electrolytes of varying [Pb(II)] at constant [OH$^-$]. Complementary data for electrolytes of varying [OH$^-$] and constant [Pb(II)] were also obtained and were of similar form to that of Figure 5.7. The exchange current density, calculated from the slope of the $i-$ $\eta_D$ curves at the origin using equation 2.18, were identical for both the anodic and cathodic processes. Figures 5.8. and 5.9. show the variation of the exchange current with [Pb(II)] and [OH$^-$] respectively.

Figure 5.10. shows the effect of temperature on the faradaic current-overpotential data from which the Arrhenius plot, figure 5.11., was obtained.

Figures 5.12. and 5.13. show typical faradaic current-overpotential data, corresponding to measurements at high overpotentials (Tafel curves), in electrolytes of varying [Pb(II)] at constant [OH$^-$] and varying [OH$^-$] at constant [Pb(II)] respectively. The kinetic parameters, transfer coefficient and apparent exchange current, obtained from the slope and intercept of the linear curve, are summarized in Table 5.1.
Fig. 5.6. Typical overpotential-time transient for $\alpha$-PbO$_2$ in alkaline electrolyte

Electrolyte: 3 mol/l$^{-1}$ K$^+$ (with added KNO$_3$)

- $[\text{Pb(II)}]$ 0.0008 mol/l$^{-1}$
- $[\text{OH}^-]$ 0.34 mol/l$^{-1}$

Cathodic pulse current 0.025 mA cm$^{-2}$
Electrode/electrolyte contact time 15 mins.
Electrode area $4.9 \times 10^{-2}$ cm$^2$
Fig. 5.7 Faradaic current-overpotential curves for $\alpha$-PbO$_2$ in alkaline electrolyte.
Fig. 5-8. Variation of exchange current with \([\text{Pb(II)}]\) for \(\alpha-\text{PbO}_2\) in alkaline electrolyte

\[\frac{\delta \log_{10} i_0}{\delta \log_{10} [\text{Pb(II)}]} = 0.25\]
Fig. 5.9. Variation of exchange current with \([\text{OH}^-]\) for \(\alpha-\text{PbO}_2\) in alkaline electrolyte

\[
\frac{\partial \log_{10} i_0}{\partial \log_{10} (\text{OH}^-)} = 0.76
\]

Electrolyte: 0.008 mol\(^{-1}\) Pb(II) 3 mol\(^{-1}\) K\(^+\) (with KNO\(_3\))

\[
\log_{10} \left( \frac{[\text{OH}^-]}{\text{mol}^{-1}} \right)
\]

\[
\log_{10} \left( i_0 / \text{mA cm}^{-2} \right)
\]
Fig. 5.11. Variation of exchange current with temperature for $\alpha$-PbO$_2$ in alkaline electrolyte

ELECTROLYTE: 0.039 mol$^{-1}$ Pb(II), 0.68 mol$^{-1}$ OH$^-$, 3 mol$^{-1}$ K$^+$ (WITH KNO$_3$)

$\log_{10}(I_y \ \text{mA cm}^{-2})$

$\left(10^3/T\right)/^\circ \text{K}^{-1}$
Fig. 5.12. Faradaic current overpotential (Tafel region) curves for α-PbO₂ at various [OH⁻] in alkaline electrolyte.
Fig. 5.13. Faradaic current–overpotential (Tafel region) curves for α-PbO\(_2\) at various [Pb(II)] in alkaline electrolyte.

Electrolyte: 3 mol\(\text{L}^{-1}\) K\(^+\) (with KNO\(_3\)), 0.68 mol\(\text{L}^{-1}\) OH\(^-\),

- 0.039 mol\(\text{L}^{-1}\) Pb(II)
- 0.021 mol\(\text{L}^{-1}\) Pb(II)
- 0.011 mol\(\text{L}^{-1}\) Pb(II)
- 0.007 mol\(\text{L}^{-1}\) Pb(II)
- 0.005 mol\(\text{L}^{-1}\) Pb(II)
Table 5.1. Characteristics of the Tafel Plots

α-PbO₂ electrodes in alkaline electrolytes at 23°C. Total ionic concentration 3 mol 1⁻¹ with added KNO₃.

<table>
<thead>
<tr>
<th>Concentration (mol 1⁻¹)</th>
<th>Cathodic Coeff. (2.3 RT / F ( \log i_o / \log \eta_D ))</th>
<th>Anodic Coeff. (2.3 RT / F ( \log i_A / \log \eta_D ))</th>
<th>Intercept at ( \eta_D = 0 ) (2 ( i_o ) mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cathodic</td>
<td>Anodic</td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td>OH⁻</td>
<td>0.29</td>
<td>0.20</td>
</tr>
<tr>
<td>0.039</td>
<td>0.68</td>
<td>0.29</td>
<td>0.19</td>
</tr>
<tr>
<td>0.021</td>
<td>0.68</td>
<td>0.28</td>
<td>0.19</td>
</tr>
<tr>
<td>0.011</td>
<td>0.68</td>
<td>0.28</td>
<td>0.19</td>
</tr>
<tr>
<td>0.0067</td>
<td>0.68</td>
<td>0.28</td>
<td>0.19</td>
</tr>
<tr>
<td>0.0052</td>
<td>0.68</td>
<td>0.29</td>
<td>0.19</td>
</tr>
<tr>
<td>0.0008</td>
<td>1.22</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>0.0008</td>
<td>1.04</td>
<td>0.30</td>
<td>0.21</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.82</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.64</td>
<td>0.28</td>
<td>0.20</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.57</td>
<td>0.28</td>
<td>0.20</td>
</tr>
</tbody>
</table>

(47)
Figures 5.14 and 5.15. show the variation of the apparent exchange current with concentration of \([\text{Pb(II)}]\) and \([\text{H}^+]\) respectively.

Figures 5.16. and 5.17. show the variation of the anodic faradaic current, at constant potential, obtained from Figures 5.11. and 5.12., with \([\text{Pb(II)}]\) and \([\text{H}^+]\) respectively. No variation of cathodic faradaic current with concentration of electroactive species was observed.

Table 5.2. summarizes the estimated differential capacitance from the overpotential time transients. The reasonably constant double layer capacitance, are satisfactory, considering the accuracies with which current and overpotential could be measured.

**Discussion of Galvanostatic Results**

The instability of \(\beta\)-PbO\(_2\) electrodes in Pb(II) containing solutions is unexpected in view of its satisfactory stability in the absence of Pb(II). Introduction of Pb(II) into the PbO\(_2\)/OH\(^-\) system has the effect of establishing an exchange process between Pb(IV) ions in the electrode lattice and Pb(II) ions in solution. A possible cause of the instability of \(\beta\)-PbO\(_2\) is that the Pb(II) species after oxidation, is laid down preferentially as \(\alpha\)-PbO\(_2\). (Considering the respective structures of the two polymorphs this simply requires the occupation of different octahedral positions by Pb(IV) ions in the close packed oxygen structure after the exchange.) Such a \(\beta\)-PbO\(_2\)/\(\alpha\)-PbO\(_2\) interconversion process could lead to disruption of the \(\beta\)-PbO\(_2\) lattice causing the observed instability.

Potential measurements at zero faradaic current flow indicate:

\[
\left( \frac{\partial \epsilon E}{\partial \log_{10} [\text{Pb(II)}]} \right) \sim -29 \text{ mV} \quad (5.3)
\]

\[
\left( \frac{\partial \epsilon E}{\partial \log_{10} [\text{OH}^-]} \right) \sim -29 \text{ mV} \quad (5.4)
\]

(48)
Fig. 5.14. Variation of apparent exchange current with $[\text{Pb(II)}]$ for $\alpha$-PbO$_2$ in alkaline electrolyte

**Electrolyte:** 3 mol l$^{-1}$ K$^+$ (with added KNO$_3$)

$[\text{OH}^-]$ 0.8 mol l$^{-1}$

- **Anodic**
- **Cathodic**

**Graph Details:**
- **Y-axis:** Log $i_s$/mA cm$^{-2}$
- **X-axis:** Log$_{10}$ $[\text{Pb(II)}]$/mol l$^{-1}$
Fig. 5. Variation of apparent exchange current with \( [\text{OH}^-] \) for \( \alpha - \text{PbO}_2 \) in alkaline electrolytes.

```latex
\text{ELECTROLYTE: 3 mol}^{-1} \text{K}^+ \text{ (WITH ADDED KNO}_3 \text{)}

\( [\text{PN]} 0.0008 \text{ mol}^{-1} \)

- \text{ANODIC}
- \text{CATHODIC}
```

\[ \log_{10}(2i_0/\text{mA cm}^{-2}) \]

\[ \log_{10}([\text{OH}^-]/\text{mol}^{-1}) \]
Fig. 5.16. Dependence of anodic current density on \([\text{Pb}(\text{II})]\) for \(\alpha-\text{PbO}_2\) in alkaline electrolyte

ELECTROLYTE: 0.68 mol\(\text{l}^{-1}\) OH\(^{-}\)
3 mol\(\text{l}^{-1}\) K\(^+\) (WITH KNO\(_3\))

\[E = 0.54 \text{V}, \] \[E = 0.515 \text{V}, \] \[E = 0.49 \text{V}, \] \[E = 0.265 \text{V}, \] \[E = 0.44 \text{V} \]

\[\frac{\delta \log_\text{a} j}{\delta \log_\text{a} [\text{Pb}(\text{II})]} = 0.48\]

\[\log_\text{a} ([\text{Pb}(\text{II})]/\text{mol} l^{-1})\]
Fig. 5.17 Dependence of anodic current density on $[\text{OH}^-]$ for $\alpha$-PbO$_2$ in alkaline electrolyte

ELECTROLYTE: 0.0008 mol l$^{-1}$ Pb(II)
3 mol l$^{-1}$ K$^+$ (WITH KNO$_3$)

$$\frac{\delta \log_i}{\delta \log_{[\text{OH}^-]}} = 1.8$$

Log$_i$(anodic current density)/mA cm$^{-2}$

Log$_{[\text{OH}^-]$/mol l$^{-1}$}
Table 5.2. \( C_L \) estimated from galvanostatic measurements.

Electrolyte total equivalent uni-univalent salt concentration 3 mol 1\(^{-1}\) (with added KNO\(_3\)).

<table>
<thead>
<tr>
<th>Concentration (mol 1(^{-1}))</th>
<th>OH(^-)</th>
<th>( C_L ) ( \mu ) F cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.039</td>
<td>0.68</td>
<td>80.1</td>
</tr>
<tr>
<td>0.021</td>
<td>0.68</td>
<td>81.2</td>
</tr>
<tr>
<td>0.011</td>
<td>0.68</td>
<td>79.7</td>
</tr>
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<td>0.0067</td>
<td>0.68</td>
<td>79.9</td>
</tr>
<tr>
<td>0.0052</td>
<td>0.68</td>
<td>80.3</td>
</tr>
<tr>
<td>0.0008</td>
<td>1.22</td>
<td>82.1</td>
</tr>
<tr>
<td>0.0008</td>
<td>1.04</td>
<td>81.5</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.82</td>
<td>81.7</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.64</td>
<td>82.0</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.57</td>
<td>80.1</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.37</td>
<td>79.7</td>
</tr>
</tbody>
</table>

(49)
corresponding to the involvement of one molecule of $\text{OH}^-$ and one molecule of Pb(II) in the equilibrium electrode reaction. The equilibrium electrode reaction can be written:

$$\text{PbO}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- = \text{Pb}^{(\text{OH})_3^-} + \text{OH}^- \quad (5.5)$$

The exact formulation of the Pb(II) species in solution has not been considered in the present work however Olin considers that in alkaline solutions Pb(II) exists as $\text{Pb}^{(\text{OH})_3^-}$.

The orders of reaction, determined from the dependence of the anodic and cathodic current densities on the concentration of the electroactive species at constant potential, indicate that the rate of the cathodic reaction is independent of both $[\text{Pb}(\text{II})]$ and $[\text{OH}^-]$. Thus, for $\alpha$-$\text{PbO}_2$, the cathodic reaction is truly zero order, which is required if the electrode does not undergo modification under the influence of the electrolyte, i.e. no change in electrode activity occurs with electrolyte concentration. It follows that the cathodic reaction does not involve the hydroxyl (or hydrogen) ion.

For the anodic reaction, the dependence of the anodic current density, $i_A$, on the concentration of electroactive species may be written:

$$i_A = k_5 \left[ \text{Pb}_{\text{aq}} \right]^x \left[ \text{OH}^- \right]^y \quad (5.6)$$

where $k_5$ is a potential dependent rate constant, $[\text{Pb}_{\text{aq}}]$ represents the measureable $[\text{Pb}^{(\text{II})}]$ in the solution and $x$ and $y$ are the orders of reaction. At high anodic potentials the faradaic current approximates to $i_A$ (Chapter 2) and the anodic orders of reaction follow from the slopes of the log $i$ vs log concentration plots, figures 5.16 and 5.17., which give:

(50)
and substituting in equation 5.6, allows values of 0.48 and 1.49 to be obtained for $x$ and $y$ respectively.

At least one molecule of Pb(II) must be involved in the charge transfer step; if more than one molecule were involved a complex reaction would be indicated which is unlikely. The experimental value of $x$ (0.48) is significantly less than unity, however, a low order of reaction with respect to the Pb(II) ion has been observed for the anodic oxidation of Pb(II) in other electrolytes. Fleischmann and Liler\(^4\) observed a value of 0.26 for the deposition of $\alpha$-PbO\(_2\) from acetate solutions and explained this in terms of adsorption of Pb(II) at the electrode. Hampson et al\(^4\) observed a reaction order of $\sim 0.8$ for the anodic reaction of $\alpha$-PbO\(_2\) in acid perchlorate solutions and proposed adsorption of H\(^+\) ions. At the present experimental potentials, negative of the pzc, adsorption of Pb(OH)\(_3\) is unlikely and H\(^+\) is not present to any significant extent for adsorption.

It is possible that neutral PbO molecules may readily be adsorbed and a sequence of reactions to represent the electrode process, involving adsorption of PbO species, can be formulated as:

\[
\text{PbO}_2 + \text{H}_2\text{O} + 2e = \text{PbO}_{\text{ads}} + 2\text{OH}^- \quad (5.9)
\]

\[
\text{PbO}_{\text{ads}} = \text{PbO}_{\text{aq}} \quad (5.10)
\]

\[
\text{PbO}_{\text{aq}} + \text{OH}^- + \text{H}_2\text{O} = \text{Pb(OH)}_3^- \quad (5.11)
\]
where PbO$_{ads}$ and PbO$_{aq}$ represent PbO adsorbed at the electrode and in the solution respectively. Such a mechanism conforms to the ideas of Gerischer$^{144}$ in that a neutral species crosses the double layer in preference to a charged species.

An estimate of the adsorption of Pb(II) species, using the method described in Chapter 2, is shown in figure 5.18, in the form of a plot of log$_10$ $\theta$ vs log$_10$[Pb(II)] where $\theta$ is approximated to Cps for alkaline electrolytes. The adsorption pseudocapacitance, Cps, was obtained by subtracting the estimated capacitance from the overpotential-time transients at $t=0$ ms from the estimated capacitance at $t=2$ ms (when adsorption affects were assumed complete). The curve is of the form:*

$$\log_{10} \theta = P_5 \log_{10} \beta_5 a + \text{const.} \quad (5.12)$$

where $P_5$ is a constant less than unity, $\beta_5$ is the adsorption coefficient, $a$ the activity and $\theta$ the surface coverage by the adsorbed species. A similar isotherm can be derived thermodynamically from the Gibbs isotherm assuming that the adsorbed layer obeys an equation of state of the form:*

$$FA = nRT \quad (5.13)$$

A similar approach for obtaining the isotherm which best fits the experimental data, using estimated adsorption pseudocapacitance was used by Gerischer$^{98}$ in a study of Ag(II) ion adsorption from ClO$_4^-$ solutions. A similar isotherm to equation 2.15, was found to apply. Hickling$^{145}$ also considered that for the adsorption of hydrogen on metals a form of this isotherm applied and recently Schiffrin$^{78}$ found that for the specific adsorption of F$^-$ ions on mercury, a Freundlich type isotherm described the surface pressure of the adsorbed ionic film.

*Footnote:* Pb(II) was used rather than activity since in the present concentration the activity coefficients are expected to be constant.
Fig. 5.18. Estimate of adsorption of Pb(II) and OH$^-$ on $\alpha$-PbO$_2$ from alkaline electrolyte.
Applying a Freundlich type isotherm of the form:

\[ \theta = k_{5f} C^P_5 \]  \hspace{1cm} (5.14)

to describe the adsorption of PbO:

\[ [\text{PbO}_{\text{ads}}] = k_{5f} [\text{PbO}_{\text{aq}}]^P_5 \]  \hspace{1cm} (5.15)

where \( k_{5f} \) is a constant and \( P_5 \) an exponent less than unity. It has been assumed that the main Pb(II) species in solution, \( \text{Pb}^{\text{aq}} \), is the singly charged hydroxy complex \( \text{Pb(OH)}_3 \) which dissociates as equation 5.11, or more simply as:

\[ \text{Pb}^{\text{aq}} = \text{PbO}^{\text{aq}} + \text{OH}^- + \text{H}_2\text{O} \]  \hspace{1cm} (5.16)

and in dilute solution, assuming \([\text{H}_2\text{O}]\) constant, an expression for \( \text{PbO}_{\text{aq}} \) can be substituted into equation 5.15, to give:

\[ [\text{PbO}_{\text{ads}}] = k_{5f} [\text{Pb}_{\text{aq}}]^{P_5}/[\text{OH}^-]^{P_5} \]  \hspace{1cm} (5.17)

For reaction 5.9, in the anodic direction:

\[ i_A = \frac{k^1_5}{x+y} [\text{PbO}_{\text{ads}}] [\text{OH}^-]^2 \]  \hspace{1cm} (5.18)

where \( k^1_5 \) is a potential dependent rate constant.

Combining equation 5.17 and 5.18, gives:

\[ i_A = \frac{k^1_5}{x+y} k_{5f} [\text{Pb}_{\text{aq}}]^P_5 [\text{OH}^-]^{2-P_5} \]  \hspace{1cm} (5.19)

comparing equation 5.6 and 5.19:

\[ x + y = 2 \]  \hspace{1cm} (5.20)
which is verified by the experimental values of $x$ and $y$.

From the low overpotential measurements, applying the rate equation (equation 2.17) to the exchange reaction, equation 5.9., assuming $[\text{PbO}_2]$ and $[\text{H}_2\text{O}]$ are unity:

$$i_0 = zF k_5^{11} [\text{PbO}_{ads}]^\alpha [\text{OH}^-]^{2\alpha} \quad (5.21)$$

where $k_5^{11}$ is a rate constant.

Substituting for $[\text{PbO}_{ads}]$ from equation 5.17:

$$i_0 = zF k_5^{11} k_{5f} [\text{Pb}_{aq}]^{\beta} S^{\alpha} [\text{OH}^-]^{2\alpha} - \beta S^\alpha \quad (5.22)$$

from which:

$$\left(\frac{\partial \log_{10} i_0}{\partial \log_{10} [\text{Pb}_{aq}]}\right) \quad [\text{OH}^-], \mu, T \quad (5.23)$$

From the slopes of the variation of the exchange current with concentration of electroactive species, figures 5.8. and 5.9., the experimental values:

$$\left(\frac{\partial \log_{10} i_0}{\partial \log [\text{Pb}_{aq}]}\right) = 0.25 \quad (5.24)$$

$$\left(\frac{\partial \log_{10} i_0}{\partial \log [\text{OH}^-]}\right) = 0.76 \quad (5.25)$$

are obtained. Substituting the experimental values into equation 5.23, gives values of $\alpha = 0.5$ and $P_5 = 0.5$. The value for $P_5$ indicates significant adsorption of PbO at the electrode.
For the measurements at high overpotentials, the mean values of the anodic and cathodic Tafel coefficients, Table 5.1., are 0.2 and 0.29 respectively. In the case of the charge transfer reaction indicated at low overpotentials (i.e. a symmetrical two electron transfer), the expected numerical sum of the Tafel coefficients is unity. The experimental values at high overpotentials are significantly different to suggest that the charge transfer at high overpotential differs from that at low overpotentials. Further evidence for a change in charge transfer mechanism is shown in the form of the Tafel curves. If anodic and cathodic reactions were the same then the anodic and cathodic Tafel slopes should be of the same order which is not the case.

In Chapter 2 thermodynamic considerations of charge transfer were discussed in which it was suggested that for a two electron transfer, a mechanism involving two consecutive single electron transfers is more favourable than a simultaneous two electron transfer. In the present case, the high overpotential measurements indicate that the charge transfer process most probably involves two consecutive single electron transfers.

Applying the theory of Lovrecek for the case of two consecutive single electron transfers, as discussed in Chapter 2, to the present high overpotential measurements, allows the transfer coefficients for both electron transfer steps to be extracted. Thus:

(i) Cathodic Tafel coefficient \( = - (n_c^* - 1 + \alpha_i) = 0.29 \) (5.26)

where \( n_c^* \) is the rate determining step in the cathodic direction and \( \alpha_i \) is the transfer coefficient of the rate determining step,

when \( n_c^* = 1 \) \( \alpha_i = \alpha_c = 0.29 \) (5.27)

(ii) Anodic Tafel coefficient \( n_A^* - \alpha_i = 0.2 \) (5.28)

where \( n_A^* \) is the rate determining step in the anodic direction and \( \alpha_i \) is the charge transfer coefficient of the rate determining step,

when \( n_A^* = 1 \) \( \alpha_i = \alpha_A = 0.2 \) (5.29)
The charge transfer process at high overpotentials can therefore be written:

\[
PbO_2 + H_2O + e^- = [PbO(OH)_2]^- \quad (5.30)
\]

\[
[PbO(OH)_2]^- + e^- = PbO + 2OH^- \quad (5.31)
\]
in which the unstable intermediate \([PbO(OH)_2]^-\) is proposed and the charge transfer coefficients are as calculated above. The formation of a Pb(III) intermediate has also been suggested by Varypaev and Fedot'yev\(^{143}\) for the slow step in the electrodeposition of PbO\(_2\) from Pb(NO\(_3\))\(_2\) solution, however, schemes based on a Pb(III) intermediate are more open to objection than those based on a transitory low charged intermediate.

In the above mechanism the formation of a hydroxyintermediate is suggested and the species that crosses the double layer is the neutral PbO thus conforming to Gerischers ideas of charge transfer\(^{144}\).

The transition of the charge transfer mechanism from a one step process at low overpotentials to a two step mechanism at high overpotentials is similar to the behaviour observed by Hampson et al\(^{45-47}\) for PbO\(_2\) electrodes in perchlorate electrolytes.

### Apparent Exchange Current

The calculation of the exchange current by extrapolation of the linear-logarithmic \(\eta - i\) data to \(\eta_D = 0\) assumes that no mechanistic change occurs in the region over which the extrapolation is made. Since in the present case a change does occur, exchange currents can only be interpreted hypothetically. On this basis the variation of the apparent exchange current with concentration of electroactive species was as shown in figures 5.14 and 5.15 from which:

\[
\left( \frac{a \log_{10} i_{oa}}{a \log_{10} [Pb(II)]} \right) \left[ OH^- \right], T, \mu = 0.15 \quad (5.32)
\]
\[
\frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [\text{OH}^-]} = 0.45 \quad (5.33)
\]

\[
\frac{\partial \log_{10} i_{ob}}{\partial \log_{10} [\text{Pb}(II)]} = 0.30 \quad (5.34)
\]

\[
\frac{\partial \log_{10} i_{ob}}{\partial \log_{10} [\text{OH}^-]} = 0.95 \quad (5.35)
\]

Applying the theory of consecutive single electron transfers \(^{105}\) (Chapter 2, equation 2.31) to the present cathodic transfer, equation 5.30, and assuming \([\text{H}_2\text{O}]\) and \([\text{PbO}_2]\) constant gives an expression for the apparent exchange current:

\[
i_{oa} = K_a [\text{PbO(OH)}_2^-]^\alpha C \quad (5.36)
\]

from which:

\[
\frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [\text{Pb}(II)]} = \alpha C \frac{\partial \log_{10} [\text{Pb}(II)]}{\partial \log_{10} [\text{OH}^-]} \quad (5.37)
\]

\[
\frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [\text{OH}^-]} = \alpha C \frac{\partial \log_{10} \text{Pb}(II)}{\partial \log_{10} [\text{OH}^-]} \quad (5.38)
\]

The L.H.S. of equation 5.37 has the numerical value 0.15 and together with the previously determined value for \(\alpha C\) of 0.15 (equation 5.27) gives:

\[
\frac{\partial \log_{10} [\text{Pb}(III)]}{\partial \log_{10} [\text{Pb}(II)]} = 1 \quad (5.39)
\]

(57)
The L.H.S. of equation 5.38 has the numerical value 0.45 giving:

\[
\left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{OH}^-]} \right)_{\text{L.H.S.}} = 3
\]

(5.40)

In the case of the anodic reaction, equation 5.31:-

\[
i_{ob} = k_a [\text{PbO(OH)}_2^+]^{1-\alpha_a} [\text{PbO}]^{\alpha_a} [\text{OH}^-]^2
\]

(5.41)

from which

\[
\left( \frac{\partial \log_{10} i_{ob}}{\partial \log_{10} [\text{Pb(II)]}} \right)_{\text{L.H.S.}} = (1-\alpha_a) \left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{Pb(II)]}} \right)_{\text{L.H.S.}} + \alpha_a
\]

(5.42)

\[
= \left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{OH}^-]} \right)_{\text{L.H.S.}} = 1
\]

(5.43)

\[
(1-\alpha_a) \left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{OH}^-]} \right)_{\text{L.H.S.}} + 2\alpha_a
\]

The L.H.S. of equation 5.42 has the numerical value 0.30 which with the previously determined value for \( \alpha_a \) of 0.65 (equation 5.29) gives:

\[
\left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{Pb(II)]}} \right)_{\text{L.H.S.}} = -1
\]

(5.44)

and the L.H.S. of equation 5.43 has the numerical value of 0.95 giving:

\[
\left( \frac{\partial \log_{10} [\text{Pb(III)]}}{\partial \log_{10} [\text{OH}^-]} \right)_{\text{L.H.S.}} = -1
\]

(5.45)

The cathodic results, equation 5.39 and 5.40, indicate an increase in the concen-
tation of the Pb(III) intermediate with increase in the concentration of OH⁻ and Pb(II)⁺. Increasing the concentration of OH⁻ and [Pb(II)] would, in effect, alter the electrode potential to more negative potentials and so enhance the cathodic reaction, i.e. increase [Pb(III)]. Similarly for the anodic reaction, equation 5.44. and 5.45. suggest that increasing the concentration of Pb(II) and OH⁻ decreases [Pb(III)]. In this case increasing the concentration of Pb(II) and OH⁻ alters the electrode potential to more negative potentials thus inhibiting the anodic reaction and formation of Pb(III) species.

The above results are further evidence that the charge transfer mechanism involves two consecutive single electron transfer steps at high overpotentials, but this must be considered in conjunction with the earlier evidence for a single two electron step at low overpotentials. The charge transfer can be considered in terms of potential energy diagrams. Figure 5.19A and 5.19B relate to the low overpotential and high overpotential conditions respectively. In figure 5.19A the reaction path (dotted line) does not cross the energy curve for the Pb(III) species, there is no transitory intermediate and a two electron charge transfer step occurs. In figure 5.19B the cathodic polarization raises curve A to curve C and the Pb(II) energy curve is intersected producing, in the overall reaction path C-D, a stable region (E) in which the Pb(III) intermediate can exist, with the result that the charge transfer process now involves two consecutive one electron transfer steps.

Temperature Dependence of the Exchange Current

From the Arrhenius plot, figure 5.11, two distinct linear regions are indicated. The values of the activation enthalpy, ΔH*, are ~ 40 kJ mol⁻¹ at the low temperatures (< 35 C) and ~ 8 kJ mol⁻¹ at higher temperatures. These results are similar to those observed by Hampson et al.⁴⁵⁻⁴⁷ in acid electrolytes. A satisfactory explanation for such a change in enthalpy with temperature is not evident. It is interesting to note that
Augstadt et al., for PbO$_2$ in H$_2$SO$_4$, observed a pronounced change in slope of the electrode potential vs temperature curves for $\alpha$-PbO$_2$.

5.3. Fast Linear Sweep Studies

The experimental procedure was as described in Chapter 3.

Results

Figures 5.20 and 5.21 show typical cathodic potential sweep curves for $\alpha$-PbO$_2$ and $\beta$-PbO$_2$ respectively. The experimental potential limits were governed by hydrogen evolution at negative potentials and oxygen evolution at positive potentials. For $\alpha$-PbO$_2$ two clearly defined current peaks (a and b) occur within the potential sweep limits. The potential of peak a corresponds to the PbO$_2$/PbO reduction potential. A slight negative shift of the potential of peak a was observed for increased sweep speeds indicating some irreversibility of the reaction. The potential of peak b corresponds to the Pb/PbO reduction potential and represents the reduction of PbO to Pb. Continuous potential cycling within the experimental potential limits did not significantly alter the form of the curves.

Figure 5.22 shows the effect of sweep rate on the maximum peak current, $I_m$, of peak a. A linear relationship between $I_m$ and $\sqrt{v}$ was observed within the experimental concentration range and the curves passed through the origin indicating that the current limiting reaction at peak a involves a diffusion reaction in solution.

Figure 5.23 shows the variation of $I_m$ with [OH$^-$]; a linear relationship was not observed. Figure 5.24 shows the $I_m$ - [OH$^-$] data in the form of a log-log plot which gave a linear relationship of slope 1.4.

For peak b a non-linear relationship between the peak current height and $\sqrt{v}$ was observed indicating that the peak does not correspond to a simple diffusion reaction but may involve a complex reaction system, possibly depending on prior reactions.
Fig. 5.20. Typical cathodic potential sweep on α-PbO₂ in NaOH electrolyte.

Electrolyte: 4.7 mol l⁻¹
Sweep Speed: 58.3 mV s⁻¹
Electrode Area: 4.49 x 10⁻² cm²
Fig. 5.22. Cathodic peak current—\(\sqrt{sweep\ rate}\) for the formation of PbO on \(\alpha\)-PbO\(_2\) electrodes in NaOH electrolyte.
Fig. 5.23. Cathodic peak current $\left[\text{OH}^-\right]$ for PbO formation on $\alpha$-PbO$_2$ electrodes in NaOH electrolyte.

- **Sweep Speeds**:
  - $58.3 \text{ mV s}^{-1}$
  - $29 \text{ mV s}^{-1}$
  - $12 \text{ mV s}^{-1}$

- **Electrode Area**: $4.49 \times 10^{-3} \text{ cm}^2$

The graph shows the relationship between cathodic peak current (mA) and concentration of OH$^-$ (mol L$^{-1}$). The data points for different sweep speeds are marked with circles, squares, and triangles, respectively.
Fig. 5.24 Variation of $I_m$ with [OH$^-$] for $\alpha$-PbO$_2$ in NaOH electrolyte.

\begin{equation}
\frac{\delta \log_{10} I_m}{\delta \log_{10} \text{[OH}^-\text{]}} = 1.3
\end{equation}

ELECTRODE AREA $4.49 \times 10^{-3} \text{ cm}^2$

- $58.9 \text{ mV s}^{-1}$
- $29 \text{ mV s}^{-1}$
- $12 \text{ mV s}^{-1}$
For $\beta$-PbO$_2$, three current peaks occur within the experimental potential limits, (c, d and e of figure 5.21). The potential of peak e corresponds to the Pb/PbO redox potential and peak d to a potential which corresponds to the potential of peak a in figure 5.21, indicating the presence of some $\alpha$-PbO$_2$ on the electrode surface. Peak c was only observed for $\beta$-PbO$_2$ and can be assumed to be due to the $\beta$-PbO$_2$/PbO redox potential. Continuous cycling within the experimental potential limits showed a decrease in peak c and an increase in peak d indicating some modification of the $\beta$-PbO$_2$ electrode surface to $\alpha$-PbO$_2$. Linear relationships between $I_m$ and $\sqrt{v}$ were not observed for any of the peaks due to the continual modification of the electrode surface.

Discussion of L.S.V. Results

Since the $I_m$ - $\sqrt{v}$ curves for $\alpha$-PbO$_2$ pass through the origin, figure 5.22, a diffusion process in solution is indicated. By considering the species present in the solution it seems reasonable to assume that the diffusing ion is the OH$^-$ ion. From the slope of the log $I_m$ - log [OH$^-$] curve, the order of reaction with respect to the OH$^-$ ion is 1.4 and, since a whole number must be involved in the reaction, the results indicate that the reaction may be complicated by intrusion of adsorbed species, confirming the galvanostatic results. The electrode reaction sequence can be represented by equation 5.9 - 5.11. Calculation of the diffusion coefficient using equation 2.47 and the slope of the $I_m$ - $\sqrt{v}$ curves, figure 5.22, yields a value of $10^{-7}$ which is too small to be the true diffusion coefficient of the OH$^-$ ion in aqueous solution (accepted value $147$ $5.23 \times 10^{-5}$). There are two possible explanations of the abnormal diffusion coefficient:

(i) diffusion of the OH$^-$ ion occurs through a layer of cathodic products and the diffusion coefficient is that of the diffusing ion in the product phase (an incomplete Pb(II)
oxide film).

(ii) diffusion of the $\text{OH}^-$ ion occurs through an adsorbed layer at the electrode. It seems in this case that the presence of an adsorbed layer, through which the $\text{OH}^-$ ion diffuses, is better supported by the galvanostatic results than the postulation of an incomplete oxide film.

**Conclusions**

In aqueous NaOH solutions (Pb(II) free) the differential capacitance curves for $\beta$-$\text{PbO}_2$ exhibit a broad minimum at $1.15\,\text{V}$ indicating that the interphase is complicated by adsorption. For $\alpha$-$\text{PbO}_2$ the capacitance curves show a very broad minimum over a fairly wide potential range indicating greater adsorption for $\alpha$-$\text{PbO}_2$.

The exchange reaction $\text{PbO}/\text{Pb(II)}$ in alkaline solution is complicated by adsorption of $\text{PbO}$ at the electrode. At potentials near the equilibrium potential the charge transfer mechanism involves a simultaneous two electron transfer. At higher overpotentials the reaction becomes two consecutive one electron transfers involving a reactive Pb(III) intermediate.

The cathodic reduction of $\alpha$-$\text{PbO}_2$ to PbO in aqueous NaOH involves mass transport control by diffusion of $\text{OH}^-$ ions in the solution but is complicated by the adsorption of products at the electrode. The cathodic reduction of $\beta$-$\text{PbO}_2$ is further complicated by modification of the surface to $\alpha$-$\text{PbO}_2$.
CHAPTER 6

THE ELECTROCHEMICAL BEHAVIOUR OF PbO₂ IN ACID PERCHLORATE SOLUTIONS

6.1. The Electrical Double Layer

Test electrode construction and experimental procedure were as described in Chapter 3.

Experimental Results

Figures 6.1 and 6.2 show typical faradaic current - bias potential curves for α and β-PbO₂ in HClO₄ and NaClO₄ solutions respectively. Electrodes were nowhere ideally polarizable in either electrolyte, but a region existed where the faradaic current flow was small and approximated to polarizability. The experimental polarizable region, extending from 1.45 - 2.1 V for α-PbO₂ and 1.45 - 2.03 V for β-PbO₂ in HClO₄ and 0.35 - 1.85 V for α-PbO₂ and 0.65 - 1.85 V for β-PbO₂ in NaClO₄ solutions, was governed by oxygen evolution at positive potentials and lattice dissolution at negative potentials.

Figures 6.3, 6.4, 6.5, and 6.6 show a series of differential capacitance - bias potential curves for α and β-PbO₂ in the respective electrolyte solutions. In both electrolytes an initial time instability of the impedance readings was observed for potentials within the experimental polarizable region. Stable impedance readings were obtained after electrode/electrolyte contact times of 3 hrs. for β-PbO₂ and 5 hrs for α-PbO₂ in HClO₄ and 2 hrs. for β-PbO₂ and 3 hrs. for α-PbO₂ in NaClO₄ solutions, readings thereafter remaining stable for at least 12 hrs. Potential excursions within the experimental polarizable region caused negligible hysteresis of impedance measurements, however, when potentials were forced outside these limits, serious irreversible changes occurred at the electrode and the impedance measurements never returned to their...
Fig. 6.1. Faradaic current-bias potential curves for \( \text{PbO}_2 \) in \( \text{HClO}_4 \) electrolyte.

**Electrolyte:** 0.0123 mol\(^{\text{m}}\) \( \text{HClO}_4 \)

- \( \beta-\text{PbO}_2 \)
- \( \alpha-\text{PbO}_2 \)
Fig. 6.2 - Faradic current - bias potential curves for PbO₂ in NaClO₄ electrolyte.
Fig. 6.3. Differential capacitance bias potential curves for α-PbO₂ in HClO₄ electrolyte

![Graph showing differential capacitance bias potential curves for different electrolyte concentrations.](image)
Fig. 6.4. Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in HClO$_4$ electrolyte

![Graph showing capacitance vs. potential for different electrolyte concentrations.]

- 0.135 mol$^{-1}$ HClO$_4$
- 0.065 mol$^{-1}$ HClO$_4$
- 0.009 mol$^{-1}$ HClO$_4$
- 0.003 mol$^{-1}$ HClO$_4$

Increasing electrolyte concentration shifts the capacitance curves to the left, indicating a lower bias potential range for the reaction to occur.
Fig. 6.5. Differential capacitance bias potential curves for α-PbO₂ in NaClO₄ electrolyte.
Fig. 6.6. Differential capacitance bias potential curves for $\beta$-PbO$_2$ in NaClO$_4$ electrolyte

Electrolyte Concentration:
- 0.12 mol/l NaClO$_4$
- 0.071 mol/l NaClO$_4$
- 0.031 mol/l NaClO$_4$
- 0.008 mol/l NaClO$_4$

Capacitance (μF/cm$^2$) vs. E(NHE) / V
original values. Replicate impedance measurements showed ~ 7% variation about a mean for both electrolytes.

Figures 6.7., 6.8., 6.9. and 6.10 show typical frequency dispersion of the differential capacitance curves. The extent of the dispersion for a frequency change 1 kHz - 500 Hz amounted to ~ 30% for HClO₄ solutions and ~ 20% for NaClO₄ solutions.

Discussion of Differential Capacitance Results

The initial time instability of the impedance data for both electrolytes can be associated with an electrode surface modification process. An initial rise in capacitance magnitude with time was also observed by Kabanov for PbO₂ electrodes in HClO₄ solutions and was associated with swelling of the PbO₂ lattice and change in the crystal structure consequently increasing the true surface area of the PbO₂. That α-PbO₂ showed the greater time instability may be due to the equilibrium process:

$$\alpha\text{PbO}_2 \leftrightarrow \text{Pb(IV)} \leftrightarrow \gamma\text{PbO}_2$$

which occurs in acid solutions.

In all the capacitance curves a clearly defined minimum was absent indicating that the interphase is complicated by adsorption at the electrode. Measurements for HClO₄ solutions showed greater capacitance values than for NaClO₄, and since a significant variation in capacitance with concentration of H⁺ ion was observed, indications are that the H⁺ ion is involved in the adsorption process. Direct adsorption of H⁺ is unlikely due to the experimental positive rational potentials but adsorption of HClO₄ molecules is a possibility (cf HNO₃ solutions). In NaClO₄ solutions the lower capacitance values may be due to the lower concentration of H⁺ ion present, reducing the possibility of adsorption of HClO₄; in this case the adsorbed species is probably
Fig. 6.7. Typical frequency dispersion of differential capacitance curves for $\alpha$-PbO$_2$ in HClO$_4$ electrolyte.
Fig. 6.8. Typical frequency dispersion of differential capacitance curves for $\beta$-PbO$_2$ in HClO$_4$ electrolyte.
Fig. 6.9. Typical frequency dispersion of differential capacitance curves for $\alpha$-PbO$_2$ in NaClO$_4$ electrolyte.
Fig. 6.10. Typical frequency dispersion of differential capacitance curves for $\beta$-PbO$_2$ in NaClO$_4$ electrolyte.
the $\text{ClO}_4^-$ ion or $\text{HClO}_4$ present to a much less extent than in the $\text{HClO}_4$ solutions.

The magnitude of the experimental polarizable region was significantly smaller in the acid solutions. The concentration of $\text{H}^+$ had most effect on the potential of lattice dissolution.

6.2. The Exchange Reaction

(a) Galvanostatic Measurements

The galvanostatic experimental procedure was as described in Chapter 3. Measurements were commenced after 20 mins electrode/electrolyte contact time in electrolytes maintained at 3 mol $\text{l}^{-1}$ uni-univalent salt concentration with added $\text{NaClO}_4$. Reproducibility was $\pm 5\%$. The ohmic overpotential was generally $< 5\%$ of $\eta_D$. Two series of experiments were performed; in the first $[\text{Pb(II)}]$ was varied and $[\text{H}^+]$ kept constant and in the second $[\text{H}^+]$ varied at constant $[\text{Pb(II)}]$.

Experimental Results

Figures 6.11. and 6.12. show examples of typical overpotential-time transients curves for $\alpha$ and $\gamma$-$\text{PbO}_2$. At higher current densities an initial gap is observed which represents the pseudo-ohmic overpotential due to the electrolyte resistance. Both transients show a steep rise initially representing the double layer charging process followed by a steadily increasing linear region from which $\eta_D$ results by extrapolation to zero time.

Figures 6.13. and 6.14. show typical faradaic current - overpotential curves for $\alpha$ and $\gamma$-$\text{PbO}_2$ respectively corresponding to measurements at low overpotentials ($\eta_D < 7 \text{ mV}$) for electrolytes of varying $[\text{Pb(II)}]$ at constant $[\text{H}^+]$. Complementary curves for electrolytes of varying $[\text{H}^+]$ and constant $[\text{Pb(II)}]$ were also obtained and were of similar form to those shown in figures 6.13. and 6.14. The exchange currents for the anodic and cathodic processes, calculated from the slope of the $i - \eta_D$ curves
Fig. 6.11. Typical overpotential-time transient for PbO₂ in perchlorate electrolyte

**Electrolyte:** 3 mol dm⁻³ ClO₄⁻ (with added NaClO₄)

\[
\begin{align*}
\text{Pb(II)} & : 0.044 \text{ mol dm}^{-3} \\
\text{H}^+ & : 0.806 \text{ mol dm}^{-3}
\end{align*}
\]

**Cathodic Pulse Current:** 0.045 mA cm⁻²

**Electrode-Electrolyte Contact Time:** 15 mins

**Electrode Area:** 4.9 x 10⁻² cm²
Fig. 6.12. Typical overpotential-time transient for PbO₂ in perchlorate electrolyte

![Graph showing typical overpotential-time transient for PbO₂ in perchlorate electrolyte.](image)

**ELECTROLYTE:** 3 mol·L⁻¹ K⁺ (WITH ADDED KNO₃)

- [Pb(II)] 0.006 mol·L⁻¹
- [H⁺] 0.9 mol·L⁻¹

**ANODIC PULSE CURRENT** 9.86 mA cm⁻²
**ELECTRODE/ELECTROLYTE CONTACT TIME** 15 mins
**ELECTRODE AREA** 4.9 x 10⁻² cm²
Fig. 6.13. Faradaic current-overpotential curves for $\alpha$-PbO$_2$ in perchlorate electrolyte.
Fig. 6.14. Faradaic current-overpotential curves for $\beta$-PbO$_2$ in perchlorate electrolyte.
at the origin, were identical. Figures 6.15. and 6.16. show the dependence of the exchange current on the concentration of the electroactive species for $\alpha$-PbO$_2$. The corresponding curves for $\beta$-PbO$_2$ are shown in figures 6.17. and 6.18.

Figures 6.19. and 6.20. show the effect of temperature on the exchange current in the form of Arrhenius plots for $\alpha$- and $\beta$-PbO$_2$ respectively.

Figures 6.21. and 6.22. show typical $i - \eta_D$ data for $\alpha$-PbO$_2$ corresponding to potential measurements at high overpotentials (Tafel curves). Complementary curves for $\beta$-PbO$_2$ are shown in figures 6.23. and 6.24. The kinetic parameters, transfer coefficient and apparent exchange current, obtained from the slope and intercept ($\eta_D = 0$) of the linear curves, and summarised in Tables 6.1. and 6.2. for $\alpha$ and $\beta$-PbO$_2$ respectively.

Figures 6.25. and 6.26. show the variation of the apparent exchange current, extracted from the Tafel curves, with concentration of electroactive species for $\alpha$-PbO$_2$. Figures 6.27. and 6.28. show corresponding curves for $\beta$-PbO$_2$.

Figures 6.29 and 6.30 show the variation of the anodic current density, at constant potential, with concentration of electroactive species for $\alpha$-PbO$_2$ in the Tafel region. Figures 6.31. and 6.32. show the variation of the cathodic current densities with concentration of electroactive species. Complementary curves for $\beta$-PbO$_2$ are shown in figures 6.33. - 6.35. Little variation of the cathodic current with $[\text{Pb(II)}]$ was observed.

Discussion of Galvanostatic Results

Potential measurements at zero faradaic current flow, figures 6.21. - 6.24. indicate that both polymorphs obey the relationship:

(66)
Fig. 6.15. Variation of exchange current with $[\text{Pb(II)}]$ for $\alpha$-$\text{PbO}_2$ in perchlorate electrolyte from galvanostatic measurements.

\[
\frac{\delta \log i_0}{\delta \log [\text{Pb(II)}]} = 0.1
\]

**ELECTROLYTE** 0.89 mol l$^{-1}$ $[\text{H}^+]$

**TOTAL ClO$_4^-$** 3 mol l$^{-1}$ (WITH NaClO$_4$)
Fig. 6.16. Variation of exchange current with \( [H^+] \) for \( \gamma-\text{PbO}_2 \) in perchlorate electrolyte from galvanostatic measurements.

\[ \log_{10}(i_0 / \text{mA cm}^{-2}) \]

- ELECTROLYTE \( 0.096 \text{ mol}^{-1} [H^+] \)
- TOTAL \( [\text{ClO}_4^-] \) \( 3 \text{ mol}^{-1} \) (WITH \( \text{NaClO}_4 \))

\[ \frac{\delta \log_{10} i_0}{\delta \log_{10} [H^+]} = 0.005 \]
Fig. 6.17. Variation of exchange current with [Pb(II)] for $\beta$-PbO$_2$ in perchlorate electrolyte from galvanostatic measurements.

\[
\frac{\Delta \log_{10} i_o}{\Delta \log_{10} [\text{Pb(II)}]} = 0.13
\]
Fig. 6.18. Variation of exchange current with $[H^+]$ for $\beta$-PbO$_2$ in perchlorate electrolyte from galvanostic measurements.

Electrolyte: 0.096 mol l$^{-1}$ [Pb(II)]
Total [ClO$_4$]: 3 mol l$^{-1}$ (with NaClO$_4$)

$$\frac{\Delta \log_{10} I_e}{\Delta \log_{10}[H^+]} = 0.26$$

log$_{10}(I_e/\text{mA cm}^{-2})$ vs log$_{10}([H^+]/\text{mol l}^{-1})$
Fig. 6.19. Variation of exchange current with temperature for $\alpha\text{PbO}_2$ in perchlorate electrolyte from galvanostatic measurements.

Electrolyte: 0.521 mol$^{-1}$ H$^+$
0.056 mol$^{-1}$ Pb(II)
TOTAL [ClO$_4^-$] 3 mol$^{-1}$ (WITH NaClO$_3$)

$\log_\circ (i_0 / \text{mA cm}^{-2})$
-0.8  -0.6  -0.4

$10^\circ / T / ^\circ K^{-1}$
3.2  3.4  3.6
Fig. 22: Faradaic current–overpotential (Tafel region) curves for α-PbO$_2$ in perchlorate electrolyte.

Electrolyte: 3 mol/l $\text{ClO}_4^-\text{H}^+$ (with added NaClO$_4$)
- 0.901 mol/l $\text{H}^+$
- 0.397 mol/l Pb(II)
- 0.24 mol/l Pb(II)
- 0.095 mol/l Pb(II)
- 0.044 mol/l Pb(II)
- 0.006 mol/l Pb(II)

Log($i$/mA cm$^2$) vs. Overpotential (mV)

- Cathodic
- Anodic

Log($i$/mA cm$^2$) vs. Overpotential (mV)
Fig.6.23. Faradaic current–overpotential (Tafel region) curves for $\beta$-PbO$_2$ in perchlorate electrolyte.

**Electrolyte:** 3 mol/l $\text{ClO}_4^-$ (with added NaClO$_4$)

0.901 mol/l $\text{H}^+$  
○ 0.397 mol/l Pb(II)  
● 0.24 mol/l Pb(II)  
△ 0.095 mol/l Pb(II)  
▲ 0.044 mol/l Pb(II)  
□ 0.006 mol/l Pb(II)

**Graph:**
- **Cathodic** and **Anodic** regions.
- Log$_e$I (mA cm$^{-2}$) vs. OVERPOTENTIAL / mV.
Fig. 6.24 Faradaic current-overpotential (Tafel region) curves for $\mu$-PbO$_2$ in perchlorate electrolyte

ELECTROLYTE: 3 mol l$^{-1}$ ClO$_4^-$ (WITH ADDED NaClO$_4$)

- 0.006 mol l$^{-1}$ Pb(II)
- 0.901 mol l$^{-1}$ H$^+$
- 0.52 mol l$^{-1}$ H$^+$
- 0.11 mol l$^{-1}$ H$^+$
- 0.044 mol l$^{-1}$ H$^+$
- 0.009 mol l$^{-1}$ H$^+$

Log$_{10}$(i/mA cm$^{-2}$)

OVERPOTENTIAL / mV

Cathodic

Anodic
Fig. 6.25. Variation of apparent exchange current with [Pb(II)] for α-PbO₂ in perchlorate electrolyte. Galvanostatic measurements.
Fig. 6.26. Variation of apparent exchange current with [H$^+$]
for α-PbO$_2$ in perchlorate electrolyte.
Galvanostatic measurements

**ELECTROLYTE:** 3 mol l$^{-1}$ ClO$_4^-$ (WITH ADDED NaClO$_4$)

[Pb(II)] 0.006 mol l$^{-1}$

- ANODIC
- CATHODIC

$\log_{10}(2i_0/mA \cdot cm^2)$ vs $\log_{10}([H^+]_\text{mol l}^{-1})$
Fig. 6.27 Variation of apparent exchange current with $[\text{Pb(II)}]$ for $\beta$-PbO$_2$ in perchlorate electrolyte. Galvanostatic measurements.

Electrolyte: 3 mol l$^{-1}$ ClO$_4^-$ (with added NaClO$_4$)

$[\text{H}^+] = 0.901$ mol l$^{-1}$

- ANODIC
- CATHODIC
Fig. 6.28. Variation of apparent exchange current with $[\text{H}^+]$ for $\beta$-PbO$_2$ in perchlorate electrolyte. Galvanostatic measurements.

Electrolyte: $3 \text{ mol L}^{-1}$ ClO$_4^-$ (with added NaClO$_4$)

Pb(II) 0.006 mol L$^{-1}$

○ ANODIC

● CATHODIC
Fig. 6.29. Dependence of anodic current density on \([\text{Pb(II)}]\) for \(\alpha-\text{PbO}_2\) in perchlorate electrolyte.

ELECTROLYTE; 3 mol\(\text{l}^{-1}\) (WITH ADDED NaClO\(_4\))

\([H^+]\) 0.901 mol\(\text{l}^{-1}\)

\[
\Delta \log_{10} i / \Delta \log_{10} ([\text{Pb(II)}]_{/\text{mol}^{-1}}) = 0.6
\]
Fig. 6.30. Dependence of anodic current density on $[H^+]$ for $\alpha$-PbO$_2$ in perchlorate electrolyte.

Electrolyte: 3 mol/l $^\text{−1}$ (with added NaClO$_4$)

$[\text{Pb(II)}] = 0.006$ mol/l $^\text{−1}$

$\frac{\delta \log_{10} i}{\delta \log_{10} [H^+]} = 0.5$

$\text{Log}_{10}(i / \text{mA cm}^2)$

$\text{Log}_{10}([H^+] / \text{mol}^\text{−1})$
Fig. 6.31. Dependence of cathodic current density on [Pb(II)] for α-PbO₂ in perchlorate electrolyte.

ELECTROLYTE: 3 mol l⁻¹ (WITH ADDED NaClO₄)

\[ [H^+] = 0.201 \text{ mol l}^{-1} \]

\[ \frac{\delta \log_{10} i}{\delta \log_{10} [\text{Pb(II)}]} = 0.18 \]
Fig. 6.32. Dependence of cathodic current density on $[H^+]$ for $\alpha\text{PbO}_2$ in perchlorate electrolyte.

Electrolyte: 3 mol $\text{l}^-$ (with added NaClO$_4$)

$[\text{Pb}(\text{II})] = 0.006 \text{ mol l}^-$

$\frac{\Delta \log_{10} i}{\Delta \log_{10} [H^+]} = 1.6$
Fig. 6.33. Dependence of anodic current density on $[\text{Pb(II)}]$ for $\beta$-PbO$_2$ in perchlorate electrolyte.

**ELECTROLYTE**: 3 mol/l$^{-1}$ (WITH ADDED NaClO$_4$)

$[\text{H}^+] = 0.901$ mol/l$^{-1}$

$\frac{\delta \log_{10} i_A}{\delta \log_{10} [\text{Pb(II)}]} = 0.52$
Fig. 6.34. Dependence of anodic current density on \([H^+]\) for \(\beta\)-PbO\(_2\) in perchlorate electrolyte.

**ELECTROLYTE:** 3 mol l\(^{-1}\) (WITH ADDED NaClO\(_4\))

\[
\left[\text{Pb}^{II}\right] = 0.006 \text{ mol l}^{-1}
\]

\[
\frac{\partial \log_{10} i}{\partial \log_{10} [H^+]} = -0.52
\]
Fig. 6.35. Dependence of cathodic current density on $[H^+]$ for $\beta$-PbO$_2$ in perchlorate electrolyte.

Electrolyte: 3 mol$^{-1}$ (with added NaClO$_4$)

$[\text{Pb(III)}] = 0.006$ mol$^{-1}$

$\frac{\delta \log_{10} i}{\delta \log_{10} [H^+]} = 1.12$

$E = 70 \text{ mV}$

$E = 50 \text{ mV}$
Table 6.1.

Characteristics of the Tafel Plots

$\alpha$-PbO$_2$ electrode in acid perchlorate electrolyte at 23°C. Total ionic concentration 3 mol l$^{-1}$ with added NaClO$_4$.

| Concentration (mol l$^{-1}$) | Cathodic Coeff. $\frac{2.3RT \log i_C}{e \eta_D}$ | Anodic Coeff. $\frac{2.3RT \log i_C}{\delta \eta_D}$ | Intercept at $\eta_D = 0(2i_0 \text{mA cm}^{-2})$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II) 0.397 0.901</td>
<td>0.81</td>
<td>0.15</td>
<td>0.200</td>
</tr>
<tr>
<td>0.24 0.901</td>
<td>0.83</td>
<td>0.14</td>
<td>0.200</td>
</tr>
<tr>
<td>0.095 0.901</td>
<td>0.83</td>
<td>0.14</td>
<td>0.182</td>
</tr>
<tr>
<td>0.044 0.901</td>
<td>0.83</td>
<td>0.14</td>
<td>0.200</td>
</tr>
<tr>
<td>0.006 0.901</td>
<td>0.82</td>
<td>0.14</td>
<td>0.105</td>
</tr>
<tr>
<td>0.006 0.52</td>
<td>0.82</td>
<td>0.15</td>
<td>0.120</td>
</tr>
<tr>
<td>0.006 0.11</td>
<td>0.84</td>
<td>0.15</td>
<td>0.110</td>
</tr>
<tr>
<td>0.006 0.044</td>
<td>0.83</td>
<td>0.14</td>
<td>0.074</td>
</tr>
<tr>
<td>0.006 0.009</td>
<td>0.81</td>
<td>0.14</td>
<td>0.105</td>
</tr>
</tbody>
</table>
Table 6.2.

Characteristics of the Tafel Plots

β-PbO₂ electrode in acid perchlorate electrolytes at 23°C. Total ionic concentration 3 mol ⁻¹ with added NaClO₄.

<table>
<thead>
<tr>
<th>Concentration (mol ⁻¹)</th>
<th>Cathodic Coeff.</th>
<th>Anodic Coeff.</th>
<th>Intercepts at η_D = 0(2i₀ mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pb(II)] [H⁺]</td>
<td>(2.3RT e log₁₀i_C) / η_D</td>
<td>(2.3RT e log₁₀i_A) / η_D</td>
<td>Cathodic</td>
</tr>
<tr>
<td>0.397 0.901</td>
<td>0.65</td>
<td>0.15</td>
<td>0.252</td>
</tr>
<tr>
<td>0.24 0.901</td>
<td>0.65</td>
<td>0.15</td>
<td>0.224</td>
</tr>
<tr>
<td>0.095 0.901</td>
<td>0.66</td>
<td>0.16</td>
<td>0.200</td>
</tr>
<tr>
<td>0.044 0.901</td>
<td>0.67</td>
<td>0.16</td>
<td>0.162</td>
</tr>
<tr>
<td>0.006 0.901</td>
<td>0.65</td>
<td>0.15</td>
<td>0.121</td>
</tr>
<tr>
<td>0.006 0.52</td>
<td>0.65</td>
<td>0.16</td>
<td>0.100</td>
</tr>
<tr>
<td>0.006 0.11</td>
<td>0.64</td>
<td>0.15</td>
<td>0.081</td>
</tr>
<tr>
<td>0.006 0.044</td>
<td>0.65</td>
<td>0.15</td>
<td>0.059</td>
</tr>
<tr>
<td>0.006 0.009</td>
<td>0.65</td>
<td>0.15</td>
<td>0.078</td>
</tr>
</tbody>
</table>
Thus the equilibrium electrode reaction involves one molecule of Pb(II) and 4 molecules of $H^+$. The equilibrium electrode reaction can be written:

$$\text{PbO}_2 + 4 \text{H}^+ + 2e^- = \text{Pb(II)} + 2 \text{H}_2\text{O} \quad (6.4)$$

The orders of reaction were obtained from the dependence of the cathodic and anodic current densities on the concentration of the electroactive species at constant potential, as discussed in Chapter 2. For reaction 6.4, the dependence of the cathodic current, $i_C$, on the concentration of electroactive species can be written as:

$$i_C = k_6^C [H^+]^x \quad (6.5)$$

and for the anodic current:

$$i_A = k_6^A [\text{Pb(II)}]^y [H^+]^z \quad (6.6)$$

where $k_6^C$ and $k_6^A$ are potential dependent rate constants, and $x$, $y$ and $z$ are the orders of reaction. Table 6.3 summarizes the experimental reaction orders obtained from figures 6.29 - 6.35.

Thus equation 6.5 and 6.6 can be rewritten as:

for $\alpha$-PbO$_2$

$$i_C = k_6^C [H^+]^{1.5} [\text{Pb(II)}]^{-0.2} \quad (6.7)$$
Table 6.3.
Experimental orders of reaction estimated from galvanostatic measurements

Electrolyte total equivalent uni-univalent salt concentration 3 mol 1⁻¹ (with added NaClO₄).

<table>
<thead>
<tr>
<th>( \frac{\partial \log_{10} i_C}{\partial \log_{10}[\text{Pb(ll)}][\text{H}^+]}, \mu, E )</th>
<th>( \alpha\text{-PbO}_2 )</th>
<th>( \beta\text{-PbO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.18</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1.52</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>0.54</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>-0.48</td>
<td>-0.52</td>
<td></td>
</tr>
</tbody>
</table>
\[ i_A = k_6A \left[ H^+ \right]^{0.6} \left[ \text{Pb(II)} \right]^{0.5} \]  \hspace{1cm} (6.8)

for $\beta$-PbO$_2$

\[ i_C = k_6C \left[ H^+ \right]^{1.1} \]  \hspace{1cm} (6.9)

\[ i_A = k_6A \left[ H^+ \right]^{0.5} \left[ \text{Pb(II)} \right]^{0.5} \]  \hspace{1cm} (6.10)

For the cathodic reaction, equation 6.4., $i_C$ should be of zero order with respect to $[\text{Pb(II)}]$, however, for $\alpha$-PbO$_2$ an order of -0.2 is observed indicating that the activity of the $\alpha$-PbO$_2$ electrode decreases with increasing $[\text{Pb(II)}]$. It is well established that in acid solutions $\beta$-PbO$_2$ is the more stable polymorph$^{22-24}$ and consequently under the conditions of the exchange reaction the proportion of $\beta$-PbO$_2$ (the less reactive) in the $\alpha$-PbO$_2$ surface may increase with increasing $[\text{Pb(II)}]$ and exchange current ($\alpha$-PbO$_2$ has a higher positive $E^0$ value than $\beta$-PbO$_2$ $^{24}$ and hence modification of $\alpha$-PbO$_2$ to $\beta$-PbO$_2$ at the electrode surface will represent a decrease in activity).

For the charge transfer step, at least one molecule of Pb(II) must be involved; more than one would indicate a complex reaction. The order of reaction with respect to Pb(II) for both polymorphs is significantly less than unity. Several explanations for the occurrence of a similar low reaction order, observed by other workers in similar electrode systems, have been suggested including Pb(II) adsorption$^{43}$ and $H^+$ adsorption$^{45-47}$ (discussed more fully in Chapter 5). In the present case direct adsorption of positive ions is unlikely due to the positive rational potentials involved, but it is possible that the adsorbed species may be in the form of neutral Pb(II) complex containing $H^+$ ions. For the low overpotential measurements, the experimental results indicate the exchange reaction involves a simultaneous two electron transfer. Hence at potentials close to the equilibrium the charge transfer reaction may involve the
following sequence of reactions:

\[
PbO_2 + 2H^+ + 2e = [Pb(OH)_2]_{ads} \quad (6.11)
\]

\[
[Pb(OH)_2]_{ads} = [Pb(OH)_2]_{aq} \quad (6.12)
\]

\[
[Pb(OH)_2]_{aq} + 2H^+ = Pb(II) + 2H_2O \quad (6.13)
\]

where \([Pb(OH)_2]_{ads}\) and \([Pb(OH)_2]_{aq}\) represent the Pb(OH)_2 species adsorbed at the electrode and in the solution respectively. In this mechanism a neutral entity, Pb(OH)_2, crosses the double layer conforming to the ideas of Gerischer. Due to the low pH of the experimental electrolyte solutions the involvement of one or more hydrogen ions in the initial adsorption and charge transfer process, i.e.

\[
PbO_2 + H^+ + 2e = PbO_2H^- \quad (6.14)
\]

\[
PbO_2 + 3H^+ + 2e = PbO_2H_3^+ \text{ or } PbOH^+ + H_2O \quad (6.15)
\]

must not be neglected, but this is unlikely since it would involve the transfer of a charged species across the double layer in preference to the neutral Pb(OH)_2. Also reaction with three hydrogen ions is unlikely since consideration of the collision theory, as applied to the liquid phase, indicates that multiple collisions as precursors to reactions are rare.

From the available thermodynamic data it seems unlikely that Pb(IV) ions exist in solution and hence, in the overall reaction, the Pb(IV) species must be involved at the electrode surface either as part of the lattice or in the adsorbed state. The proposed species, Pb(OH)_2, may be considered to arise as a surface species formed as
the product of weakly adsorbed H\(^+\) ions and lattice oxygen atoms on the surface, weakening the bonds between the surface lead and the underlying fully co-ordinated oxygen atoms of the PbO\(_2\) and enhancing the reduction to Pb(II).

An estimate of the adsorption of Pb(II) species is shown in figures 6.36 and 6.37, for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively, in the form of a \(\log_{10} \theta\) vs \(\log_{10} [\text{Pb(II)}]\) plot where \(\theta\) is approximated to \(C_{\text{ads}}\). Complementary data for the H\(^+\) ion are plotted on the same diagrams. The adsorption pseudocapacitance was obtained in a similar manner to that used for alkaline electrolytes and was greatest for the Pb(II) species. The adsorption behaviour approximates to the relationship:

\[
\log_{10} \theta = P_6 \log_{10} \rho_6 a + \text{const} \quad (6.16)
\]

which can also be written as:

\[
\theta = k_{6f} C^P_6 \quad (6.17)
\]

Combining equation 6.17 and 6.12 gives:

\[
\left[ [\text{Pb(OH)}_2]^\text{ads} \right] = k_{6f} \left[ [\text{Pb(OH)}_2]^\text{aq} \right]^{P_6} \quad (6.18)
\]

where \(k_{6f}\) is a constant and \(P_6\) less than unity. Substituting for \([\text{Pb(OH)}_2]^\text{aq}\) from equation 6.13:

\[
\left[ [\text{Pb(OH)}_2]^\text{ads} \right] = k_{6f}^{\frac{1}{P_6}} [\text{Pb(II)}]^P_6 / [\text{H}^+]^{2P_6} \quad (6.19)
\]

For reaction 6.11, at high overpotentials in the anodic direction:

\[
i_A = k_6 \left[ [\text{Pb(OH)}_2]^\text{ads} \right] [\text{H}^+]^{-2} \quad (6.20)
\]
Fig. 6.36. Estimate of adsorption of Pb(II) and H$^+$ at α-PbO$_2$ from perchlorate electrolyte.

Galvanostatic measurements.
Fig. 6.37. Estimate of adsorption of Pb(II) and H\(^+\) at αPbO\(_x\) from perchlorate electrolyte. Galvanostatic measurements.
where \( k_6 \) is a potential dependent rate constant. Combining equation 6.19 and 6.20:

\[
i_A = k_6 k_{6f}^1 \left[ \text{Pb(II)} \right] P_6 \left[ H^+ \right]^{-2(1-P_6)}
\]

Comparing equation 6.6 and 6.21 indicates that:

\[
y + z = -2 - P_6
\]

from the experimental anodic reaction orders; table 6.3:

\[
y + z = 1.02
\]

\[
P_6 = 0.98
\]

Allowing for experimental inaccuracies \( P_6 \) approximates to unity indicating that Pb(II) species are not adsorbed at the electrode to any appreciable extent under the present experimental conditions. Similar reasoning for \( \beta \)-PbO\(_2\) indicates that \( P_6 \) approaches unity and consequently little or no adsorption is involved at the electrode.

At low overpotentials the magnitude of the exchange current, which is slightly larger for \( \alpha \) than \( \beta \)-PbO\(_2\), indicates that the exchange reaction is slow. Applying the rate equation, equation 2.17, to the exchange reaction, equation 6.11., and assuming \([\text{PbO}_2]\) and \([H_2O]\) are unity gives:

\[
i_o = zF k_6^0 \left[ [\text{Pb(OH)}_2]^\text{ads} \right]^{-2} \left[ H^+ \right]^{-2(1-\alpha)}
\]

substituting for \([\text{Pb(OH)}_2]^\text{ads}\) from equation 6.13:

\[
i_o = zF k_6^1 \left[ H^+ \right]^{2(1-\alpha)} - 2\alpha P_6 \left[ \text{Pb(II)} \right]^{\alpha} P_6
\]
The experimental concentration dependencies, obtained from figures 6.14, 6.15, 6.16, and 6.17, are summarized in Table 6.4.

Table 6.4.
Exchange current dependencies on concentration of electroactive species estimated from galvanostatic measurements. Electrolyte total equivalent uni-univalent salt concentration 3 mol l$^{-1}$ (with added NaClO$_4$)

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-PbO$_2$</th>
<th>$\beta$-PbO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\partial \log_{10} i_0 \over \partial \log_{10} [\text{H}^+] [\text{Pb(II)}], \mu, T$</td>
<td>0.05</td>
<td>0.26</td>
</tr>
<tr>
<td>$\partial \log_{10} i_0 \over \partial \log_{10} [\text{Pb(II)}] [\text{H}^+], \mu, T$</td>
<td>0.1</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Substituting the experimental values for $\alpha$-PbO$_2$ into equation 6.27 and 6.28 gives values of $\alpha = 0.87$ and $P_6 = 0.115$ indicating the presence of adsorption of Pb(II) species at the electrode. Similarly for $\beta$-PbO$_2$ values of $\alpha = 0.74$ and $P_6 = 0.176$ can be extracted.

Hence, although at high overpotentials PbO$_2$ electrodes appear to be relatively uncomplicated by adsorption, at low overpotentials Pb(OH)$_2$ is adsorbed, the extent of
which is slightly greater at \( \alpha\)-PbO\(_2\) electrodes. The reason for the absence of adsorption at high overpotentials may lie in the greater potentials at the electrode.

The kinetic parameters of the reaction at high overpotentials are summarised in Tables 6.1 and 6.2 for \( \alpha\) and \( \beta\)-PbO\(_2\) respectively. Mean values of the anodic and cathodic Tafel coefficients are 0.14 and -0.82 for \( \alpha\)-PbO\(_2\) and 0.16 and -0.65 for \( \beta\)-PbO\(_2\). The results indicate that in the Tafel region the exchange reaction differs from that involved at low overpotentials and probably involves two consecutive single electron transfers. Evidence of such a mechanistic change is found in the different apparent exchange current densities for the anodic and cathodic processes at high overpotentials and also the anodic and cathodic Tafel slopes differ.

Interpretation of the Tafel region data using Lovrecek's theory\(^{105}\) (Chapter 2), allows rational values for the charge transfer coefficients, corresponding to the first and second charge transfer reactions, to be obtained. In a similar manner to that for alkaline electrolytes, the first charge transfer step in both the anodic and cathodic directions emerges as the rate determining step.

Applying the expressions obtained by Lovrecek to the present experimental results for \( \alpha\)-PbO\(_2\):

Cathodic Tafel Coefficient = \(- (n^*_c - 1 + \alpha_c) = -0.82\) \hspace{1cm} (6.29)

where \( n^*_c \) is the rate determining step in the cathodic direction and \( \alpha_c \) is the transfer coefficient of that step.

when \( n^*_c = 1, \quad \alpha_c = \alpha_1 = 0.82\) \hspace{1cm} (6.30)

Anodic Tafel Coefficient = \( n^*_A - \alpha_a = 0.14\) \hspace{1cm} (6.31)

where \( n^*_A \) is the rate determining step in the anodic direction, and \( \alpha_a \) is the charge transfer coefficient of that step.
when \( n^*_A = 1 \), \( \alpha_a = \alpha_2 = 0.86 \) \hspace{1cm} (6.32)

Similar analysis for \( \beta \)-PbO\(_2\) yields, \( \alpha_1 = 0.65 \) and \( \alpha_2 = 0.84 \).

The charge transfer reaction at high overpotentials may involve the following sequence of reactions:

\[
\begin{align*}
PbO_2 + 2H^+ & = [Pb(OH)_{2}^{2+}] \hspace{1cm} (6.33) \\
[Pb(OH)_{2}^{2+}] + e & = [Pb(OH)_{2}^{+}] \hspace{1cm} (6.34) \\
[Pb(OH)_{2}^{+}] + e & = Pb(OH)_2 \hspace{1cm} (6.35) \\
Pb(OH)_2 + 2H^+ & = Pb(II) + H_2O \hspace{1cm} (6.36)
\end{align*}
\]

\([Pb(OH)_2^{2+}]\) is formed as a surface species. The slow, rate determining step is considered to be reaction 6.34, in which the reactive hydroxy intermediate, \([Pb(OH)_2^+]\) is formed. The existence of a Pb(III) intermediate species was discussed in Chapter 5.

It is also possible that the Pb(III) intermediate may exist as \([PbOOH]\) or \([PbOH.H_2O^{++}]\) but, if this was the case, the transfer across the double layer would involve charged species which is less favourable than transfer of neutral species.

**Apparent Exchange Current**

Table 6.5 summarizes the experimental apparent exchange current dependencies on the concentration of electroactive species obtained from figures 6.25. - 6.29.

Using a similar analysis to that used in the case of alkaline electrolytes, the apparent cathodic exchange current at high overpotentials for the charge transfer process can be expressed as:

(77)
\[ i_{oa} = k_{oa} [Pb(III)]^{a} [H^+]^{2(1-a)} \] (6.37)

For the charge transfer reaction in the anodic direction, equation 6.35.:

\[ i_{ob} = k_{ob} [Pb(III)]^{1-a} [Pb(II)]^{b} [H^+]^{-2a} \] (6.38)

Table 6.5.

Apparent exchange current dependence on concentration of electroactive species.

Electolyte total equivalent uni-univalent salt concentration 3 mol 1⁻¹ (with added NaClO₄)

<table>
<thead>
<tr>
<th>( \frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [Pb(II)]} ), ( \mu ), ( T ) [( [Pb(II)] ), ( [H^+] )]</th>
<th>( \alpha-PbO_2 )</th>
<th>( \beta-PbO_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [H^+]} ), ( \mu ), ( T )</th>
<th>( \alpha-PbO_2 )</th>
<th>( \beta-PbO_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.59</td>
<td>0.59</td>
<td></td>
</tr>
</tbody>
</table>

Both cathodic and anodic expressions contain a term involving the Pb(III) species, the concentration of which is unlikely to be independent of potential and consequently the apparent exchange may only be discussed qualitatively.

From equation 6.37.:--
\[
\left(\frac{\partial \log_{10} \frac{1}{\alpha a}}{\partial \log_{10} \left[ \text{Pb}(11) \right]} \right)_{[H^+], \mu, T} = a_a \left(\frac{\partial \log_{10} \left[ \text{Pb}(111) \right]}{\partial \log_{10} \left[ \text{Pb}(11) \right]} \right)_{[H^+], \mu, T}
\]

and
\[
\left(\frac{\partial \log_{10} a}{\partial \log_{10} [\text{Pb}(11)]} \right)_{[H^+], \mu, T} = 2(1-a_0) + a_a \left(\frac{\partial \log_{10} \left[ \text{Pb}(111) \right]}{\partial \log_{10} [H^+]} \right)_{[\text{Pb}(11)], \mu, T}
\]

similarly from equation 6.39:
\[
\left(\frac{\partial \log_{10} \frac{1}{\alpha b}}{\partial \log_{10} \left[ \text{Pb}(11) \right]} \right)_{[H^+], \mu, T} = (1-a_b) \left(\frac{\partial \log_{10} \left[ \text{Pb}(111) \right]}{\partial \log_{10} \left[ \text{Pb}(11) \right]} \right)_{[H^+], \mu, T} + a_b
\]

and
\[
\left(\frac{\partial \log_{10} \frac{1}{\alpha b}}{\partial \log_{10} [H^+] \left[ \text{Pb}(11) \right]} \right)_{[H^+], \mu, T} = (1-a_b) \left(\frac{\partial \log_{10} \left[ \text{Pb}(111) \right]}{\partial \log_{10} [H^+]} \right)_{[\text{Pb}(11)], \mu, T} - 2a_b
\]

By substituting the experimental values, Table 6.5., into the respective equations gives the experimental concentration dependencies shown in Table 6.6.

The cathodic results, for both polymorphs, indicate an increase in the concentration of the Pb(II) intermediate with increase in the concentration of Pb(II) and decrease in concentration of H\(^+\). These concentration changes would, in effect, alter the electrode potential to more negative potentials and thus enhance the cathodic reaction.

The anodic results indicate a decrease in the concentration of Pb(III) with increase in concentration of Pb(II) and decrease in concentration of H\(^+\). The potential changes caused by the concentration changes in this case would be expected to inhibit the
Table 6.6.

Estimation of the dependence of the concentration of the Pb(III) species on the concentration of the electroactive species.

Electrolyte total equivalent uni-univalent salt concentration 3 mol l⁻¹ (with added NaClO₄)

<table>
<thead>
<tr>
<th></th>
<th>Cathodic (iₒa)</th>
<th>Anodic (iₒb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-PbO₂</td>
<td>β-PbO₂</td>
</tr>
<tr>
<td>[\alpha \log_{10}[\text{Pb(III)}] ] [\beta \log_{10}[\text{H}^+]], (T)</td>
<td>0.17</td>
<td>0.2</td>
</tr>
<tr>
<td>[\beta \log_{10}[\text{H}^+]] [\alpha \log_{10}[\text{Pb(II)}]], (T)</td>
<td>-0.42</td>
<td>-0.81</td>
</tr>
</tbody>
</table>

anodic reaction. A similar energy profile, as discussed for alkaline electrolytes (figure 5.19), will also apply in this case.

**Temperature Dependence of Exchange Current**

From the Arrhenius plots, figures 6.19 and 6.20, two linear regions for α-PbO₂ exist, but for β-PbO₂ only one such region is observed. For α-PbO₂ activation enthalpies for 25.2 kJ mol⁻¹ (temperatures < 35°C) and 10 kJ mol⁻¹ (temperatures < 35°C) were indicated. For β-PbO₂ the enthalpy of activation was 41.6 kJ mol⁻¹. The values of the enthalpies of activation and existence of two linear regions for α-PbO₂, are similar to that observed for alkaline electrolytes.
Faradaic Impedance Measurements

The faradaic impedance method and treatment of results was as described in Chapter 3. Measurements, taken at the potential of zero faradaic current, were commenced after 24 hrs. electrode/electrolyte contact time during which the test electrode was kept on open circuit.

Experimental Results

As a first step in analysing the faradaic impedance data the measurements were represented as a transformation in the complex plane. Such a representation is shown in figure 6.38 and 6.39 for α and β-PbO\textsubscript{2} respectively. A single straight line is obtained in each case rather than a circular one, characteristic of kinetic control. This indicates that the major rate controlling process is diffusion in solution. It is clear from figures 6.38 and 6.39 that values of the electrode capacitance and the electrolyte resistance cannot be obtained, however, since such a representation indicates a diffusion rate controlling process then it seems feasible to match the impedance data in accordance with the method of Randles described in Chapter 2, i.e. to match the data to the correct behaviour of the Warburg impedance. Figures 6.40 and 6.41 show typical sets of impedance data for α and β-PbO\textsubscript{2} respectively, treated in this way. Two parallel straight lines were obtained for the in-phase and out-of-phase components in the experimental frequency range (40 Hz - 5 kHz). Table 6.8 summarizes the double layer capacitance required for the correct behaviour of the Warburg impedance. The value of the electrolyte resistance, \( \sim 240 \, \Omega \, \text{cm}^2 \), agreed fairly well with \( R_E \) values observed in the double layer studies. Two series of experiments were performed; in the first \([H^+]\) was varied at constant \([\text{Pb(II)}]\) and in the second \([\text{Pb(II)}]\) varied at constant \([H^+]\).

Figures 6.42 and 6.43 show the variation of the exchange density with \([H^+]\) obtained by extrapolation of the impedance plots to infinite frequency and using
Fig. 6.38. Complex plane impedance plot for $\alpha$PbO$_2$

in perchlorate electrolyte

ELECTROLYTE 3 mol l$^{-1}$ (WITH ADDED NaClO$_4$)

$[\text{Pb(II)}] = 0.043$ mol l$^{-1}$

$[\text{H}^+] = 1.0$ mol l$^{-1}$

ELECTRODE/ELECTROLYTE CONTACT TIME 24 hrs

ELECTRODE AREA $4.9 \times 10^{-4}$ cm$^2$
Fig. 6.39. Complex plane impedance plot for $\beta$-PbO$_2$ in perchlorate electrolyte.

ELECTROLYTE 3 mol$^{-1}$ (WITH ADDED NaClO$_4$)

$\left[\text{Pb (II)}\right] 0.043$ mol$^{-1}$

$\left[\text{H}^+\right] 1.0$ mol$^{-1}$

ELECTRODE/ELECTROLYTE CONTACT TIME 24 hrs

ELECTRODE AREA $4.9 \times 10^{-3}$ cm$^2$
Fig. 6.40. Typical impedance curves for PbO₂ in perchlorate electrolyte.

Electrolyte: 0.015 mol/l Pb(II)
1.0 mol/l H⁺
Total ClO₄⁻ 3 mol/l (with added NaClO₄)
Electrode/electrolyte contact time 24 hrs
Electrode area 4.9 x 10⁻⁹ cm²

\( \text{Impedance } / \Omega \)

\( \frac{1}{\omega C} \)

\( R_f \)
Fig. 6.41. Typical impedance curves for $\beta$-PbO$_2$ in perchlorate electrolyte.

**Electrolyte:**
- $0.015 \text{ mol}^{-1}$ Pb(II),
- $1.0 \text{ mol}^{-1}$ H$^+$
- Total $[\text{ClO}_4^-]$ = 3 $\text{ mol}^{-1}$ (with NaClO$_4$)

**Electrode/Electrolyte Contact Time:** 24 hrs.

**Electrode Area:** $4.9 \times 10^{-2}$ cm$^2$
Fig. 6.42. Variation of exchange current with $[H^+]$ for $\alpha$-PbO$_2$ in perchlorate electrolyte from impedance measurements.

**Diagram:**

- **ELECTROLYTE** 0.001 mol l$^{-1}$ [Pb(II)]
- **TOTAL [ClO$_4^-$] 3 mol l$^{-1}$ (WITH NaClO$_4$)

Log$_e$($i_o$/mA cm$^{-2}$) vs. log$_e$([H$^+$]/mol l$^{-1}$)

\[ \frac{\delta \log_e i_o}{\delta \log_e [H^+]} = 0.02 \]
Fig 6.43. Variation of exchange current with $[H^+]$ for $\beta$-PbO$_2$ in perchlorate electrolyte from impedance measurements.
Table 6.8.

$C_L$ obtained from impedance measurements

Electrolyte total equivalent uni-univalent salt concentration 3 mol $1^{-1}$ (with added NaClO$_4$)

<table>
<thead>
<tr>
<th>Concentration (mol $1^{-1}$)</th>
<th>$C_L \mu F \ cm^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>H$^+$</td>
</tr>
<tr>
<td>0.068</td>
<td>0.99</td>
</tr>
<tr>
<td>0.044</td>
<td>0.99</td>
</tr>
<tr>
<td>0.015</td>
<td>0.99</td>
</tr>
<tr>
<td>0.0072</td>
<td>0.99</td>
</tr>
<tr>
<td>0.0029</td>
<td>0.99</td>
</tr>
<tr>
<td>0.001</td>
<td>0.99</td>
</tr>
<tr>
<td>0.001</td>
<td>0.15</td>
</tr>
<tr>
<td>0.001</td>
<td>0.063</td>
</tr>
<tr>
<td>0.001</td>
<td>0.019</td>
</tr>
<tr>
<td>0.001</td>
<td>0.0054</td>
</tr>
</tbody>
</table>
equation 2.19, for $\alpha$-PbO$_2$ and $\beta$-PbO$_2$ respectively. Figures 6.44. and 6.45. show complementary curves for the variation of [Pb(II)].

Figures 6.46. and 6.47. show the variation of the exchange current density with temperature in the form of Arrhenius plots. Throughout the whole experimental temperature range the impedance plots gave two parallel straight lines from which $R_D$ could be estimated.

Discussion of Impedance Results

The value of the frequency independent capacitance shunting the faradaic reaction, can be seen from Table 6.8. to be of the order of 150 - 210 $\mu$F cm$^{-2}$ in the case of the a.c. experiments and from Table 6.7., 90 - 115 $\mu$F cm$^{-2}$ from galvanostatic measurements. These latter values are in agreement with previously reported data$^{45-47}$. Even though a greater degree of uncertainty can be attached to the geometrically measured data, the difference between the two sets of results is significant. Both sets are considerably greater than the value of the double layer capacitance estimated from double layer measurements in non-interacting nitrate electrolyte solutions, allowing for concentration differences. It is clear that in the presence of the exchange reaction the double layer capacitance is abnormally high.

Since the faradaic impedance curves, figures 6.40. and 6.41, show no effects that can be ascribed to relaxation processes occurring at the electrode, the increased 'apparent' double layer capacitance can be regarded as an additional frequency independent capacitance due to adsorption, in parallel with the 'true' double layer capacitance and the faradaic impedance. The difference between the double layer capacitance values in the presence and absence of Pb(II) allows a value of the adsorption pseudocapacitance, $C_{ps}$, to be obtained. Since the adsorption pseudocapacitance is proportional to the coverage of the electrode by the adsorbed species, a guide to the form of the adsorption isotherm is given by the relationship between $C_{ps}$ and concen-
Fig. 6.44. Variation of exchange current with $[\text{Pb(III)}]$ for $\alpha$-$\text{PbO}_2$ in perchlorate electrolyte from impedance measurements.
Fig. 6.45. Variation of exchange current with $[\text{Pb}(\text{II})]$ for $\beta\text{PbO}_2$ in perchlorate electrolyte from impedance measurements.

$\begin{align*}
\frac{\delta \log_{10} i_0}{\delta \log_{10} [\text{Pb}(\text{II})]} &= 0.17 \\
\log_{10} \left( \frac{[\text{Pb}(\text{II})]}{\text{mol l}^{-1}} \right) &\leq -3.0 \\
\log_{10} \left( i_0 \right) &\geq 1.4
\end{align*}$
Fig. 6.46. Variation of exchange current with temperature for $\alpha$-PbO$_2$ in perchlorate electrolyte from impedance measurements.

ELECTROLYTE: 0.068 mol$^{-1}$ Pb(II)
1.0 mol$^{-1}$ H$^+$
TOTAL [ClO$_4^-$] 3 mol$^{-1}$ (WITH NaClO$_4$)

$\log_{10}(i_0)$ (mA cm$^{-2}$) vs. $\left(10^3/T\right)/K$
Fig. 6.47. Variation of exchange current with temperature for $\beta$-PbO$_2$ in perchlorate electrolyte from impedance measurements.
tration of adsorbed species in the bulk electrolyte. Figures 6.48. and 6.49. show plots of $\log_{10} \theta$ vs $\log_{10} [\text{Pb(II)}]$, where $\theta$ has been approximated to $C_{ps}$ for both polymorphs. The curves obey the relationship:

$$\log_{10} \theta = P_6 \log_{10} \beta_6 \alpha + \text{const} \quad (6.43)$$

or

$$\theta = \beta_6 \alpha^P_6 \quad (6.44)$$

which confirms the use of a similar isotherm in the interpretation of the galvanostatic measurements. Using such an isotherm to describe the possible adsorption at the electrode and the reaction mechanism indicated in equation 6.11 - 6.13, the exchange current can be expressed as:

$$i_o = z F k_6^0 \left[[\text{Pb(OH)}_2]_{\text{ads}}\right]^\alpha [\text{H}^+]^{2(1-\alpha)} \quad (6.45)$$

from which:

$$\left(\frac{\partial \log_{10} i_o}{\partial \log_{10} [\text{Pb(II)]}}\right)_{[\text{H}^+],\mu,T} = \alpha P_6$$

$$\left(\frac{\partial \log_{10} i_o}{\partial \log_{10} [\text{H}^+]\right)_{[\text{Pb(II)]},\mu,T} = 2(1-\alpha) - 2\alpha P_6$$

Table 6.9. summarizes the experimental concentration dependencies obtained from figures 6.42 - 6.45.

Using similar analysis to that used for the galvanostatic measurements to extract $\alpha$ and $P_6$ from the experimental values of Table 6.8. indicates that for $\alpha$-PbO$_2$, 

(85)
Fig. 6.48. Estimate of adsorption of Pb(II) on $\alpha$-PbO$_2$ from perchlorate electrolyte. Impedance measurements.
Fig. 6.49. Estimate of adsorption of Pb(II) on $\beta$-PbO$_2$

in perchlorate electrolyte. Impedance measurements.

**Graph Description:**
- **Y-axis:** $\log_{10}(C_{ads}/\mu F \text{ cm}^{-2})$
- **X-axis:** $\log_{10}([\text{Pb}]/\text{mol} \text{ l}^{-1})$
- **Total Electrolyte Concentration:** 3 mol l$^{-1}$ (with added NaClO$_4$)
- **H$^+$ Concentration:** 1.0 mol l$^{-1}$
Table 6.9.
Exchange current dependence on concentration of electroactive species estimated from impedance measurements.

Electrolyte total equivalent uni-univalent salt concentration 3 mol 1⁻¹ (with added NaClO₄)

<table>
<thead>
<tr>
<th></th>
<th>α-PbO₂</th>
<th>β-PbO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial \log_{10} i_0}{\partial \log_{10} [\text{Pb(II)}] [H^+], \mu, T} )</td>
<td>0.255</td>
<td>0.17</td>
</tr>
<tr>
<td>( \frac{\partial \log_{10} i_0}{\partial \log_{10} [H^+] [\text{Pb(II)}], \mu, T} )</td>
<td>0.02</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\( \alpha = 0.7 \) and \( P = 0.36 \) and for \( \beta \)-PbO₂, \( \alpha = 0.7 \) and \( P = 0.25 \).

Hence it can be concluded that adsorption of a Pb(II) species at the electrode occurs confirming the galvanostatic measurements, however, the impedance results indicate less adsorption than do the galvanostatic measurements.

Examination of the slope of the impedance curves for both polymorphs indicates that the Warburg coefficient varies with concentration in the expected manner, i.e. slope increases with decreasing \([\text{Pb(II)}] \) and \([H^+] \), but values are several orders of magnitude higher than expected from equation 2.38. It is clear from these results that for diffusion and double layer formation at the electrode/electrolyte interphase only a fraction of the total surface area is active. An estimate of the electrode area that is active can be calculated using equation 6.46.

\[
A = \frac{\sigma^{\text{calc}}}{\sigma^{\text{obs}}} \quad (6.46)
\]
where A is the active area and σ the Warburg coefficient. Table 6.10 summarizes the estimated active areas indicated in the present studies. Throughout the experimental concentration range the estimated active area never exceeded 9% of the total geometric area.

The reduction of the apparent surface area may be associated with the presence of a film on the electrode which significantly blocks the electrode reaction and reduces the double layer capacitance, but the high capacitance values and the exchange current densities obtained from the impedance measurements contradict such an effect. Alternatively, the surface of the electrode may contain a limited number of active sites at which the exchange reaction can proceed. Such active sites may be due to partial coverage of the electrode by an insoluble film of an oxide or oxy salt of Pb(II) rather than PbO which, with a low dielectric constant, would seriously reduce the frequency independent capacitance on the nucleation and thickening of a new phase.

The linearity of the impedance plots over the whole experimental concentration range indicates the absence of effects due to lattice building (crystallisation). Under the most favourable conditions, relaxation occurs over a spectrum of 100 fold change in frequency and consequently there would appear to be little possibility of crystallisation effects occurring in the present case. The electrode process therefore, is one of charge transfer at active sites on the electrode followed by direct transfer of Pb(II) species across the double layer and diffusion in solution.

The apparent greater active area of β-PbO₂ electrodes compared with α-PbO₂ could be an electrode geometric surface area effect. The double layer studies indicated that capacitance values for α-PbO₂ on the whole, were larger than for β-PbO₂ which suggests that the α-form has the larger true surface area. Under the conditions of exchange it has also been suggested that the α-form undergoes modification to the more acid stable β-form 47, equation 6.1., and such a process would also be expected to cause a surface expansion.
Table 6.10.

Estimate of the active area of electrodes from Warburg slopes

Electrolyte total equivalent uni-univalent salt concentration 3 mol 1⁻¹ (with added NaClO₄)

<table>
<thead>
<tr>
<th>Concentration mol 1⁻¹</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>H⁺</td>
<td>β-PbO₂</td>
<td>α-PbO₂</td>
<td></td>
</tr>
<tr>
<td>0.068</td>
<td>0.99</td>
<td>1.3</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>0.044</td>
<td>0.99</td>
<td>1.3</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>0.99</td>
<td>3.1</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>0.0072</td>
<td>0.99</td>
<td>5.0</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>0.0029</td>
<td>0.99</td>
<td>2.8</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.99</td>
<td>3.2</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.15</td>
<td>4.1</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.063</td>
<td>3.6</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.019</td>
<td>4.1</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.0054</td>
<td>4.1</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>

Temperature Dependence of Impedance Data

The Arrhenius plots, figures 6.45 and 6.46, indicate one linear relationship for both polymorphs. The activation enthalpy obtained from these plots was 15.5 kJ mol⁻¹ for β-PbO₂ and 34.4 kJ mol⁻¹ for α-PbO₂.

Comparison of Galvanostatic and Faradaic Impedance Results

The experimental values of the exchange current obtained by the faradaic impedance method are considerably greater than observed using the galvanostatic pulse technique. The reason for the significant difference seems to lie in the effect of rep-
etition of potential stimuli on the PbO$_2$ electrodes. To test this galvanostatic pulse experiments were designed so that the frequency of electrode potential perturbations in the a.c. experiments were approached by those of the galvanostatic measurements.

Figure 6.50. shows the potential response transients obtained for $\beta$-PbO$_2$ electrodes to which multiple current pulses have been applied (similar for $\alpha$-PbO$_2$). The magnitude of the overpotential is very significantly reduced as the frequency of the square pulse is increased. At a repetition time of 30 min. the transients were unaffected, the overpotentials being everywhere a maximum. The maximum value of the overpotential (adjusted for concentration overpotential to time = 0) gave a value of the exchange current predicted by the present galvanostatic experiments. The overpotential corresponding to the highest repetition rate experimentally available (lowest $\eta$) approached the exchange current obtained from faradaic impedance measurements in electrolyte solutions of similar concentration.

The behaviour can be explained as follows. It was suggested for the impedance measurements that the PbO$_2$ lattice is not completely reactive but contains isolated active sites. Each of these active sites has a life time, $\tau$, and if $\omega$ is the frequency of the a.c. applied, then three sets of conditions may be considered.

1. If $\omega \gg \tau$ the exchange current observed, $i_0 T$, will be a maximum since all the centres will be active.

2. If $\omega \sim \tau$ the observed exchange current, $i_{\text{app}}$, is much less than $i_0 T$ since not all the centres are active.

3. If $\omega \ll \tau$ the value of the observed exchange current, $i_0$, represents the equilibrium number of centres.

In the faradaic impedance method the frequency of the a.c. used (minimum repetition time of 20 times sec$^{-1}$) used was much greater than $\tau$ and the exchange current
Fig. 6.50. Effect of repetition of short current pulses (60 ms) on overpotential-time transients for $\beta$-PbO$_2$.

CURRENT DENSITY 1 mA cm$^{-2}$
PULSE DELAY 20 ms.
NO. OF PULSES - (a) 1; (b) 10; (c) 20; (d) 100; (e) 200.

```
[Graph showing overpotential-time transients with curves labeled a through e.]
```
observed is $i_0$. It is noteworthy that the impedance curves always showed a tendency to depart from "ideal behaviour", at frequencies $< 40$ Hz. Therefore $\tau$ must be less than $\sim 25$ ms. In the galvanostatic measurements pulse times of $70$ ms were used in order to extract the required overpotential data, i.e. the time span of the experiment was much greater than the life time of an active site.

It is the potential excursion which apparently results in the formation of active centres for although current was passing across the interphase continually, figure 6.51. shows that the overpotential ultimately approaches that of the "long time" experiment. Thus "activation" is due to potential changes rather than the passage of charge across the interphase.

Conclusions

In aqueous $\text{HClO}_4$ and $\text{NaClO}_4$ solutions, the differential capacitance curves indicate that the electrode/electrolyte interphase is complicated by adsorption.

The exchange reaction in acid perchlorate solutions is complicated by adsorption of $\text{Pb(OH)}_2$ from solution. The rate of the exchange reaction, measured by the faradaic impedance method, is considerably greater in magnitude than that measured using the galvanostatic single pulse method. The general features of the reaction agree well for both methods and indicate that the reaction takes place in steps and involves a charge transfer reaction involving a simultaneous two electron transfer. For galvanostatic measurements at high overpotentials a charge transfer reaction involving two consecutive single electron transfers is indicated. It would seem that the reason for the higher exchange current densities as measured by the a.c. method is due to lattice activation by the application of repetitive potential stimulli.

(90)
Fig. 6.51. Effect of "long time" polarisation on overpotential for a $\beta$-PbO$_2$ electrode previously activated by repeated short time (60 ms) pulses.

**CURRENT DENSITY 1 mA cm$^{-2}$**

(a) NO PREVIOUS PULSES

(b) 200 PREVIOUS PULSES
CHAPTER 7

THE ELECTROCHEMICAL BEHAVIOUR OF PbO₂ IN SULPHATE ELECTROLYTES

7.1. The Electrical Double Layer

Test electrodes and experimental procedure were as described in Chapter 3.

Results

Figure 7.1 shows typical faradaic current - bias potential curves for α and β-PbO₂ in H₂SO₄ solutions indicating experimental polarizable regions of ~ 1.25 - 1.95 V for α-PbO₂ and ~ 1.25 - 1.85 V for β-PbO₂. The potential of zero faradaic current flow was slightly more positive for α-PbO₂ than for β-PbO₂. The electrodes were no-where ideally polarizable.

Figures 7.2. and 7.3. show a series of differential capacitance - bias potential curves for α and β-PbO₂ respectively. For potential within the experimental polarizable region stable impedance measurements were obtained after 24 hrs. electrode/electrolyte contact time for both polymorphs. Initial electrode/electrolyte contact was accompanied by an appreciable capacitance rise, being a maximum after ~ 12 hrs, thereafter falling slightly until stable and reproducible results were obtained. The initial rise in the capacitance was accompanied by a fall in the electrode resistance. For both polymorphs serious hysteresis of the impedance measurements was observed for potential excursions outside the experimental polarisable limits and impedance measurements never returned to their original values. Potential excursions within the polarizable region resulted in negligible hysteresis. Reproducibility of impedance measurements showed a 10% variation about a mean. Figures 7.4. and 7.5. show the extent of the frequency dispersion of the capacitance curves. The dispersion amounted to
Fig. 7.1. Faradaic current-bias potential for PbO₂ in H₂SO₄ electrolyte.
Fig. 72. Differential capacitance-bias potential curves for \( \alpha \)-PbO\(_2\) in \( H_2SO_4 \) electrolyte

Electrolyte conc.
- 0.17 mol\(^{-1}\)
- 0.056 mol\(^{-1}\)
- 0.031 mol\(^{-1}\)
- 0.017 mol\(^{-1}\)
- 0.0046 mol\(^{-1}\)

Frequency 120 Hz
Fig. 7.3. Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in H$_2$SO$_4$ electrolyte.
Fig. 74. Typical frequency dispersion of differential capacitance curves for \( \alpha \)-PbO\(_2\) in \( H_2SO_4 \) electrolyte.
Fig. 7.5 Typical frequency dispersion of differential capacitance curves for $\beta$-PbO$_2$ in $\text{H}_2\text{SO}_4$ electrolyte.

ELECTROLYTE 0.031 mol$^{-1}$ $\text{H}_2\text{SO}_4$

- ○ 120 Hz
- ⋄ 300 Hz
- △ 500 Hz
- ▲ 1000 Hz
\[\sim 40\%\text{ for a frequency change }1 \text{ k Hz} - 500 \text{ Hz}.\]

Figure 7.6. shows typical faradaic current - bias potential curves for \(\alpha\) and \(\beta\)-PbO\(_2\) in K\(_2\)SO\(_4\) solutions. The experimental polarizable region amounted to \(\sim 0.5 \text{ V}\) for both polymorphs. In both cases the position of the experimental polarizable region was strongly dependent upon pH; at pH 12 the range 0.95 - 1.45 V was available whereas at pH 1.8 the region had shifted to more positive potentials 1.45 - 1.95 V.

Figures 7.7. and 7.8. show a series of differential capacitance - bias potential curves for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively for the pH range 1.8 - 12. When potentials were confined to within the experimental polarizable region some time variation of the impedance measurements was observed within the first 3 hrs. of electrode/electrolyte contact; thereafter impedance readings remained fairly stable for \(\sim 10 \text{ hrs.}\) and showed little hysteresis for potential excursions within the experimental polarizable region. For potential excursions outside the experimental polarizable region hysteresis was observed and impedance values never returned to their original values.

Figures 7.9. and 7.10. show the extent of the dispersion of capacitance with frequency for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively. The dispersion was greatest at low pH.

**Discussion of the Differential Capacitance Results**

The form of the differential capacitance curves in both H\(_2\)SO\(_4\) and K\(_2\)SO\(_4\) solutions is completely unlike those obtained in nitrate solutions. The broad capacitance minimum indicates the possibility of adsorption of solution species at the interphase. The in-phase (resistive) component of the electrode impedance was fairly constant throughout the polarizable region for both H\(_2\)SO\(_4\) and K\(_2\)SO\(_4\) solutions, indicating little or no change of the double layer structure in this region, however, at the extremities an abrupt rise was observed. The positive limit of the experimental polarizable region can be associated with the oxygen evolution reaction and the negative
Fig. 7.6. Faradaic current-bias potential curves for PbO$_2$ in K$_2$SO$_4$ electrolyte.
Fig. 7.7. Differential capacitance - bias potential curves for $\alpha$-PbO$_2$ in sulphate electrolyte.
Fig. 7.8. Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in sulphate electrolyte.

- Electrolyte: 0.034 mol$^{-1}$ $K_2$SO$_4$
- pH Values: 1.8, 2.5, 3.0, 3.4, 3.8, 6.0, 12.0
- Frequency: 120 Hz

Capacitance / $\mu$F cm$^{-2}$ vs. $E_{(NHE)}$ / V
Fig. 7.9. Typical frequency dispersion of differential capacitance curves for $\alpha$-PbO$_2$ in sulphate electrolyte.

Electrolyte: 0.034 M K$_2$SO$_4$, pH 3.4

- 120 Hz
- 300 Hz
- 500 Hz
- 1000 Hz
Fig. 7.10. Typical frequency dispersion of differential capacitance curves for \( \beta \)-PbO\(_2\) in sulphate electrolyte.
limit with the onset of the development of a layer of lead sulphate on the reduced electrode. Potential excursions negative of the experimental polarizable region caused the capacitance to decrease significantly and, at a fixed potential, the capacitance was time dependent, inferring a possible thickening of the lead sulphate film and capacitance reduction in accordance with the 'parallel plate' formula.

The form of the capacitance curves is similar for each pH value studied but, in H$_2$SO$_4$ solutions, due to the severe breakdown of the electrode at the negative extremity of the polarizable region, potential excursions were never made such that a capacitance peak could be observed as for K$_2$SO$_4$ solutions. The magnitude of the capacitance and frequency dispersion of capacitance increases as pH decreases indicating participation of H$^+$ ions in the structure of the interphase. The direct adsorption of H$^+$ ions at the electrode is unlikely since, in the present experiments, the experimental polarizable region is at positive rational potentials. The possibility of adsorption of SO$_4^{2-}$, HSO$_4^-$ or H$_2$SO$_4$ exists and also reactions of the type:-

$$H^+ + SO_4^{2-} \text{ads} = HSO_4^- \text{ads} \quad (7.1)$$

$$4 HSO_4^- \text{ads} + PbO_2 + 2e = PbSO_4 \text{ads} + 3SO_4^{2-} + 2H_2O \quad (7.2)$$

would lead to a pseudocapacitance. The pseudocapacitance peak at negative potentials can be associated with reactions of the type indicated in equation 7.2. At high pH values, although similar reactions to equation 7.1 and 7.2 are less favoured, it is likely that OH$^-$ ions will be adsorbed and may even displace sulphate. Under conditions of high pH the potential of lattice dissolution would be expected to occur at increasingly negative potentials as reactions 7.1 and 7.2 are suppressed, and this is observed in practice (figures 7.7 and 7.8).

The difference between the behaviour of $\alpha$ and $\beta$-PbO$_2$ electrodes in sulphate
electrolytes is only marginal. It would appear that the adsorption of sulphate and presence of surface reactions of the type discussed above obscure surface structural differences between the two polymorphs.

7.2. The Exchange Reaction

(a) Galvanostatic Measurements

The galvanostatic experimental procedure was as described in Chapter 3. Measurements were commenced after 20 mins. electrode/electrolyte contact time in electrolytes maintained at 3 mol \(1^{-1}\) uni-univalent salt concentration with added \(\text{NaClO}_4\). Reproducibility was \(\pm 7\%\) and the ohmic overpotential was generally < 5% of \(\eta_D\). Two series of experiments were performed; in the first \([H^+]\) was varied at constant \([\text{SO}_4^{2-}\]) and \([\text{Pb(II)}]\) and in the second \([\text{SO}_4^{2-}\]) varied at constant \([\text{Pb(II)}]\) and \([H^+]\). No experiments were performed at varying \([\text{Pb(II)}]\) due to the very low solubility of \([\text{Pb(II)}]\) salts in sulphate electrolytes.

Experimental Results

Figure 7.11. shows a typical overpotential - time transient for \(\alpha-\text{PbO}_2\). Transients for \(\beta-\text{PbO}_2\) were of a similar form. The form of the transients for both polymorphs were similar to those observed in perchlorate electrolytes. Values of \(\eta_D\) were obtained by extrapolation of the linear section of the transient to zero time.

Figures 7.12. and 7.13. show typical faradaic current - overpotential curves for \(\alpha\) and \(\beta-\text{PbO}_2\) respectively, corresponding to measurements at low overpotentials \((\eta_D < 7 \text{ mV})\) in electrolytes of varying \([H^+]\) at constant \([\text{SO}_4^{2-}\]) and \([\text{Pb(II)}]\). Complementary data for electrolytes of varying \([\text{SO}_4^{2-}\]) at constant \([H^+]\) and \([\text{Pb(II)}]\) were also obtained. The exchange current, calculated from the slope of the \(i-\eta_D\) curves at the origin, was identical for both anodic and cathodic processes.
Fig. 7.11. Typical overpotential-time transient for PbO₂ in sulphate electrolyte

Electrolyte: 3 M total equivalent uni univalent ionic concentration (with added NaClO₄)

\[
\begin{align*}
\text{[Pb(II)]} & \quad 0.000018 \text{ mol} \\
\text{[H⁺]} & \quad 0.009 \text{ mol} \\
\text{[SO₄²⁻]} & \quad 0.2 \text{ mol l} \\
\end{align*}
\]

Cathodic pulse current: 0.14 mA cm²
Electrode/electrolyte contact time: 30 min.
Electrode area: 4.9 x 10⁻² cm²
Fig. 7.12. Faradaic current - overpotential curves for \( \alpha \)-PbO\(_2\) in sulphate electrolyte.
Fig. 7.13. Faradaic current-overpotential curves for $\beta$-PbO$_2$ in sulphate electrolyte.

ELECTROLYTE 0.2 mol$^{-1}$ SO$_4^{2-}$
TOTAL ANION CONC 3 mol$^{-1}$
(WITH KClO$_4$)

- 0.006 mol$^{-1}$ H$^+$
- 0.047 mol$^{-1}$ H$^+$
- 0.148 mol$^{-1}$ H$^+$
Figures 7.14. and 7.15. show the variation of the exchange current with \([H^+]\) for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively. No change in the exchange current was observed for varying \([SO_4^{2-}]\).

Figures 7.16. and 7.17. show the effect of temperature on the exchange current in the form of Arrhenius plots. Throughout the whole of the experimental temperature range the anodic and cathodic exchange current densities were alike.

Figures 7.18. and 7.19. show typical faradaic current - overpotential curves for \(\alpha\) and \(\beta\)-PbO\(_2\) in electrolytes of varying \([H^+]\) at constant \([SO_4^{2-}]\) and \([\text{Pb(II)}]\) corresponding to anodic and cathodic measurements at high overpotentials (Tafel plots). Complementary curves for varying \([SO_4^{2-}]\) at constant \([H^+]\) and \([\text{Pb(II)}]\) showed little variation with concentration. The kinetic parameters, transfer coefficient and apparent exchange current, obtained from the slope and intercept of the linear curve, are summarized in Tables 7.1. and 7.2. for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively,

Figures 7.20. and 7.21. show the variation of the apparent exchange current with \(H^+\) for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively.

Figures 7.22. and 7.23. show the variation of the anodic current, at constant potential, with concentration of \(H^+\) for \(\alpha\) and \(\beta\)-PbO\(_2\) respectively and figures 7.24. and 7.25. the variation of the cathodic faradaic current at constant potential with concentration of \(H^+\).

Discussion of Galvanostatic Results

Potential measurements at zero faradaic current flow indicate that both polymorphs obey the relationship:

\[
\left( \frac{\varepsilon E}{\delta [H^+] [\text{Pb(II)}]_{SO_4^{2-}} \mu, T} \right)_0 = +118 \text{ mV}
\]  

(7.3)

which corresponds to the involvement of 4 molecules of \(H^+\) in the equilibrium reaction.
Fig. 7.14. Variation of exchange current with $[H^+]$ for $\alpha$-PbO$_2$ in sulphate electrolyte from galvanostatic measurements.

ELECTROLYTE: 0.2 mol l$^{-1}$ SO$_4^{2-}$
TOTAL ANION CONC 3 mol l$^{-1}$ (WITH KClO$_4$)
0.000018 mol l$^{-1}$ Pb(II)

\[
\frac{\delta \log i_0}{\delta \log [H^+]} = 0.49
\]
Fig. 7.15. Variation of exchange current with $[H^+]$ for $\beta$-PbO$_2$ in sulphate electrolyte from galvanostatic measurements.

**Diagram:**
- **Electrolyte:** 0.2 mol l$^{-1}$ (SO$_4^{2-}$)
- **Total Anion Conc.** 3 mol l$^{-1}$ (with KCIO$_4$
- **0.000018 mol l$^{-1}$ Pb(II)

**Equation:**
\[
\frac{\delta \log_{10} i_0}{\delta \log_{10} [H^+]} = 0.47
\]
Fig. 7.16 Variation of exchange current with temperature for $\alpha$-PbO$_2$ in sulphate electrolyte from galvanostatic measurements.

Electrolyte: $0.018$ mol/l $H^+$
$0.2$ mol/l $SO_4^{2-}$
Total anion conc. $3$ mol/l (with KClO$_4$)
$0.000018$ mol/l $Pd(II)$
Fig. 7.17: Variation of exchange current with temperature for $\beta$-PbO$_4$ in sulphate electrolyte from galvanostatic measurements.

Electrolyte:
- 0.018 mol$^{-1}$ H$^+$
- 0.2 mol$^{-1}$ [SO$_4^{2-}$]
- Total anion conc 3 mol$^{-1}$ (with KClO$_4$)
- 0.000018 mol$^{-1}$ Pb(II)

$log_{10}(i_0 \text{ mA cm}^{-2})$

$(10^3/\theta)_K^*$
Fig. 7.19 Faradaic current-overpotential (Tafel region) curves for PbO$_2$ in sulphate electrolyte.

ELECTROLYTE 3 mol/l$^{-}$ (WITH ADDED NaClO$_4$)
- 0.2 mol/l$^{-}$ SO$_4^{2-}$
- 0.006 mol/l$^{-}$ H$^+$
- 0.013 mol/l$^{-}$ H$^+$
- 0.03 mol/l$^{-}$ H$^+$
- 0.047 mol/l$^{-}$ H$^+$
- 0.099 mol/l$^{-}$ H$^+$
- 0.148 mol/l$^{-}$ H$^+$

CATHODIC

ANODIC

$\log(I/\text{mA cm}^{-2})$ vs. OVERPOTENTIAL/$\nu$
Fig. 7.20. Variation of apparent exchange current with \([H^+]\) for \(\alpha-PbO_2\) in sulphate electrolyte. Galvanostatic measurements.

**ELECTROLYTE** 3 mol l\(^{-1}\) (WITH ADDED \(NaClO_4\))

- 0.2 mol l\(^{-1}\) \(SO_4^{2-}\)
- 0.000018 mol l\(^{-1}\) \(Pb(II)\)

○ ANODIC
● CATHODIC
Fig. 7.21. Variation of apparent exchange current with \([H^+]\) for \(\beta\)-PbO\(_2\) in sulphate electrolyte.

Galvanostatic measurements.
Fig. 722. Dependence of anodic current on \([H^+]\), Tafel region measurements, for \(\gamma\)-PbO\(_2\) in sulphate electrolyte.

**Diagram:**

- **Electrolyte:** 3 mol\(\text{l}^{-1}\) (with added NaClO\(_4\))
  - 0.2 mol\(\text{l}^{-1}\) \(\text{SO}_4^{2-}\)
  - 0.000018 mol\(\text{l}^{-1}\) Pb(II)

\[
\frac{\Delta \log_{10} i}{\Delta \log_{10} [H^+]} = 0.46
\]

**Equation:**

\[
\log_{10}(i/\text{mA cm}^{-2})
\]

\[
\log_{10}([H^+] / \text{mol l}^{-1})
\]
Fig. 7.23. Dependence of anodic current on $[\text{H}^+]$, Tafel region measurements, for $\beta$-PbO$_2$ in sulphate electrolyte.

ELECTROLYTE 3 mol$^{-1}$ (WITH ADDED NaClO$_4$)

0.000018 mol$^{-1}$ Pb(II)

0.2 mol$^{-1}$ SO$_4^{2-}$

$\frac{\Delta \log_{10} i}{\Delta \log_{10} [\text{H}^+]} = 0.5$

$E = 0.15 \text{ V}$

$E = 0.2 \text{ V}$
Fig. 724: Variation of cathodic current with $[H^+]$, Tafel region measurements, for $\alpha$-PbO$_2$ in sulphate electrolyte.

ELECTROLYTE 3 mol l$^{-1}$ (WITH ADDED NaClO$_4$)

0.2 mol l$^{-1}$ SO$_4^{2-}$

0.000018 mol l$^{-1}$ Pb(II)

$E = -0.4\text{V}$

$E = -0.3\text{V}$

$E = -0.2\text{V}$

$\frac{\delta \log i}{\delta \log [H^+]} = 1.4$
Fig. 7.25. Dependence of cathodic current on \([H^+]\), Tafel region measurements, for \(\beta\)-PbO\(_2\) in sulphate electrolyte.

![Graph showing the dependence of cathodic current on \([H^+]\) for \(\beta\)-PbO\(_2\) in sulphate electrolyte. The graph includes a line with a slope of 0.9 and points at different potentials: E = -0.4 V, E = -0.3 V, and E = -0.2 V. The electrolyte is 3 mol\(\text{l}^{-1}\) with added NaClO\(_4\), containing 0.00018 mol\(\text{l}^{-1}\) Pb(II), 0.2 mol\(\text{l}^{-1}\) SO\(_4^{2-}\).]
Characteristics of Tafel Plots

\( \text{PbO}_2 \) electrode in acid sulphate electrolytes at 23°C. Total equivalent uni-univalent ionic concentration 3 mol l\(^{-1}\) with added NaClO\(_4\). [SO\(_4^{2-}\)] 0.2 mol l\(^{-1}\). [Pb(II)] 0.000018 mol l\(^{-1}\).

<table>
<thead>
<tr>
<th>Concentration (mol (l^{-1}))</th>
<th>Cathodic Coeff.</th>
<th>Anodic Coeff.</th>
<th>Intercept at ( \eta_D = 0 ) (2 (i_0 ) mA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cathodic</td>
<td>Anodic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coeff.</td>
<td>Coeff.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{2.3RT \varepsilon \log_{10}i_c}{zF \partial \eta_D} )</td>
<td>( \frac{2.3RT \varepsilon \log_{10}i_A}{zF \partial \eta_D} )</td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td>H(^+)</td>
<td>Cathodic</td>
<td>Anodic</td>
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<tr>
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<td>0.0061</td>
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<td>0.047</td>
<td>0.18</td>
<td>0.80</td>
</tr>
<tr>
<td>0.000013</td>
<td>0.099</td>
<td>0.18</td>
<td>0.80</td>
</tr>
<tr>
<td>0.000013</td>
<td>0.148</td>
<td>0.18</td>
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<td>0.891</td>
<td>6.31</td>
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</tr>
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</table>
Table 7.2.

Characteristics of Tafel Plots

$\beta$-PbO$_2$ electrode in acid sulphate electrolytes at 23$^\circ$C. Total equivalent uni-univalent ionic concentration 3 mol $1^{-1}$ with added NaClO$_4$. $[SO_4^{2-}]$ 0.2 mol $1^{-1}$. [Pb(II)] 0.000018 mol $1^{-1}$.

<table>
<thead>
<tr>
<th>Concentration (mol $1^{-1}$)</th>
<th>Cathodic Coeff. $-\left(\frac{2.3 RT}{zF} \log_{10} \frac{i_c}{\eta D}\right)$</th>
<th>Anodic Coeff. $\frac{2.3 RT}{zF} \log_{10} \frac{i_A}{\eta D}$</th>
<th>Intercept at $\eta D = 0$ (2mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>$H^+$</td>
<td>$H^+$</td>
<td>$H^+$</td>
</tr>
<tr>
<td>0.000013</td>
<td>0.061</td>
<td>0.16</td>
<td>0.57</td>
</tr>
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<td>0.000013</td>
<td>0.013</td>
<td>0.17</td>
<td>0.58</td>
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<td>0.17</td>
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<td>0.58</td>
</tr>
<tr>
<td>0.000013</td>
<td>0.148</td>
<td>0.17</td>
<td>0.57</td>
</tr>
</tbody>
</table>
These results are in agreement with the electrode reaction:

\[ \text{PbO}_2 + 4 \text{H}^+ + 2 \text{e} = \text{Pb(II)} + 2 \text{H}_2\text{O} \]  \hspace{1cm} (7.4)

The dependence of the cathodic current density for reaction 7.4., \( i_c \), on the concentration of electroactive species can be written as:

\[ i_c = k_{7c} [\text{H}^+]^x \]  \hspace{1cm} (7.5)

and for the anodic reaction:

\[ i_A = k_{7A} [\text{Pb(II)}]^y [\text{H}^+]^z \]  \hspace{1cm} (7.6)

where \( k_{7c} \) and \( k_{7A} \) are potential dependent rate constants, \( x \), \( y \) and \( z \) are the orders of reaction. Table 7.3 summarises the experimental orders of reaction obtained from figures 7.22 - 7.25.

As complementary data for the variation \([\text{Pb(II)}]\) could not be obtained a full mechanistic picture can not be proposed. Comparison of the \( \text{H}^+ \) ion orders of reaction with the corresponding data for perchlorate electrolytes (Chapter 6) indicates that the reaction in sulphate electrolytes has similar characteristics. In perchlorate electrolytes it was proposed that the electrode reaction involved diffusion in solution and the present experimental results in sulphate electrolytes indicate that a similar process may occur.

That a diffusion process is involved is in contrast with a number of examples of insoluble film formation on solid electrodes which have usually followed a solid state nucleation and growth mechanism directly at the electrode surface \( 149,150 \). It is also interesting that for the formation of \( \text{PbSO}_4 \) on electropolished Pb, Archdale and Harrison \( 151 \) suggested that the rate controlling reaction is diffusion of \( \text{Pb(II)} \) from the electrode into the solution which forming a weak complex with \( \text{SO}_4^{2-} \) ions.
Table 7.3.

Experimental orders of reaction estimated from galvanostatic measurements

Electrolyte total equivalent uni-univalent ionic concentration 3 mol l⁻¹ (with added NaClO₄). [SO₄²⁻] 0.2 mol l⁻¹, [Pb(II)] 0.000018 mol l⁻¹

<table>
<thead>
<tr>
<th></th>
<th>α-PbO₂</th>
<th>β-PbO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>α log₁₀ i₀</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>α log₁₀ [H⁺] [Pb(II)], μ, T, E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(α log₁₀ iₐ)</td>
<td>-0.46</td>
<td>-0.51</td>
</tr>
<tr>
<td>α log₁₀ [H⁺] [H⁺], μ, T, E</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus a reaction mechanism that may describe the electrode process involved at PbO₂ electrodes in sulphate electrolytes is that proposed for perchlorate electrolytes viz. equation 6.11 - 6.13, involving diffusion of Pb(II) species in solution.

From the measurements at low overpotentials the values of the exchange current densities indicate that the reaction is slow. The apparent charge transfer coefficient, obtained from figures 7.14 and 7.15, approximates to 0.5 which would be expected of a symmetric reaction relatively uncomplicated by adsorption, however, more than qualitative deductions cannot be made from the present experiments.

From measurements at high overpotentials the mean values for the anodic and cathodic Tafel coefficients, Tables 7.1 and 7.2, are 0.87 and -0.18 for α-PbO₂ and 0.58 and -0.17 for β-PbO₂. The apparent exchange current densities for the anodic and cathodic measurements are significantly different from each other to suggest that, at high overpotentials, the anodic and cathodic processes are different.
For the cathodic Tafel curves, although the apparent exchange current densities are different for the two polymorphs, the Tafel coefficients are essentially the same indicating that the same cathodic reaction applies for both polymorphs. Comparison of the Tafel coefficients for sulphate and perchlorate electrolytes show significant differences, however, in perchlorate systems the reaction is relatively uncomplicated by insoluble Pb(II) products whereas for sulphate solutions the reaction is complicated by intrusion of insoluble PbSO$_4$. The PbSO$_4$ may not necessarily intrude on the electrode surface but may reduce diffusion of Pb(II) species to the electrode resulting in the lower Tafel slopes observed.

At high anodic overpotential, there exists the possibility of more than one reaction occurring at the electrode. The theoretical standard potential for the $\text{O}_2/\text{H}_2\text{O}$ reaction is 1.23 V and for the PbO$_2$/PbSO$_4$ electrode ~ 1.7 V. Thus thermodynamically water should decompose upon contact with PbO$_2$ and the fact that PbO$_2$ is essentially stable in aqueous solutions is due to the slowness of the $\text{O}_2$ evolution reaction, which requires relatively high overpotential to proceed at significant rates. Hence, although at potentials close to the equilibrium potential the oxygen evolution reaction is slow and has a negligible effect on the overall electrode reaction, as the anodic potential increases $\text{O}_2$ evolution will increase and may no longer be neglected. A further complication arises due to the low concentration of Pb(II) present. At high anodic potentials, the electrolyte layers in the immediate vicinity of the electrode will rapidly become depleted of Pb(II) species and diffusion of the Pb(II) species in the solution will become the rate determining step. Diffusion of the Pb(II) species will be relatively slow due to the complex formation of Pb(II) with SO$_4^{2-}$. Thus at high anodic overpotentials only a qualitative estimation of the kinetics of the electrode reaction can be made.

A number of workers have studied the oxygen evolution on PbO$_2$ electrodes (appendix 1) and have indicated Tafel slopes of ~ 0.14 for $\beta$-PbO$_2$ and ~ 0.07 for $\alpha$-PbO$_2$. (100)
Both these values approximate to the experimental Tafel slopes indicating that under the present experimental conditions the predominant electrode reaction is \( \text{O}_2 \) evolution. Ruetschi concluded\(^{152}\) that the Tafel slope for \( \alpha\text{-PbO}_2 \) is characteristic of a two electron change whilst for \( \beta\text{-PbO}_2 \) the rate determining step involves a one electron change. \( \alpha\text{-PbO}_2 \) behaves to some extent like an oxygen electrode in alkaline solution but \( \beta\text{-PbO}_2 \) is similar to many metals in acid solutions\(^{153}\).

Assuming that a two electron change is involved in the rate determining step in the case of oxygen evolution on \( \alpha\text{-PbO}_2 \) and that the experimental Tafel slopes correspond almost solely to this reaction, then an apparent exchange coefficient of \( \sim 0.44 \) is obtained. Similarly for \( \beta\text{-PbO}_2 \), assuming a one electron exchange, an apparent exchange coefficient of 0.58 is obtained.

Thus the different behaviour observed in the anodic branches of the Tafel curves for perchlorate and sulphate solutions may be due to the relative solubilities of the \( \text{Pb(II)} \) products in the respective solutions. In perchlorate solutions, the electrolyte layers in the vicinity of the electrode will contain sufficient \( \text{Pb(II)} \) to enable the \( \text{Pb(II)}/\text{Pb(IV)} \) exchange reaction to take place in preference to the oxygen evolution reaction. In sulphate solutions the low solubility of \( \text{Pb(II)} \) severely restricts the \( \text{Pb(II)}/\text{Pb(IV)} \) reaction and the oxygen evolution reaction predominates.

**Temperature dependence of the galvanostatic measurements**

In the low overpotential region, the Arrhenius plots, figures 7.16 and 7.17, indicate enthalpies of activation of 46.8 kJ mol\(^{-1}\) for \( \beta\text{-PbO}_2 \) and 54.3 kJ mol\(^{-1}\) for \( \alpha\text{-PbO}_2 \). Both these values compare with values obtained in other electrolyte systems. For Tafel region measurements, temperature increases caused an increase in the Tafel coefficients for both polymorphs, however, at the higher temperatures overpotential measurements became less reproducible, and measurements unreliable.

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Faradaic Impedance Measurements

The faradaic impedance method and treatment of results was as described in Chapter 3. Measurements were commenced after 24 hrs. electrode/electrolyte contact time during which time the test electrodes were kept on open circuit.

Experimental Results

As a first step in analysing the faradaic impedance results the experimental data was represented as a transformation in the complex plane. Such a representation is shown in figures 7.26 and 7.27. for α and β-PbO₂ respectively. A single line, of slope 45°, is obtained for both polymorphs indicating that the major rate controlling process is diffusion in solution. Clearly from figures 7.26. and 7.27., values of the electrode capacitance and electrolyte resistance cannot be obtained, however since a diffusion controlled reaction is indicated, it seems feasible to match the impedance data to the correct behaviour of the Warburg impedance, in accordance with the method described in Chapter 3.

Figures 7.28. and 7.29. show sets of typical faradaic impedance data matched to the correct behaviour of the Warburg impedance for α and β-PbO₂ respectively. Two parallel straight lines were obtained for the in-phase and out-of-phase components in the experimental frequency range (80 - 5000 Hz). Two series of experiments were performed; in the first [H⁺] was varied at constant [Pb(II)] and [SO₄²⁻] and in the second [SO₄²⁻] varied at constant [H⁺] and [Pb(II)].

Figures 7.30. and 7.31. show the variation of the exchange current with [H⁺] for α and β-PbO₂ respectively. Exchange current densities were obtained by extrapolation of the impedance plots to infinite frequency. Figures 7.32. and 7.33. show the variation of the exchange current density with [SO₄²⁻].

Figures 7.34. and 7.35. show the variation of the exchange current density with
Fig. 7.26. Complex plane impedance plot for $\alpha$-PbO$_2$ in sulphate electrolyte.

ELECTROLYTE 3 mol/l TOTAL EQUIVALENT UNI-UNIVALENT IONIC CONC. (WITH ADDED NaClO$_4$)

- $[\text{Pb}^{II}] = 0.00018$ mol/l
- $[\text{H}^+] = 0.17$ mol/l
- $[\text{SO}_4^{2-}] = 0.2$ mol/l

ELECTRODE/ELECTROLYTE CONTACT TIME 26 hrs., ELECTRODE AREA $4.9 \times 10^{-2}$ cm$^2$. 
Fig. 7.27: Complex plane impedance plot for $\beta$-PbO$_2$ in sulphate electrolyte.

ELECTROLYTE: 3 mol/l TOTAL EQUIVALENT UNI-UNIVALENT IONIC CONC. (WITH ADDED NaClO$_4$

- [Pb(II)] $0.000018$ mol/l
- [$H^+$] $0.64$ mol/l
- [$SO_4^{2-}$] $0.2$ mol/l

ELECTRODE/ ELECTROLYTE CONTACT TIME 26 hrs ELECTRODE AREA $4.9 \times 10^{-3}$ cm$^2$
Fig. 7.29. Typical impedance curves for $\beta$-PbO$_2$ in sulphate electrolyte.

**ELECTROLYTE** 3 moll$^{-1}$ TOTAL EQUIVALENT UNI-UNIVALENT IONIC CONC. (WITH ADDED NaClO$_4$)

\[
\begin{align*}
[Pb(II)] &\quad 0.000018 \text{ moll}^{-1} \\
[H^+] &\quad 0.17 \text{ moll}^{-1} \\
[SO_4^{2-}] &\quad 0.2 \text{ moll}^{-1}
\end{align*}
\]

ELECTRODE/ELECTROLYTE CONTACT TIME 26 hrs
ELECTRODE AREA $4.9 \times 10^{-3} \text{ cm}^2$
Fig. 7.30. Variation of exchange current with \([H^+]\) for \(\alpha\)-PbO\(_2\) in sulphate electrolyte from impedance measurements.

\[
\text{TOTAL ELECTROLYTE EQUIVALENT UNI-UNIVALENT IONIC CONCENTRATION (WITH ADDED NaClO\(_4\))}
\]

- \([\text{Pb (II)}]\) 0.000018 mol/l
- \([\text{SO}_4^{2-}\)] 0.2 mol/l

\[
\text{Log}_{10}(i_0/\text{mA cm}^{-2})
\]

\[
\text{Log}_{10}([H^+]_\text{mol/l})
\]
Fig. 7.31. Variation of exchange current with \([H^+]\) for \(\beta\)-PbO\(_2\) in sulphate electrolyte from impedance measurements.

**ELECTROLYTE 3 mol\(^{-1}\) TOTAL EQUIVALENT UNI-UNIVALENT IONIC CONC. (WITH ADDED NaClO\(_4\))**

- \([\text{Pb}^{(II)}]\) 0.000018 mol\(^{-1}\)
- \([\text{SO}_4^{2-}\)] 0.2 mol\(^{-1}\)
Fig. 7.32. Variation of exchange current with \([SO_4^{2-}]\) for \(\alpha\)-PbO\(_2\) in sulphate electrolyte from impedance measurements.

ELECTROLYTE 3 mol\(^{-1}\) TOTAL EQUIVALENT UNI-UNIQUAVENT
IONIC CONC. (WITH ADDED NaClO\(_4\))

\[
\begin{align*}
[\text{Pb (II)}] & \quad 0.000018 \text{ mol}\,\text{l}^{-1} \\
[H^+] & \quad 0.51 \text{ mol}\,\text{l}^{-1}
\end{align*}
\]
Fig.7.33. Variation of exchange current with \([\text{SO}_4^{2-}]\) for \(\beta\)-PbO\(_2\) in sulphate electrolyte from impedance measurements.

**Electrolyte:** 3 mol\(^{-1}\) total equivalent uni- univalent ionic concentration (with added NaClO\(_4\))

\[[\text{Pb}^{2+}] \quad 0.00018\text{mol} \, \text{l}^{-1}\]

\[[\text{H}^+] \quad 0.51\text{mol} \, \text{l}^{-1}\]
Fig. 7.34. Variation of exchange current with temperature for α-PbO₂ in sulphate electrolyte from impedance measurements.

ELECTROLYTE: 3 mol l⁻¹ TOTAL EQUIVALENT
UNI-UNIVALENT IONIC CONC. (WITH ADDED NaClO₄)

\[
\begin{align*}
[\text{Pb(II)}] &\quad 0.00018 \text{ mol}^{-1} \\
[H^+] &\quad 0.007 \text{ mol}^{-1} \\
[SO₄^{2-}] &\quad 0.2 \text{ mol}^{-1}
\end{align*}
\]
Fig. 7.35. Variation of exchange current with temperature for $\beta$PbO$_2$ in sulphate electrolyte from impedance measurements.

ELECTROLYTE: 3 mol$^{-1}$ TOTAL EQUIVALENT UNI-UNIVALENT IONIC CONC (WITH ADDED NaClO$_4$)

- [Pb(II)] $0.00018$ mol$^{-1}$
- [H$^+$] $0.064$ mol$^{-1}$
- [SO$_4^{2-}$] $0.2$ mol$^{-1}$

Log$_{10}$($i$/$mA cm$^{-2}$) vs. $(10^3 / T) / ^\circ K$
temperature, for $\alpha$ and $\beta$-PbO$_2$ respectively, in the form of Arrhenius plots. The impedance data fitted classical behaviour at all temperatures below 40°C however at higher temperatures the data was more difficult to match.

Discussion of Faradaic Impedance Results

The value of the frequency independent capacitance estimated from faradaic impedance measurements, shunting the faradaic reaction can be seen from Table 7.5. to be of the order of $239 - 300 \ \mu$F cm$^{-2}$ for $\beta$-PbO$_2$ and $559 - 770 \ \mu$F cm$^{-2}$ for $\alpha$-PbO$_2$. For the galvanostatic measurements, Table 7.4., capacitance values of $\sim 130 \ \mu$F cm$^{-2}$ for $\beta$-PbO$_2$ and $\sim 140 \ \mu$F cm$^{-2}$ for $\alpha$-PbO$_2$ were obtained from the initial slope of the overpotential - time transients. The value of $R_E$ agreed fairly well with the electrolyte resistance obtained in the previously discussed double layer studies. The capacitance values obtained from the galvanostatic measurements are comparable with those observed for complementary measurements in perchlorate electrolytes. The faradaic impedance values are significantly different from the complementary data for perchlorate electrolytes, particularly in the case of $\alpha$-PbO$_2$. Both sets of capacitance values are considerably greater than those estimated from measurements in non-interacting electrolytes, (Chapter 4) allowing for the present concentration differences, and it is clear that in the presence of a faradaic reaction the double layer capacitance is abnormally high.

Since the faradaic impedance curves do not show any relaxation within the experimental frequency range the additional 'apparent' double layer capacitance must be regarded as resulting from the presence of an additional frequency independent capacitance in parallel with the true double layer capacitance and faradaic impedance.

The value of the experimental Warburg coefficient, obtained from the slope of the impedance curves, is considerably greater than the theoretical value, calculated from
Table 7.4.

$C_L$ estimated from the galvanostatic measurements

Electrolyte total equivalent uni-univalent salt concentration 3 mol $1^{-1}$ (with added NaClO$_4$). $[\text{SO}_4^{2-}]$ 0.2 mol $1^{-1}$, $[\text{Pb(II)}]$ 0.000018 mol $1^{-1}$.

<table>
<thead>
<tr>
<th>$[\text{H}^+]$ mol $1^{-1}$</th>
<th>$C_L \mu F \text{cm}^{-2}$</th>
<th>$\beta$-PbO$_2$</th>
<th>$\alpha$-PbO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.148</td>
<td>134</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>0.099</td>
<td>131</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>0.047</td>
<td>131</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>0.018</td>
<td>126</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>0.013</td>
<td>128</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>0.0061</td>
<td>131</td>
<td>143</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.5.

$C_L$ obtained from impedance measurements

Electrolyte total equivalent uni-univalent salt concentration 3 mol $1^{-1}$ (with added NaClO$_4$). $[\text{SO}_4^{2-}]$ 0.2 mol $1^{-1}$, $[\text{Pb(II)}]$ 0.000018 mol $1^{-1}$.

<table>
<thead>
<tr>
<th>$[\text{H}^+]$ mol $1^{-1}$</th>
<th>$C_L \mu F \text{cm}^{-2}$</th>
<th>$\beta$-PbO$_2$</th>
<th>$\alpha$-PbO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.41</td>
<td>300</td>
<td>770</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>291</td>
<td>692</td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>291</td>
<td>611</td>
<td></td>
</tr>
<tr>
<td>0.064</td>
<td>273</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>0.021</td>
<td>256</td>
<td>571</td>
<td></td>
</tr>
<tr>
<td>0.007</td>
<td>239</td>
<td>559</td>
<td></td>
</tr>
</tbody>
</table>
equation 2.38., particularly in the case of $\beta$-PbO$_2$. Due to the low concentration of Pb(II) in the electrolyte, the theoretical Warburg slope is almost independent of H$^+$. Table 7.6 summarizes the experimental Warburg slopes observed.

Table 7.6. 

Experimental Warburg Slopes

<table>
<thead>
<tr>
<th>[H$^+$] mol $1^{-1}$</th>
<th>Warburg slope $\Omega s^{-1}$</th>
<th>$\beta$-PbO$_2$</th>
<th>$\alpha$-PbO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.41</td>
<td>5100</td>
<td>1490</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>5500</td>
<td>1510</td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>5450</td>
<td>1510</td>
<td></td>
</tr>
<tr>
<td>0.064</td>
<td>5800</td>
<td>1525</td>
<td></td>
</tr>
<tr>
<td>0.021</td>
<td>5900</td>
<td>1530</td>
<td></td>
</tr>
<tr>
<td>0.007</td>
<td>6200</td>
<td>1520</td>
<td></td>
</tr>
</tbody>
</table>

The Warburg slope for $\beta$-PbO$_2$ is considerably greater than the theoretical value and shows an increase with decreasing [H$^+$]. For $\alpha$-PbO$_2$ the experimental Warburg slope is approximately constant throughout the experimental concentration range.

Changes in [SO$_4^{2-}$] had little effect on the slopes. An estimate of the active area of the electrode is given by equation 6.46 and indicates that for $\beta$-PbO$_2$ the active area never exceeded ~ 22% and for $\alpha$-PbO$_2$ ~ 70% of the geometric area.

The magnitude of the exchange current ($i_o \sim 10^1$ mA cm$^{-2}$) density was considerably larger than those observed in the galvanostatic measurements. Table 7.7 summarizes the exchange current dependencies on the concentration of solution species.
obtained from figures 7.30. - 7.33.

Table 7.7.

Exchange current dependence on concentration of electroactive species estimated from galvanostatic measurements

Electrolyte total equivalent uni-univalent salt concentration 3 mol 1⁻¹ (with added NaClO₄). [Pb(II)] 0.000018 mol 1⁻¹

<table>
<thead>
<tr>
<th></th>
<th>β-PbO₂</th>
<th>α-PbO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial \log_{10} i_0}{\partial \log_{10} [\text{H}^+] \cdot [\text{SO}_4^{2-}] \cdot [\text{Pb(II)}], \mu, T} )</td>
<td>0.34</td>
<td>0.32</td>
</tr>
<tr>
<td>( \frac{\partial \log_{10} i_0}{\partial \log_{10} [\text{SO}_4^{2-}] \cdot [\text{Pb(II)}], [\text{H}^+], \mu, T} )</td>
<td>0</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Although the galvanostatic measurements did not show any variation of exchange current with [SO₄²⁻], for the faradaic impedance results in the case of α-PbO₂ a slight reduction was observed for increasing [SO₄²⁻]. For both polymorphs the hydrogen ion dependency was less than that observed in the galvanostatic measurements.

The faradaic impedance results indicate that in sulphate electrolytes, as in perchlorate electrolytes, application of rapidly changing potential stimuli to the electrode causes an apparent activation of the PbO₂ lattice. The linearity of the impedance plots over the whole range of experimental frequencies indicates that no effects due to lattice building (crystallization) were present. The characteristics of the electrode process show similarities to the process proposed for perchlorate electrolytes. Consequently the process involves charge transfer at active sites followed by direct

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transfer of a Pb(II) species across the double layer and diffusion in solution.

The increase in the observed frequency independent capacitance with increasing [H+] can be explained as due to reactions of the type indicated in equations 7.1 and 7.2. Activating the lattice by application of ac stimuli promotes these reactions due to the increased number of active sites formed, leading to the observed experimental pseudocapacitance. The observed capacitance values are in agreement with such an electrode process since it is estimated that α-PbO₂ has the larger active surface area and the larger frequency independent capacitance.

The apparent larger active surface area of α-PbO₂ electrodes could be a consequence of the α/β-PbO₂ interconversion process. Alternatively, it may be that α-PbO₂ is more reactive than β-PbO₂. In acid solutions the tendency for α-PbO₂ to convert to the more stable β-PbO₂ will create surface irregularities which may present the charge transfer with more active sites.

Temperature Dependence of Faradaic Impedance Results

The Arrhenius plots, figures 7.34 and 7.35, indicate enthalpies of activation of 7.3 kJ mol⁻¹ for α-PbO₂ and 8.4 kJ mol⁻¹ for β-PbO₂. These values are considerably smaller than those observed in the galvanostatic experiments and may be a result of the apparent lattice activation.

7.3. Linear Sweep Voltammetry

Figure 7.36 shows a typical fast cathodic potential sweep curve for α-PbO₂.

Within the experimental potential limits (determined by oxygen evolution at the positive extremity and hydrogen evolution at the negative extremity) three peaks occur. Peak a occurs at the PbO₂/PbSO₄ potential and corresponds to the reduction of α-PbO₂ to PbSO₄. Peak b occurs at approximately the PbSO₄/Pb potential and corresponds to the
Fig. 7.36. Typical potential sweeps for $\alpha$-PbO$_2$ in H$_2$SO$_4$ electrolyte.

- Electrolyte: 4.41 mol/l H$_2$SO$_4$
- Electrode area: 4.49 x 10$^{-2}$ cm$^2$
- Sweep speed: 58.3 mV s$^{-1}$
- ANODIC SWEEP
- CATHODIC SWEEP
reduction of PbSO$_4$ to Pb. At low potential sweep speeds (< 10 mV s$^{-1}$) peak a showed the presence of a current shoulder at the negative side of the main peak indicating the occurrence of two reactions at approximately the same potential. Repetitive cycling in the limited potential range +2200 mV to +1400 mV, allowing negligible rest time between each sweep, caused a progressive increase in the magnitude of the current shoulder and a decrease of the main peak. Fast anodic sweeps on the α-PbO$_2$ electrode, after an initial fast cathodic sweep (broken line in figure 7.3.), showed only one peak within the experimental potential range corresponding to the oxidation of Pb to PbSO$_4$. A linear relationship between $I_m$ and $\sqrt{v}$ for peak a was not observed indicating that the reaction corresponding to this peak is complex and does not involve only diffusion in solution.

Peaks b and c of figure 7.36 were difficult to separate from each other and also peak c tended to merge with the cathodic current produced by the H$_2$ evolution reaction. Consequently it was difficult to measure true values of $I_m$ for these peaks and reliable plots of $I_m$ vs $\sqrt{v}$ could not be obtained.

Figure 7.37. shows a typical fast cathodic potential sweep curve for β-PbO$_2$. Within the experimental potential limits two clearly defined peaks (d and e) are observed. Peak d occurs at approximately the PbO$_2$/PbSO$_4$ potential and corresponds to the reduction of β-PbO$_2$ to PbSO$_4$. Peak e occurs at approximately the PbSO$_4$/Pb potential and corresponds to the reduction of PbSO$_4$ to Pb.

Figure 7.38. shows the effect of sweep rate on the cathodic peak height for the PbO$_2$/PbSO$_4$ reduction process (peak d). At the lowest sweep speeds applied a linear relationship exists between $I_m$ and $\sqrt{v}$, passing through the origin. $I_m$ was directly proportional to the concentration of H$_2$SO$_4$ throughout the whole of the experimental concentration range in agreement with equation 2.45, indicating that the faradaic current flow is controlled by diffusion of a solution species. At higher sweep speeds an
Fig. 7.37. Typical potential sweeps for $\beta$-PbO$_2$ in $H_3$SO$_4$ electrolyte.

- CATHODIC SWEET
- ANODIC SWEET

ELECTROLYTE: 5.56 mol/Hz $H_2SO_4$
ELECTRODE AREA: 4.9 x $10^{-3}$ cm$^2$
SWEEP RATE: 58.3 mV/s
Fig. 7.38. Cathodic peak current $\sqrt{\text{sweep rate}}$ for formation of PbSO$_4$ on $\beta$-PbO$_2$ in H$_2$SO$_4$ electrolyte.

**ELECTROLYTE CONC.-**
- 7.64 mol$^{-1}$
- 6.8 mol$^{-1}$
- 5.56 mol$^{-1}$
- 4.88 mol$^{-1}$
- 3.77 mol$^{-1}$
- 2.63 mol$^{-1}$
- 2.21 mol$^{-1}$
- 1.28 mol$^{-1}$

**ELECTRODE AREA** $4.49 \times 10^{-3}$ cm$^2$

**Diagram**
- Cathodic current (mA) vs. $\sqrt{\text{sweep rate}}$ (mV$^{1/2}$ s$^{-1/2}$)
- Lines for different electrolyte concentrations
abrupt change in the slope of the $I_m$ vs $\sqrt{v}$ curves is observed which occurs at progressively lower sweep speeds for increasing $H_2SO_4$ concentrations and gives significant intercepts on the current axis.

Figure 7.39 shows $(\partial I_m/\partial u^{1/2})$ vs concentration of $H_2SO_4$ for the peak corresponding to the $\beta$-$PbO_2$/$PbSO_4$ reduction. A straight line was obtained which extrapolated through the origin. From the slope of this line the diffusion coefficient of the species involved in the rate determining step was obtained using equation 2.45. The value obtained, $\sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, is considerably higher than that reported for the sulphate ion $^{147}$ but may indicate that the electrode is 'rough' as would be expected for electrodeposited $PbO_2$ electrodes.

It was not possible to correlate $I_m$ and $v$ for peak e since this peak corresponds to the reduction of more than one substance (a duplex structure of $PbSO_4$ and underlying $\beta$-$PbO_2$).

When a cathodic sweep was followed by an anodic sweep, with a negligible rest time between the two, a trace (broken line of figure 7.37) was obtained that was similar to anodic potential sweep traces on polycrystalline Pb (Appendix 6). Only one clearly defined peak was obtained within the potential limits and this corresponded to the oxidation to $PbSO_4$ of the Pb previously deposited on the $\beta$-$PbO_2$ by the cathodic sweep. No consistent relationship between $I_m$ and $v$ was obtained due to the dependence of this reaction on the two previous reduction reactions involved in the cathodic sweep.

Discussion of the L.S.V. Results

The behaviour of the $\beta$-$PbO_2$ electrode can be interpreted in terms of two processes occurring other than charge transfer:

(i) the diffusion of $SO_4^{2-}$ and $HSO_4^-$ ions in the solution,
Fig. 7.39. Slope of $I_n - \sqrt{V}$ curves vs $[\text{SO}_4^{2-}]$ for $\beta$-PbO$_2$ in $\text{H}_2\text{SO}_4$ electrolyte.
the transport of mass and charge through an insoluble layer of PbSO$_4^*$ at the electrode.

At low sweep speeds and low concentrations of H$_2$SO$_4$ current limitation is caused by a shortage of anions in the electrolyte layers in the immediate vicinity of the electrode. At higher concentrations of H$_2$SO$_4$ there is always an adequate supply of SO$_4^{2-}$ ions available at the electrode, however, the progressive growth of the PbSO$_4$ layer hinders the transport of charge through the electrode and the current density is therefore limited. The rate determining process is now the diffusion of ions through the layer of PbSO$_4$ at the electrode so that a linear $i_m$ vs $\sqrt{v}$ relationship is to be expected. The concentrations and diffusion coefficients of the reacting species in equation 2.45, now refer to the solid phase and the slopes of the $i_m$ vs $\sqrt{v}$ lines undergo a change in value corresponding to the change in current limitation mechanism. Extrapolation of the $i_m$ vs $\sqrt{v}$ curves, corresponding to the solid phase limitation mechanism, to zero sweep speed does not yield a zero value of $i_m$ but gives a significant intercept. The magnitude of this intercept is a measure of the charge necessary to cover the electrode with the solid phase of PbSO$_4$.

Increasing the concentration of H$_2$SO$_4$ in the electrolyte solution should cause a progressive reduction in the sweep speed at which the changeover from one mechanism of current limitation to the other occurs since limitation due to shortage of SO$_4^{2-}$ ions

*Footnote* The solubility of PbSO$_4$ when plotted against the concentration of H$_2$SO$_4$ shows a maximum of $\sim 6$ mg $1^{-1}$ at 1 mol $1^{-1}$ H$_2$SO$_4$. The solubility then progressively decreases to a minimum of 1 mg $1^{-1}$ in $\sim 6$ mol $1^{-1}$ H$_2$SO$_4$ thereafter remaining fairly constant with further changes in H$_2$SO$_4$ concentration. The solubility of PbSO$_4$ in the present electrolyte will therefore account for the removal of some Pb(II) ions from the electrode but this will be relatively minor.
becomes progressively more unlikely. This is observed in practice (figure 7.37.).

The sweep speed at which change over from one mechanism to the other occurs is determined by the thickness of the film and the diffusion coefficient as expressed by the physical structure of the film. A number of workers have commented on the structural changes that occur in the reduced layer at the electrode as the concentration of H$_2$SO$_4$ increases in the range 1 - 8 mol 1$^{-1}$, the most marked changes being reported at $\sim$ 5 mol 1$^{-1}$. This is in the region at which $I_m$ begins to exhibit a marked change in its relationship with concentration, figure 7.37, and it may be that the same factor applies in this case.

It is interesting to note that the apparent changes in the mechanism of current limitation occur at concentrations of H$_2$SO$_4$ approximately 2 mol 1$^{-1}$ higher for the case of the cathodic reduction of $\beta$-PbO$_2$ than for the anodic oxidation of Pb (Appendix 6). It is considered that the reason for this lies in the nature of the products of the respective reactions involved:

\[
Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e
\]

\[
\beta$\text{-PbO}_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_2O.
\]

For the $\beta$-PbO$_2$ reaction the molecules of H$_2$O produced during the reduction process will cause a change in the concentration of the electrolyte in the immediate vicinity of the electrode so that effectively this corresponds to a lowered H$_2$SO$_4$ concentration compared with the Pb reaction.

Previous work$^{43}$ established that in acid electrolytes $\alpha$-PbO$_2$ undergoes structural modification to give the more stable $\beta$-polymorph:

\[
\alpha$\text{-PbO}_2 \overset{H^+}{\rightleftharpoons} \text{Pb(IV)} \overset{\text{Pb(IV)}}{\rightleftharpoons} \beta$\text{-PbO}_2
\]
Also the relative \( \text{PbO}_2/\text{PbSO}_4 \) reduction potentials for the \( \alpha \)- and \( \beta \)-polymorphs show a potential difference of \( \sim 0.007 \) V (\( \alpha \)-\( \text{PbO}_2/\text{PbSO}_4; +1.7085 \pm 0.0005 \) V and \( \beta \)-\( \text{PbO}_2/\text{PbSO}_4; +1.715 \pm 0.0005 \) V).

Results of the repetitive sweeps indicate that the main peak initially observed at the \( \text{PbO}_2/\text{PbSO}_4 \) potential corresponds to the reduction of \( \alpha \)-\( \text{PbO}_2 \) to \( \text{PbSO}_4 \) and the current shoulder of peak b to the reduction of a small amount of \( \beta \)-\( \text{PbO}_2 \) present due to the modification of the \( \alpha \)-\( \text{PbO}_2 \) surface. Repetitive sweeps in acid solutions would tend to increase the proportion of \( \beta \)-\( \text{PbO}_2 \) at the \( \alpha \)-\( \text{PbO}_2 \) electrode surface until the \( \beta \)-polymorph is the dominant form involved in the reduction process hence explaining the shift of potential of the main peak a to a slightly negative potential. A tentative but by no means final explanation of the appearance of peak b in potential sweeps performed only on \( \alpha \)-\( \text{PbO}_2 \) and not in similar sweeps on \( \beta \)-\( \text{PbO}_2 \) is the reduction of some lead compound underneath the \( \text{PbSO}_4 \) layer. It is well established that in \( \text{H}_2\text{SO}_4 \) the \( \text{PbO}_2 \) electrode behaves similarly to the \( \text{Pb} \) electrode in that immediately underneath the \( \text{PbSO}_4 \) layer alkaline conditions exist which would favour the existence of \( \alpha \)-\( \text{PbO}_2 \) in preference to any modified \( \beta \)-\( \text{PbO}_2 \). Consequently peak b may correspond to a direct reduction of underlying \( \alpha \)-\( \text{PbO}_2 \) to \( \text{Pb} \).

Conclusions

In aqueous \( \text{H}_2\text{SO}_4 \) and \( \text{K}_2\text{SO}_4 \), the differential capacitance curves indicate that the electrode/electrolyte interphase is complicated by adsorption.

The exchange reaction in acid sulphate electrolytes has similar characteristics as determined by both the galvanostatic and faradaic impedance techniques. An apparent lattice activation by the application of repetitive potential stimuli is observed.

The L.S.V. measurements indicate the existence of two rate controlling steps for the \( \text{PbO}_2/\text{PbSO}_4 \) reaction. At low sweep speeds and low concentrations of \( \text{H}_2\text{SO}_4 \) the rate determining step involves diffusion in solution however at higher concentrations of acid a solid phase diffusion process becomes rate controlling.
A STUDY OF THE DIFFERENTIAL CAPACITANCE OF THE PbO_2/AQUEOUS PHOSPHATE SOLUTION INTERPHASE

It is fairly well established that additions of phosphoric acid to the normal lead-acid cell electrolyte result in an enhanced cycle life of the positive electrode. It is consequently of some interest to understand the behaviour of the phosphate ion at the PbO_2 electrode.

Early work by Feitknecht and Gauman suggested that during the charging process in the lead-acid cell intermediate plumbic compounds are formed which are not stable in the cell electrolyte (40% H_2SO_4) and spontaneously decompose or undergo hydrolysis,

\[
PbSO_4 + SO_4^{2-} + 2 H_2O = \left[ Pb(OH)_2 (SO_4)_2 \right]^{2-} + 2 H^+ + 2e \tag{1}
\]

\[
\left[ Pb(OH)_2 (SO_4)_2 \right]^{2-} = PbO_2 + H_2SO_4 + SO_4^{2-} \tag{2}
\]

or

\[
PbSO_4 + SO_4^{2-} = Pb(SO_4)_2 + 2e \tag{3}
\]

\[
Pb(SO_4)_2 + 2 H_2O = PbO_2 + 2 H_2SO_4 \tag{4}
\]

If a mixture of H_2SO_4 and H_3PO_4 replaces the conventional electrolyte, analogous and relatively stable plumbic salts are obtained. Feitknecht and Gauman assumed that OH radicals are formed which react with the plumbous phosphate to give plumbic phosphate.

(113)
\[ \text{OH}^- = \text{OH} + e \]  

or

\[ \text{H}_2\text{O} = \text{OH} + e + \text{H}^+ \]  

\[ \text{PbHPO}_4 + 2 \text{OH} = \text{H} \left[ \text{Pb(OH)}_2 \text{PO}_4 \right] \]  

It was suggested that decomposition of the phosphate resulted in an increased proportion of \( \alpha\text{-PbO}_2 \) on the electrode as compared with the hydrolysis of the sulphate salt due to migration of \( \text{H}^+ \) ions into the solution leaving an alkaline condition at the electrode which is conducive to the formation of \( \alpha\text{-PbO}_2 \). Several workers have suggested that \( \alpha\text{-PbO}_2 \) aids cycle life of positive plates.

**Results**

Figures 8.1. and 8.2. show the extent of the experimental polarizable regions for \( \alpha\text{-PbO}_2 \) and \( \beta\text{-PbO}_2 \) in \( \text{H}_3\text{PO}_4 \), \( \text{KH}_2\text{PO}_4 \) and \( \text{K}_2\text{HPO}_4 \) solutions respectively. The limits of experimental polarizability for \( \alpha\text{-PbO}_2 \) in \( \text{H}_3\text{PO}_4 \), \( \text{KH}_2\text{PO}_4 \) and \( \text{K}_2\text{HPO}_4 \) were \( \sim 1.4 - 1.9 \text{ V} \), \( \sim 1.15 - 1.8 \text{ V} \) and \( \sim 0.95 - 1.75 \text{ V} \) respectively and for \( \beta\text{-PbO}_2 \) \( \sim 1.35 - 1.9 \text{ V} \), \( \sim 1.05 - 1.85 \text{ V} \) and \( \sim 0.95 - 1.65 \text{ V} \) respectively. The extent of the polarizable regions increased in the series \( \text{H}_3\text{PO}_4 - \text{K}_2\text{HPO}_4 \) and shifted to more negative potentials with increasing pH.

Figures 8.3. - 8.4. show differential capacitance - bias potential curves for the experimental electrolyte solutions. Stability of the impedance measurements was lowest for \( \text{H}_3\text{PO}_4 \) solutions in which 5 hrs. electrode/electrolyte contact time was required before stable impedance readings were obtained. The capacitance - time variation amounted to \( \sim 20\% \) of the final impedance value.

Figures 8.9. and 8.10. show typical frequency dispersion of the differential
Fig. 8.1. Faradaic current-bias potential curves for $\alpha$-PbO$_2$ in phosphate electrolyte

ELECTROLYTE:

- $0.18$ mol l$^{-1}$ K$_2$HPO$_4$
- $0.093$ mol l$^{-1}$ KH$_2$PO$_4$
- $0.13$ mol l$^{-1}$ H$_3$PO$_4$
Fig. 8.2. Faradaic current-bias potential curves for $\beta$-PbO$_2$ in phosphate electrolyte.
Fig. 8.3. Differential capacitance - bias potential curves for $\alpha$-PbO$_2$ in H$_3$PO$_4$ electrolyte.
Fig. 8.4. Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in H$_3$PO$_4$ electrolyte.
Fig. 8.6. Differential capacitance-bias potential curves for $\beta$PbO$_2$ in KH$_2$PO$_4$ electrolyte.
Fig. 8.7 Differential capacitance-bias potential curves for $\alpha$-PbO$_2$ in K$_2$HPO$_4$ electrolyte.
Fig. 8.8. Differential capacitance-bias potential curves for $\beta$-PbO$_2$ in $K_2HPO_4$ electrolyte.
Fig. 8.9. Frequency dispersion of differential capacitance curves for $\alpha$-PbO$_2$ in $H_3$PO$_4$ electrolyte

**Diagram Description:**
- **Electrolyte:** 0.131 mol/l $H_3$PO$_4$
- **Graph:**
  - Open circles: 120 Hz
  - Filled circles: 300 Hz
  - Filled triangles: 500 Hz
  - Open triangles: 1000 Hz
- **Axes:**
  - $C_L / \mu F \ cm^2$
  - $E(NHE) / V$

**Note:**
- The graph shows the variation of differential capacitance, $C_L$, with the potential $E(NHE)$ at different frequencies.
Fig. 8.10. Frequency dispersion of differential capacitance curves for $\beta$-PbO$_2$ in H$_3$PO$_4$ electrolyte.

ELECTROLYTE 0.131 mol l$^{-1}$ H$_3$PO$_4$

- 120 Hz
- 300 Hz
- 500 Hz
- 1000 Hz

$C_s / \mu F \ cm^{-2}$ vs. $E_{(NHE)} / V$
capacitance curves for $\alpha$-PbO$_2$ and $\beta$-PbO$_2$ respectively in H$_3$PO$_4$ in which dispersion was greatest for the three electrolytes tested. Frequency dispersion is similar to that observed in H$_2$SO$_4$ solutions and increases with decreasing acidity.

Discussion of Differential Capacitance Results

The forms of the differential capacitance curves are similar to those obtained in aqueous sulphate solutions (Chapter 7) but unlike those in nitrate solutions (Chapter 4). The form and absence of a minimum, which progressively deepens with decreasing electrolyte concentration, in the capacitance curves indicates that the interphase is complicated by adsorption.

The rise in capacitance at the positive extremity of the polarizable region is a pseudocapacitance peak associated with oxygen evolution, and the rise (to a spike) at the negative limit marks the onset of the reduction of the PbO$_2$ electrode to the Pb(II) state. The in-phase (resistive component of the electrode impedance is fairly constant within the experimental polarizable region indicating little change in the double layer structure within these potential limits.

At potentials more negative than the pseudocapacitance spike in KH$_2$PO$_4$ and K$_2$HPO$_4$ solutions, the capacitance decreases markedly as potential becomes more negative due probably to the thickening of the Pb(II) film (the form of which was not determined). The magnitude of the capacitance variation with concentration is greater for K$_2$HPO$_4$ than KH$_2$PO$_4$ indicating that film formation is favoured by increased pH. For H$_3$PO$_4$ solutions a significant reduction of the capacitance at potentials more negative than the polarizable region is absent indicating that lattice reduction is not accompanied by the development of an insoluble layer on the electrode surface.

The capacitance magnitude, which is considerably greater than observed in nitrate solutions, decreases progressively in the series H$_3$PO$_4$ - KH$_2$PO$_4$ - K$_2$HPO$_4$ indicating the influence of the H$^+$ ion on the system. The direct adsorption of the
H⁺ ion at the present positive rational potentials seems unlikely, however, due to the low solubility of lead phosphates, it is likely that PO₄³⁻, HPO₄²⁻ and H₂PO₄⁻ ions are directly adsorbed. It is suggested that the observed high electrode capacitance values arise from adsorption reactions of the type:

\[
PbO₂ + 2 H_3PO₄_{ads} + 2e = PbHPO₄_{ads} + HPO₄²⁻_{ads} + 2 H_2O \quad (8.8)
\]

\[
PbO₂ + 4 H_2PO₄_{ads} + 2e = PbHPO₄_{ads} + HPO₄²⁻_{ads} + 2 H_2O \quad (8.9)
\]

\[
PbO₂ + 5 HPO₄²⁻_{ads} + 2e = PbHPO₄_{ads} + HPO₄³⁻_{ads} \quad (8.10)
\]

A large number of reactions of this type can be formulated. These reactions (equations 8.8. - 8.10) are favoured by decreasing the pH of the electrolyte, thus the lower the pH (higher [H⁺]) the greater the adsorption capacitance as observed in practice.

The behaviour of both polymorphs was similar in all three electrolytes, however any differences which may have occurred would tend to be obscured by the pseudo-capacitance developed as a result of the participation of the H⁺ ion in the double layer structure and reactions of the type of equation 8.8. - 8.10. Overall the magnitude of the capacitance was greater for α-PbO₂ than for β-PbO₂ indicating that the true surface area of α-PbO₂ is possibly greater than for β-PbO₂.

Comparison of PO₄³⁻ and SO₄²⁻ Systems

The significant difference observed between the double layer structure in SO₄²⁻ and in PO₄³⁻ is the absence of an apparent adherent insoluble film in phosphate solutions for potential excursions negative of the polarizable region. There are two possible explanations:

(1) the lead (II) phosphate produced under these conditions has sufficient solubility
to leave the electrode.

(2) the lead (II) phosphate film formed is only poorly held at the electrode and is unable to act as a dielectric.

Conclusions

The PbO$_2$/aqueous phosphate solution interphase is complicated by adsorption of solution species. Reversible redox reactions, involving H$^+$ and phosphate ions adsorbed at the electrode, occur within the polarizable region. These reactions give rise to a pseudocapacitance. Highly adherent insulating films characteristic of the PbO$_2$/K$_2$SO$_4$ system are not developed as a product the reduction of the PbO$_2$ lattice.
CHAPTER 9

FINAL DISCUSSION AND CONCLUSIONS

9.1. The PbO₂/Aqueous Solution Interphase

(a) The Potential of Zero Charge

The study of the differential capacitance of PbO₂ electrodes is restricted by a limited potential region in which the electrode is uncomplicated by faradaic reactions. This potential region is defined at the negative extremity by lattice dissolution and at the positive extreme by oxygen evolution and is strongly influenced by pH, i.e. by decreasing the pH the region was significantly decreased. In general the concentration of H⁺ ions had a marked effect on the potential of lattice dissolution.

The pzc, estimated from measurements in neutral nitrate solutions, occurs at 1.07 ± 0.01 V for α-PbO₂ and 1.15 ± 0.01 V for β-PbO₂. Thus at the equilibrium potential, E⁰ (~ 1.69 V²²⁻²⁴), the PbO₂ electrode has a positive charge with respect to the bulk electrolyte and anionic adsorption will be favoured at the electrode. This compares with solid metal electrodes where the equilibrium potential is usually more positive than E_z, e.g. lead, E⁰ = 0.126 V¹⁵⁸, E_z = 0.60 V¹⁵⁹; silver, E⁰ = 0.799 V¹⁵⁸, E_z = 0.7 V¹⁶⁰.

An 'a priori' study of the pzc and the interphasial structure has been shown to be important in the present exchange reaction studies where, by consideration of the experimental potentials involved, the nature of adsorbed intermediates and products were estimated.

(b) Double Layer Structure

In KNO₃ solutions the differential capacitance curves resemble, in form, those for mercury in aqueous NaF solutions¹²⁴. In the most concentrated solutions a well de-
fined hump in the capacitance curves was obtained which, on dilution, progressed into a well defined capacitance minimum that was independent of concentration. From a comparison of the magnitude of the capacitance of PbO$_2$ electrodes with that for mercury electrodes, a roughness factor of $\sim 5 - 10$ for PbO$_2$ electrodes is indicated which was further evinced by the observed frequency dispersion of the capacitance curves. Allowing for surface roughness, the electrode behaved very much as predicted by the Gouy-Chapman theory, specific adsorption of solution species being absent. At all potentials the capacitance magnitudes of equilibrated electrodes was greater for $\alpha$-PbO$_2$ than for $\beta$-PbO$_2$ indicating a greater surface area for the $\alpha$-polymorph.

In other electrolyte solutions experimental results show that the double layer is complicated by adsorption. The adsorption appears to be strongly influenced by pH. In general, the magnitude of the capacitance for a particular electrolyte increased with decreasing pH. Since the experimental polarizable regions were generally at positive rational potentials the direct adsorption of H$^+$ is unlikely and it is probable that H$^+$ is involved in adsorption processes of the type indicated in equation 7.1. - 7.2. and 8.8. - 8.10, which are favoured by decreasing pH, and also in the adsorption of molecules, e.g. HNO$_3$, H$_2$SO$_4$, HClO$_4$.

(c) **Surface Equilibrium**

Investigations of the differential capacitance of a number of solid metals have shown that, in contrast to amalgam electrodes, considerable variation of the electrode impedance invariably occurs with electrode/electrolyte contact time before stable values are obtained. It has been suggested that the pretreatment of a solid metal electrode probably produces a surface of different metallurgical configuration from that corresponding to an equilibrated electrode. The initially observed electrode activity is probably due to a rearrangement of the surface to produce a surface of minimum surface area (for differential capacitance measurements can only take place by self
diffusion of metal ions on the electrode surface).

In the case of PbO₂ electrodes, a variation of the electrode impedance with electrode/electrolyte contact time was observed, in contrast to solid metal electrodes, the magnitude of the capacitance rises with contact time (accompanied by a decrease in electrode resistance) until stable values were obtained. Time instability was greatest for low pH electrolytes. Two processes may account for such time instability:

(1) the electrodeposited PbO₂ has a high initial surface energy and in order to achieve a more stable lower energy the electrodes undergo a surface expansion process. In the case of α-PbO₂, the electrode is further complicated by a surface modification of the type:

\[ \alpha\text{-PbO}_2 + H^+ \rightarrow \text{Pb(IV)} + H^+ \rightarrow \beta\text{-PbO}_2 \]  \hspace{1cm} (9.1)

which would possibly cause further surface expansion.

(2) the adsorption processes occurring at the PbO₂ electrode are time dependent. Also adsorption will tend to hinder surface expansion and thus lengthen the equilibration time. The effect of adsorption on the equilibration time is illustrated by the lowest time instability being observed for the case of KNO₃ solutions, where adsorption was absent. If adsorption does involve ion pairs or molecules, as indicated by the capacitance measurements in acid solutions, then it may be expected that adsorption will be slower than ionic adsorption.

It seems most probable that the initial equilibration period is connected with both the above effects. The exact degree to which each effect is involved cannot be ascertained with accuracy. Kabanov and co-workers²⁵,²⁸,²⁹,³ⁱ,³⁴,³⁷,⁴⁰ considered that the initial instability was due solely to a surface expansion. Since in the present experiments time instability was smallest for KNO₃ solutions, in which adsorption is considered absent,
and greatest in solutions of high $H^+$ concentration, the conclusions of Kabanov and co-workers are not fully justified. In the present case it is apparent that adsorption certainly plays an important role in determining the stability of the electrode.

(d) Relative Surface Area of $\alpha$ and $\beta$-PbO$_2$

Capacitance values obtained for PbO$_2$ electrodes on immediate contact with electrolyte solutions were generally greater in magnitude for $\beta$-PbO$_2$ than for the $\alpha$-form, however, after equilibration the reverse is true. Thus, for PbO$_2$ electrodes on immediate contact with the electrolyte, the surface area of the $\beta$-polymorph is greater than that of the $\alpha$-form, however, for equilibrated surfaces the surface area of $\alpha$-PbO$_2$ is larger. The reason for this may be related to a higher surface energy of $\alpha$-PbO$_2$ or due to an increased adsorption causing $\alpha$-PbO$_2$ to show a larger adsorption pseudocapacitance; a number of workers have suggested that $\alpha$-PbO$_2$ adsorbs to a lesser extent than $\beta$-PbO$_2$. Thus it appears that $\alpha$-PbO$_2$ is deposited with a higher surface energy than $\beta$-PbO$_2$. The possibility of surface modification of $\alpha$-PbO$_2$ electrodes via reaction 9.1 cannot be neglected as a possible cause of the larger surface area of equilibrated $\alpha$-PbO$_2$ electrodes but, since equilibrated $\alpha$-PbO$_2$ electrodes in alkaline solutions showed greater capacitance values than $\beta$-PbO$_2$, this cannot be the dominant factor.

9.2. The Charge Transfer Reaction

(a) Under Galvanostatic Conditions

For the case of exchange reactions at solid metals, Bockris and Conway$^{100}$ established that the most probable path of metal deposition reactions from calculations of the free energies of the various possible reaction paths. They indicated that the most probable mechanism involved consecutive single electron transfers and estimated that
the most probable reaction path is the transfer of an ion to a plane surface site, diffusion to a step site, diffusion along the step to a kink site, and finally, incorporation into the lattice accompanied by electron transfer. Calculations by Hush\textsuperscript{161}, Mott and Watts-Tobin\textsuperscript{162}, however, showed that direct electron transfer between the surface of the metal and a hydrated ion could not be ignored.

In the present exchange reaction studies, it is considered that the charge transfer process in both acid and alkaline electrolyte solutions at PbO\textsubscript{2} electrodes involves transfer of electrons on the surface of the electrode with surface Pb(IV) ions to form adsorbed Pb(II) species which are then directly transferred across the double layer as neutral Pb(II) species. The transfer of a neutral species across the double layer is in agreement with ideas of Gerischer\textsuperscript{144} who suggested that the most likely species to cross the double layer would be a neutral or low charged species.

The charge transfer reaction is slow and a change in the charge transfer mechanism is indicated as potential excursions from the equilibrium potential are increased. At high overpotentials the charge transfer process involves two consecutive single electron transfers in preference to a single simultaneous two electron transfer at low overpotentials. It is probable that even at low overpotentials the exchange reaction involves two consecutive single electron transfers, however, at such potentials the time interval and the energy of activation difference between the two electron transfers is small. Due to the experimental limitations, e.g. current pulse times employed, it was not possible to distinguish between the two processes.

It would be of interest to compare the exchange reaction at the PbO\textsubscript{2} electrode with that at other oxide electrodes, but comparison with all oxides is not possible due to the unique metallic characteristics displayed by PbO\textsubscript{2} compared with most oxides. For the oxides closest in resemblance to PbO\textsubscript{2}; AgO, MnO\textsubscript{2}, TiO\textsubscript{2} and Tl\textsubscript{2}O\textsubscript{3}, it is clear that some similarities exist; thus there is a possible intermediate valence state between reactant and product of a reduction reaction. For AgO it has been suggested

(122)
that a solid state reaction predominates, the rate controlling step being the diffusion of Ag⁺ or OH⁻ ions in the oxide lattice. In the case of MnO₂, in neutral electrolyte solutions, the reaction involves an intermediate Mn(III) species, viz.:

\[
\text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnOOH} \quad (9.2)
\]

which then undergoes further reaction to give the Mn(II) oxide. The rate determining step is the diffusion of Mn(II) ions in the solid phase. Discharge mechanisms similar to that for MnO₂ have also been proposed for Tl₂O₃, in which the unstable Tl(II) is involved and diffusion of Tl(II) ions in the solid phase is rate determining. For TiO₂ the reaction is considered to occur in the solid state, however, no intermediate valence state between reactant and product exists. Thus PbO₂ cannot be satisfactorily compared with these four oxides since whereas for PbO₂ a solution reaction is involved in the case of the above four oxides the reaction occurs in the solid phase. The possibility of the existence of unstable reaction intermediates seems to be a common feature of the exchange reaction of all the oxides except TiO₂ where no possible intermediate valence state exists.

(b) Under Conditions of Repetitive Potential Stimuli

The general kinetic characteristics of the exchange reaction, i.e. concentration dependencies of the exchange current and the exchange mechanism, were similar for both galvanostatic and faradaic impedance measurements. A significant difference occurred in the magnitude of the exchange current observed. The exchange current extracted from the impedance measurements was generally of the order of 10 times greater than those determined by the galvanostatic method. Thus it appears that the application of rapidly changing potential stimuli to the PbO₂ electrode causes an apparent activation of the PbO₂ lattice. This apparent lattice activation can be
explained by consideration of the response of 'active sites' on the PbO$_2$ surface to a.c. In the case of impedance measurements the frequency of the applied a.c. is much greater than the life time of the active sites and the exchange current density observed is a maximum since all the active sites are available for exchange. In the case of galvanostatic measurements, the experimental current pulse times used were greater than the life time of an active site and the exchange current corresponds to the equilibrium number of active sites on the surface. It was noted that for frequencies < 40 Hz, deviations from ideal behaviour of the impedance data occurred. Such a frequency is equivalent to a galvanostatic pulse time of 25 ms. Thus the estimated life time of an active site is < 25 ms.

(c) Adsorption Isotherm Employed

In all the experimental measurements the adsorption isotherm which best fitted the experimental results was one that is similar to the Freundlich isotherm. Attempts to force the experimental results into other possible isotherms, e.g. those discussed in Chapter 2, were unsuccessful.

A great deal of knowledge and understanding of adsorption at metal electrodes has been gained by use of the Langmuir isotherm however, in many cases conditions were such that significant deviations from Langmuir behaviour occurred. Recently the variation of the heat or the apparent standard free energy of adsorption with coverage, has been considered, leading to the use of isotherms of similar form to the Frumkin isotherm. Detailed complex isotherms have been applied to describe adsorption on mercury electrodes 68,164-166 these, however, are only useful for liquid metals where the charge on the electrode can be measured with a relatively high degree of accuracy. At solid electrodes, and in particular oxide electrodes, further understanding of adsorption is restricted by uncertainties of the real surface areas and hence partial surface coverage.

In general the Freundlich isotherm has found limited use in describing adsorption at electrodes, however, Hickling 145 found that for the adsorption of hydrogen on metals, a
form of Freundlich isotherm fitted the experimental results. More recently Schriffrin, from an investigation of the specific adsorption of fluoride ions on mercury, found that a modified Freundlich type isotherm described the surface pressure of the adsorbed ionic film and that a similar isotherm possibly explained the behaviour of other weakly adsorbed ions at mercury. Hills and Reeves also concluded that the adsorption of PF$_6^-$ from KPF$_6$ and KF mixtures followed a modified Freundlich isotherm. In previous work concerning PbO$_2$ electrodes, Jones et al used a Freundlich type isotherm to describe hydrogen adsorption. Thus although the Freundlich isotherm has found limited use, in certain cases it has been found to be the most applicable.

9.3. Further Work

(1) Most lead acid cells are fabricated with grids of Pb–Sb alloy; normally from 4–12% by weight of Sb. Primarily the purpose of the antimony is to strengthen the grid metal so that it can be cast and fabricated with greater ease than pure lead, which is very soft and easily deformed. The action of the antimony, however, is not solely metallurgical. It is leached from the grid metal and causes detrimental, as well as beneficial, side reactions. It has been reported that the presence of antimony gives rise to an increased content of $\alpha$-PbO$_2$ in the formed positive active material.

Further work could be performed in an attempt to understand the effect of antimony on the PbO$_2$ electrode more fully. When the exact function of antimony in the cell is known then it may be possible to designate a substitute for use in the lead acid cell that has the same beneficial properties and is free of the detrimental ones.

(II) There is little reported work, as yet, concerning the effect of organic additives on the behaviour of PbO$_2$ electrodes. The use of organic expanders in the battery plates and organic separators between the plates presents good cause to further
investigate the effect of organic additives to the cell electrolyte

(III) In the present work the experimental test electrodes consisted of electrodeposited samples on platinum bases. The deposits were of known polymorphic form (either \( \alpha \) or \( \beta \)). It would be of interest to carry out further work on electrodes consisting of mixtures of the two polymorphs in fixed proportions.

(IV) In this work \( \text{PbO}_2 \) was formed on platinum, however, in the lead acid battery system the positive active material is formed on \( \text{Pb} - \text{Sb} \) alloy. Further work is required on such electrodes to see if the different base substrates have any effect on the kinetics of the electrode reactions.
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