Electrochemical reactions at lead dioxide electrodes

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ELECTROCHEMICAL REACTIONS AT
LEAD DIOXIDE ELECTRODES

BY

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SUMMARY

Preliminary passivation studies established that kinetic measurements could be made at α- and β- lead dioxide electrodes, in perchloric acid electrolytes, without the intrusion of solid films.

The kinetics of the rate controlling exchange reaction at α- and β-PbO₂ have been investigated using the galvanostatic pulse technique. The overpotential-current density data was interpreted in terms of two rate controlling charge transfer mechanisms. Around the equilibrium potential the reaction mechanism appears as a simultaneous two-electron transfer which changed to two consecutive single-electron transfer steps at high overpotential. Possible reaction mechanisms have been discussed on the basis of the observed kinetic parameters.

Differential capacitance-potential data for α- and β-PbO₂ has been measured in inert electrolytes.

A comparison of the electrochemical behaviour of α- and β-PbO₂ has been made.
ACKNOWLEDGEMENT

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During the last few decades oxide electrodes, produced by anodic oxidation of electrolytes in solution, have attracted considerable attention. This has largely been due to the progress made in the development of techniques for investigating electrochemical reactions and to the improvements made in the conditions under which such reactions may be studied (1,2).

The purpose of the present investigation, has been to examine the electrode kinetic behaviour of one such oxide-electrolyte system, and, if possible to interpret this behaviour in terms of possible mechanisms of exchange between the oxide lattice and ions in solution.

A review has been made of a number of well defined oxide electrode systems in which the oxides are produced anodically on electroperoxidation.

1.1. THEORETICAL PRINCIPLES

The Electrical Double Layer. A knowledge of the structure of the electrical double layer is essential in order to elucidate the kinetics of electrode processes. This is due to the fact that the properties of an electrode surface are affected by the charge density at the interphase, while the potential difference across the interphase and the electrical field in the immediate vicinity of the interphase both influence the transfer of charge from one phase to another.
An electrical layer is established when an electrode makes contact with an electrolyte. It consists of two layers of electric charge of opposite sign and equal magnitude separated by a distance of a few Angstrom units. The existence of an electrical double layer depends on an inhomogeneity in the medium and is always closely associated with a phase boundary. The two layers 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; naturally the two types of double layer may co-exist.

In general solid electrode - electrolyte interphases can be classified into a) ideally polarizable interphases and b) non-polarizable interphases. An ideally polarizable interphase may be defined as a system for which at equilibrium every charged component is finite (or measurable) in one phase only. This means there is no passage of charge across the interphase although a charge separation can occur by movement of charges round the external circuit involving the polarizing p.d. In the case of non-polarizable electrodes the presence of a potential determining ion in both phases leads to a p.d. across the interphase determined by the Nernst equation.

2.
Theories of the structure of the double layer. The first concept of the structure of the double layer was due to Helmholtz, who considered it as two surface layers of charge separated by a constant distance. This early theory would require a constant double layer capacitance and is therefore incomplete.

Gouy (3) and Chapman (4) have extended the Helmholtz concept of the double layer structure to the extent of assuming a diffuse (rather than a compact) layer which would be affected by the thermal motion of the ions. Whereas ions are treated as point charges in the Gouy – Chapman theory, allowing them to approach the electrode within any distance, Stern (5), postulated that ions cannot reach the electrode beyond the plane of closest approach. On the ideas of Stern, the double layer can be divided into two regions, the compact double layer between the electrode and the plane of closest approach, and the diffuse double layer from the plane of closest approach into the bulk of the solution.

The usefulness of the Stern concept as a working hypothesis for the electrical double layer has been enhanced by Grahame (6), who elaborated the theory in terms of the finite size of ions and has considered the question of their solvation in the double layer. Devanathan and Tilak (7) have postulated a third layer of unsolvated ions specifically adsorbed in the Helmholtz layer.

This latter concept makes possible, for example, the interpretation of the observed shape of capacitance -
potential curves for the mercury - electrolyte interphase.

**Electrochemical equilibrium.** The study of the electrical double layer is the study of its relation to the phase boundary potential. Most systems have at the interphase an equilibrium potential which cannot be changed without altering the composition of the system. At equilibrium the electrochemical potential of each charged component in one phase is equal to that in the other phase. A change in the concentration of a charged component in one phase would result in a change in the phase boundary potential. Attainment of equilibrium at the new concentration results in a new value for the phase boundary potential.

**Basic kinetic steps.** The basic reaction paths for the exchange between metal ions in solution and in a lattice have been treated by various authors (8-10). One such reaction path could be the direct transfer of an ion from the solution to a half crystal position [see Gerischer (11)] which may be a screw dislocation or an otherwise incomplete crystal layer. Alternatively, the reaction path could be a two-step mechanism involving the transfer of ions to any surface site on the crystal planes followed by transport of such ions by surface diffusion to half crystal positions.

The fundamental difference between these two reaction paths is that crystallization and charge transfer are
simultaneous steps in the first case, but consecutive involving
two separate reaction steps in the second.

**Definition of kinetic parameters.** For a simple electrode
process the rate determining step can be identified with the
overall reaction

\[ 0 + Ze = R \] \[ 1.1 \]

The free energy barrier for such a process is shown in
Figure 1 and has been fully discussed elsewhere (12).

The relationship between activation overpotential and
current passing across the electrode interphase, following
the ideas of Butler (13), Erdey-Gruz and Volmer (14) and
Frumkin (15) is*

\[ i = i_C - i_A = i_o \left( \exp \left( \frac{\Delta G}{RT} \right) \eta_D - \exp \left[ \left( 1 - \alpha \right) \frac{\Delta F}{RT} \right] \eta_D \right) \] \[ 1.2 \]

\[ i_C = i_A = i_o \] at the equilibrium potential (when the
overall faradaic current, \( i = 0 \))

\( \alpha \), is the cathodic transfer coefficient.

Figure 1b shows the relationship, (equation \[ 1.2 \]), for
the case \( \alpha = 0.5, Z = 2, T = 298 \, ^\circ \text{K} \); the first term in the
series expansion is also shown. Below about 7 mV a linear
relationship exists between over-potential and current
density. Thus, equation \[ 1.2 \] becomes

\[ \frac{\eta_D}{i} = \frac{-RT}{ZF i_o} \] \[ 1.3 \]

for \( \eta_D \ll \frac{RT}{\Delta G F} \) (or \( \eta_D \ll \frac{RT}{(1-\alpha)ZF} \))

* An alphabetical list of the symbols used throughout is given
in Appendix 1.
FIG 1a

THE CHARGE TRANSFER PROCESS.

Free energy barrier and general rate equation

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

for \( \alpha = 0.5 \)

\( Z = 2 \)

\( T = 298^\circ K \)

--- First term in polynomial expansion

\[ \frac{i}{i_0} = \frac{\eta ZF}{RT} \]
The quantity \((-\partial \eta_d/\partial i)_{i_0}\) has the dimensions of resistance and is called the reaction resistance \(R_d\).

However, when the perturbation of the process is high, i.e. \(|\eta_d| > 50\text{mV}\), the rate of the reaction in the direction opposed by the overpotential is reduced to negligible proportions and the second term in equation [1.2] can be ignored.

Equation [1.2] then conforms to the Tafel equation:-

\[
\eta_d = a - b \log_{10} i \quad \quad \quad \quad [1.4]
\]

where for the cathodic process

\[
a = \left( \frac{2.303RT}{\alpha ZF} \right) \log_{10} i_0
\]

and \(b = 2.303RT/\alpha ZF \quad \quad \quad \quad [1.5]\)

\((1-\alpha)\) replaces \(\alpha\) for the anodic process.

The dependence of exchange current \((i_0)\) on reactant concentration can be established \((16,17)\) provided the concentrations in the pre-electrode state are known functions of the concentrations outside the diffuse layer. In the case represented by equation [1.1] we have:-

\[
i_0 = ZFk^0 a_R^\alpha a_0^{1-\alpha} \quad \quad \quad \quad [1.6]
\]

\(a_R\) and \(a_0\) are replaced by the corresponding concentrations \(c_R\) and \(c_0\) since activities are usually unknown. The standard rate constant \(k^0\) (units cm sec\(^{-1}\) for concentrations in mole cm\(^{-3}\)) is defined accordingly. For the charge transfer
Polarization resistance. The quantity \( \frac{d\eta}{di} \eta = 0 \) at the equilibrium potential \( E_0 \) (i.e. \( \eta = 0 \)) is called the polarization resistance \( R_p \). This is a quantity, having the dimensions of ohmic resistance and is related to the physical and chemical changes which occur across the interphase. The magnitude of the polarization resistance depends on the experimental conditions, and in general on the charge transfer resistance, diffusion polarization, ohmic polarization and crystallization resistance. Diffusion and concentration polarization arise from some slow step in the discharge (or deposition) stages involving components at the phase boundary. It would include such terms as polarization due to diffusion or any subsequent electrode reaction.

The modified form of equation \([1.2]\) for processes where concentrations at the interphase differ from bulk concentrations is

\[
i = i_0 \frac{C_0}{\sigma_{\text{C}_0}} \exp(-\alpha ZF \eta_D / \text{RT}) - \frac{C_R}{\sigma_{\text{C}_R}} \exp(1-\alpha) ZF \eta_D / \text{RT}\]

\[\ldots [1.7] \]

where \( i_0 \) corresponds to bulk concentrations \( \sigma_{\text{C}} \).

When \( |\eta_D| < RT / \alpha ZF \), equation \([1.7]\) becomes

\[
i = i_0 \left\{ \frac{C_0}{\sigma_{\text{C}_0}} - \frac{C_R}{\sigma_{\text{C}_R}} - \frac{ZF \eta_D}{\text{RT}} \right\} \ldots \ldots \ldots \ldots \ldots \ldots \ldots [1.8] \]
1.2. SPECIFIC ELECTRODE SYSTEMS

A comparison of mercury and amalgam electrodes with solid metal electrodes. The foundation of modern electrode kinetics was established by experiments using the mercury electrode. Tafel (18) established his experimental law using such an electrode while Frumkin (15), basing his arguments on results obtained on Hg, introduced the concept of double layer influence on electrode kinetics.

Results on solid metal electrodes, however, are more difficult to interpret than are those at mercury electrodes. This is mainly due to surface characteristic variables. Although metallurgical techniques have made it possible both to examine such surface variables and also to produce electrodes of very high purity. The problems at solid metal electrodes may be summarized as:-

i) Whereas an amalgam electrode is homogeneous, the surfaces of solid metal electrodes are usually inhomogeneous in the physical sense i.e. they are often composed of a number of crystal planes, each exposed plane being a potentially different surface. Low index and therefore close packed planes would be expected to possess a different reactivity than high index planes in which the atoms were further apart. Hence 'smooth' metal surfaces possess a range of reactivities at equilibrium.

ii) The surfaces of solid metal electrodes are often inhomogeneous in the chemical sense, and may, for example be partly covered by oxides or absorbed molecules or ions.
iii) Mercury and liquid amalgam electrodes provide structureless, smooth surfaces of readily determinable area. The true surface area of a solid metal is rarely equal to its superficial area. A multiplicity of crystal planes, dislocations contribute to the surface topography giving rise to surface roughness.

**Oxide electrodes.** The difficulties encountered with solid metal electrodes will also be expected to apply in the case of solid oxide electrodes. In addition, there are several further factors to be considered related to the structure of oxides as compared with that of metallic elements. These include the participation of both oxygen and metal atoms which usually differ from each other in size. The electronegativity of each atom is also generally different which means that the bonding electrons are not equally shared between the metal and oxygen atoms. Metals can exist in more than one oxidation state, due to the presence of partially filled orbitals, and hence various stoichiometries have also to be considered, and particularly so with oxides of the transitional metals.

The requirements of an 'ideal' oxide electrode can be summarized as:-

i) Perfect lattice containing no holes, fissures, grain boundaries, permeable to the electrolyte.

ii) Readily obtainable in a reproducible state of minimum free energy and should not occur in different polymorphic forms.
iii) Non-reactive nature so that it is stable in the electrolyte and free of films.

iv) No adsorption of reactant ions at the interphase or the presence of adsorbed intermediates and/or reaction products on the surface which will influence the reaction rate.

v) Small charge separation between the ion in the lattice and ion on the electrolyte side of the interphase.

1.3. REVIEW OF THE WELL DEFINED - OXIDE ELECTROLYTE SYSTEMS

Silver oxide - alkaline system. Silver forms two oxides of stoichiometric compositions $\text{Ag}_2O$ and $\text{AgO}$, both of which are stable in alkali over a limited pH range. The anodic oxidation of silver electrodes in sodium hydroxide electrolyte first produces the lower oxide with a well marked potential arrest before the start of the formation of the higher oxide.

The structure of the lower oxide is well established as containing univalent Ag with a ZnS structure. The structure of the higher oxide has been the centre of much controversy, the general consensus of opinion being divided, between considering it as a mixture of Ag(I) and Ag(III) oxides or a definite monoclinic structure with two distinct Ag-O distances. Both oxides are semi-conductors, the higher oxide having a conductivity several orders of magnitude greater than the lower oxide and so suggests itself for electrochemical study. However, its uncertain structure, poor conductivity in
relation to other oxide electrodes and the fact that it requires no cationic involvement in solution for its formation, coupled with the disadvantages which arise from the use of sodium hydroxide electrolyte, restricts the scope of making electrode kinetic measurements in such systems.

Manganese dioxide - alkaline system. Manganese dioxide exists in four polymorphic forms of which the $\beta$-form, pyrolusite, has the lowest free energy. Anodic oxidation of acid - manganous sulphate electrolytes at a carbon electrode produces the unstable $\gamma$-MnO$_2$.

Surface area measurements of the latter modification, by gas adsorption, reveal an extremely large surface area (i.e. $10^5$ times the superficial surface area). MnO$_2$ electrodes also have the disadvantage in that they absorb a wide variety of cations from solution with the liberation of hydrogen ions. From the study of the discharge characteristics of MnO$_2$ electrodes in ammonium salt electrolyte at pH8, Vosburgh (19) suggested that a reaction occurs within the oxide lattice producing a change of surface composition to MnOOH. The electrode potential varies as the composition of the oxide at the surface exposed to the solution changes.

Lead dioxide - acid system. Lead dioxide exists in two modifications either of which may be prepared relatively free of the other by electroperoxidation of lead electro-
lytes under carefully controlled experimental conditions. \( \alpha \)-PbO\(_2\) may be formed from plumbite, neutral nitrate and acetate electrolytes while the more stable \( \beta \)-modification is prepared from acid electrolytes. The deposits are hard, dense and metallic in appearance.

In general, there is good agreement on the physical and chemical properties of lead dioxide. The excellent conductivity (related to its nonstoichiometric composition) is nearer to that of metals than semiconductors. The conductivity decreases with increase in temperature whereas that of semiconductors increases. The marked contradiction of semiconductor properties is a significant factor in favour of PbO\(_2\) as compared with the other oxides where such properties might interfere with the kinetic measurements. The negative sign of the Hall index indicates that the current carriers are also negative; their high mobility demonstrates that they are more probably electrons than negative ions.

**Other oxides systems.** Mark and Vosburgh (20) have investigated the discharge characteristics of thallium (III) oxide in alkali, titanium (IV) oxide in acid, tin (IV) oxide and cerium (IV) oxide in ammonium sulphate buffered to pH 5. They concluded that whereas thallium (IV) oxide gave reasonably reproducible overpotentials the other oxides did not; also there was evidence that the exchange reaction at the latter oxides was very slow.
Thallium (IV) oxide and titanium (IV) oxide (blue) are good conductors of electricity while TiO$_2$, CeO$_2$ and SnO$_2$ are much poorer conductors in relation to the former oxides.

1.4. CHOICE OF THE OXIDE - ELECTROLYTE SYSTEM

In view of the advantages outlined above (namely: only two polymorphs formed, both prepared by electro-peroxidation, with well defined structures, both thermodynamically stable and having exceptional conductivity) it was decided to investigate the PbO$_2$ - H$^+$ system.

The influence of the electrolyte anion on electrode processes in which it plays no overall part had also to be considered. Three anions were considered, namely sulphate, nitrate and perchlorate.

The complexing action of lead with both nitrate and sulphate anions influences the double layer region both electrostatically and sterically. Lead, however, forms no complexes with perchlorate ions. Adsorption effects of particular anions will be very specific, strongly potential dependent but will be least for non-deformable anions such as perchlorate ions. Both nitrate and perchlorate anions give freely soluble systems which are attractive experimentally since the kinetics may be studied over a wide range of plumbous ion concentration. The limiting solubility and poor conductivity of PbSO$_4$ might be expected to introduce its own further complications. Furthermore, the perchlorate ion is thermodynamically more stable than...
either the sulphate or nitrate ions (e.g. nitrate ions are cathodically reducible).

Whereas sulphate and nitrate electrolytes have attracted a great deal of attention, perchlorate electrolytes have not and in view of this and the advantages outlined above it was decided to study the mechanism of exchange between PbO₂ and plumbous ions in acid-lead perchlorate electrolytes.

1.5. STRUCTURAL CONSIDERATIONS

Tetragonal PbO₂ (β-) has a rutile structure, Figure 2), the unit cell of which is a distorted cube and can be described as a body-centred cubic arrangement of metal atoms with oxygen atoms in positions of three-fold coordination. Orthorhombic PbO₂ (α-) has a columbite structure (Figure 3), consisting of an hexagonal close-packed assembly of oxygen atoms in which half the octahedral holes are occupied by metal ions.

The non-stoichiometric compositions of α- and β-PbO₂, according to Butler and Copp (21), are PbO₁.₈₃₋₂.₀₂ and PbO₁.₉₅₋₂.₀ respectively.

Lower oxides of lead. The lower oxides and hydroxides of lead are of interest as possible products of reduction of lead dioxide. Two polymorphic forms of the next lower oxide, PbO, have been described and are designated tetragonal and orthorhombic PbO. The structure of the former is well established (22), Figure 4. The oxygen
FIG 2  The crystal structure of tetragonal PbO$_2$
FIG 3  The crystal structure of orthorhombic PbO₂
FIG 4  The crystal structure of tetragonal PbO
atoms lie between every other pair of lead layers and each lead atom has four oxygen atom neighbours lying to one side. With the rhombic form it was impossible to locate the oxygen atoms from the intensities of X-ray reflections but their positions have been determined by neutron diffraction. The basic structure unit is a chain, Figure 5, in which the lead atom is bonded to two oxygen atoms (at 2.21 Å) and these chains are then weakly bonded into layers by two Pb-O bonds of lead (2.49 Å). The layer is a puckered version of tetragonal PbO where there are four equal Pb-O bonds.

Olin (23) has shown, from a potentiometric study of the hydrolysis of lead (II) in a perchlorate medium, that there is good evidence for a Pb(OH)$^+$ complex; Pb(OH)$_2$ also exists and is stable in electrolytes of high pH. As regards the hydroxo complexes of lead (IV) very little is known and the existence of Pb(IV) ions in solution is uncertain (24).

1.6. LITERATURE REVIEW

The electrochemical aspects of the lead dioxide-acid system have attracted considerable attention following the development of the lead-acid storage battery by Planté in 1859. During recent years interest has continued following the discovery of $\alpha$-PbO$_2$ by Kameijama and Fukeumoto (25) while Zaslavsky and his co-workers
FIG 5  The crystal structure of rhombic PbO
(26,27) later showed this modification to have an orthorhombic structure.

The chemical processes occurring in a lead-acid battery can be represented by the overall equation,

$$\text{PbO}_2 + \text{Pb} + 2 \text{H}_2\text{SO}_4 = 2 \text{PbSO}_4 + 2 \text{H}_2\text{O} \quad \ldots \ldots \text{[1.9]}$$

This proposed scheme was named the "double sulphonation theory" and was formulated by Glasstone and Tribe (28). Fundamental research into this theory was performed inter alia by Dolezalik (29), Hamer (30) and Beck and Wynne-Jones (31), the latter workers in particular contributing significantly in support of the double sulphonation theory.

More detailed suggestions have since been forwarded for the actual mechanism. Feitknecht and co-workers (32,33) have investigated the passivation of lead electrodes in $\text{H}_2\text{SO}_4$ electrolyte and concluded that $\beta$-$\text{PbO}_2$ is formed by the oxidation of plumbous ion by hydroxyl radicals.

$$\text{Pb}^{++} + 2 \text{OH} = \beta\text{-PbO}_2 + 2 \text{H}^+ \quad \ldots \ldots \ldots \text{[1.10]}$$

Spahrbier (34), however, found that the reactions occurring during $\beta$-$\text{PbO}_2$ formation may be summarized as:

$$\text{H}_2\text{O} = \text{H}^+ + \text{OH}_\text{ads} + e \quad \ldots \ldots \ldots \text{[1.11]}$$

$$\text{Pb}^{++} + \text{H}_2\text{O} = \text{Pb(OH)}^{++} + \text{H}^+ + e \quad \ldots \ldots \text{[1.12]}$$

At present it has been generally accepted that the
mechanism upon which passivation is based begins with OH\(^-\) ions discharging followed by hydroxyl radical adsorption at the electrode surface. The Pb(OH)\(_2\) formed from the adsorbed radicals is immediately oxidized into one or both forms of PbO\(_2\) (35). The suggestion of plumbic ion participation in the exchange reaction has attracted considerable interest (35, 36). Bone, Fleishmann and Wynne-Jones (37) when investigating the kinetics of exchange between plumbous ions in solution and \(\alpha\)- and \(\beta\)-PbO\(_2\) have shown that plumbic ions were not involved in the oxidation process. Using a radioactive tracer technique the exchange between plumbous ions and PbO\(_2\) in a nitrate electrolyte was examined by measuring the rate at which plumbous ions in solution become active. It was found that the total exchange occurred very quickly and without exception at the available and accessible surface.

Fleischmann and co-workers (38, 39), using the potentiostatic technique, have studied the nucleation of \(\alpha\)-PbO\(_2\) from acetate and neutral nitrate electrolytes and the nucleation of \(\beta\)-PbO\(_2\) from acid-perchlorate, nitrate and sulphate electrolytes. A mechanism has been suggested (38) for the deposition of \(\alpha\)-PbO\(_2\) from acetate electrolytes and the charge transfer coefficients have been summarized for a series of electrolytes (39). The magnitude of the exchange current is not quoted in the literature and attempts to calculate it
from reported $\eta_d - i$ data suggests that the reaction is slow e.g. $i_0 \approx 0.1 \text{ mA cm}^{-2}$ in an electrolyte of sulphuric acid saturated with lead sulphate.

Although the mechanism of discharge remains obscure, discharge characteristics of $\beta$-PbO$_2$ in sulphuric and perchloric acid electrolytes are quite well known (20,40,41). There is little similar such information available however concerning $\alpha$-PbO$_2$ (42-44).

Self discharge effects have been observed by a number of investigators (20,40), although the magnitude of this effect is somewhat uncertain. Beck, Lind and Wynne-Jones (40) found a rate of discharge equivalent to 0.6 mA cm$^{-2}$ when studying the anodic oxidation of lead whereas Mark and Vosburgh (20) reported a value 1.8 x 10$^{-4}$ mA cm$^{-2}$ in the deposition of PbO$_2$ onto a platinum substrate from an acid-lead perchlorate electrolyte.

The charging and discharging of a lead accumulator occurs at appreciable overvoltages and hence the overvoltage of oxygen evolution has attracted considerable attention (45-51). Rüetschi and co-workers (45,50) found agreement with the Tafel equation with a slope of 0.121 V/ decade of current for $\beta$-PbO$_2$ which is in good agreement with that observed by other workers (47,49).
CHAPTER 2. PRELIMINARY CATHODIC POLARIZATION STUDIES

This part of the investigation records the results of the galvanostatic polarization of $\alpha$- and $\beta$-$\text{PbO}_2$ electrodes in acid-perchlorate electrolytes until the passive state is obtained. Analogous anodic studies of metals have shown that passivation occurs when the faradaic current has exceeded a critical value and the onset of passivation is marked by a steep rise of potential with respect to time.

The object of these experiments is to provide information regarding the cathodic behaviour of the electrode in acid-perchlorate electrolytes and to explore the feasibility of making kinetic measurements uncomplicated by the intrusion of solid films.

Experimental

Electrolytic cell. Polarization experiments were made in a cell similar to that illustrated in Figure 6. All cell fittings used were lubrication-free ground glass joints. The cell was connected to the borosilicate glass nitrogen line using minimum lengths of flexible neoprene tubing. Exhaustive laboratory tests had shown that the release of impurities from neoprene into the electrolytic system was negligible.
A, test electrode; B, reference electrode; C, counter electrode; D, purification limb containing activated charcoal; and E, nitrogen lift pump.
Electrodes. Counter, test and reference electrodes were of identical material prepared by electrodeposition of either $\alpha$- or $\beta$-PbO$_2$ onto etched (1:1 HNO$_3$/H$_2$SO$_4$) platinum. The deposition procedure is given in Appendix 2. The purity of the electrodeposits was checked by X-ray diffraction (Philips diffractometer type P.W. 1051) and in addition, their electrode potentials were measured in acid-lead perchlorate electrolytes, as reported in Appendix 3. The test electrode was the cross section of a platinum rod (area, $3.14 \times 10^{-2}$ cm$^2$) sealed in lead-free soda glass and connected to the electrical circuit via the usual mercury-iron contact, also used for the reference and counter electrodes. The counter electrode was a gauze cylinder of large surface area and the reference electrode a small flat sheet.

An optical examination of the platinum-glass seal was made prior to electrodeposition to ensure that no crevices were present.

Materials. All materials were of A.R. quality. Water was twice distilled from deionized stock and had a conductivity of $< 1$ $\mu$mho cm$^{-1}$. Charcoal was purified by Soxhlet extraction and pure nitrogen was obtained from commercial "oxygen-free" nitrogen as described in Appendix 4.

Purification procedure. All the vessels used in the
electrolyte preparation and the electrolytic cells and their components were cleaned (1 week) with 50-50 concentrated sulphuric and nitric acid. They were then washed with 10 changes of distilled water followed by double distilled water and were allowed to remain in the latter for two days. On completion of the washing procedure all glassware was dried in an oven at 120°C. A criterion of successful cleaning was freedom from attaching drops on the glass above the solution.

Continuous purification of the electrolyte to remove traces of impurity, which might interfere with the polarization studies or electrode kinetic measurements, was achieved by passing the electrolyte through active charcoal. Circulation was via a nitrogen-activated lift pump.

Tests with sitting-drop mercury electrodes in inert electrolytes had shown that a satisfactory level of electrolyte cleanliness was attained after four days continuous circulation, at a rate of approximately 25 ml min\(^{-1}\). The criterion used for electrolyte cleanliness was conformation of the differential capacitance curves with established data (52) and a change of less than 1% over 24 hours. Hampson and Larkin (53) using the same purification procedure, as described above, have observed \(C_L\) stability for extended periods up to 10 days. Satisfactory \(C_L\) stability was
achieved using $\beta$-PbO$_2$ electrodes in inert electrolytes when at least four days circulation was allowed before experiments were made (see Chapter 6).

Electrical circuit (Fig 7). For polarization times greater than 0.1 sec, the potential source was a battery (138 V) switched in the conventional manner. For the experimental polarization-time range the rise-time of the current was too small to be of consequence in the present work. When passivation times were less than 0.1 sec, the battery source was replaced by a pulse generator (Solartron, type GO 1005). The pulse generator also provided a prepulse which was used to trigger the time base of the oscilloscope (Hewlett Packard type 130C fitted with camera type 196B) just before the pulse developed. The pulse generator output, 100V into 2500$\Omega$ at a maximum amplitude of 40 mA, was continuously variable with a risetime of 0.3 $\mu$sec. The potential of the pulse generator was initially and finally at earth; providing that counter and test electrodes were of identical material, this was not important.

Experimental procedure. Experiments were made in air thermostats at temperatures of 23 ± 1°C. Electrolytes, maintained at constant total concentration (6.85M) with NaClO$_4$, were unstirred during polarisation experiments. A freshly prepared electrode was withdrawn from the electrodeposition circuit, washed with
FIG 7  Electrical circuit

C, counter electrode; C<sub>r</sub>, standard resistance;
L, load resistance; P, potential source;
R, reference electrode; T, test electrode.
double distilled water and test electrolyte and fitted into the electrolytic cell. After 20 min. contact with the electrolyte, polarisation was commenced. Once passivated, electrodes were discarded, since with such electrodes even after rest periods sufficiently long for cathodic products to leave the vicinity of the electrode, repassivation times significantly longer than the original were sometimes recorded. Potential-time oscilloscope traces were generally recorded photographically. The passivation time was measured from the instant the current pulse rose to the time the cathode potential fell abruptly. Experiments were repeated to ensure reproducibility, mean values being determined. Passivation times were recorded as functions of current density and electrolyte composition.

After passivation, cathodes were cleaned, etched and recoated with lead dioxide.
2.1. THE CATHODIC BEHAVIOUR OF $\beta$-PbO$_2$ IN ACID-PERCLORATE ELECTROLYTES.

Experimental Results

Figure 8 shows a typical overpotential - time trace for the polarization of $\beta$-PbO$_2$. The point of passivation, A, (first transition time) is precisely determined and marks the termination of the reaction

$$\beta$-PbO$_2$ + 4H$^+$ + 2e = Pb$^{2+}$ + 2H$_2$O \ldots \ldots \ldots \text{[2.1]}$$

The second transition which occurs at point B represents the change in the process between

$$\text{Pb}^{2+} + 2(\text{ClO}_4^-) + 2e = \text{Pb} + 2(\text{ClO}_4^-) \ldots \ldots \text{[2.2]}$$

and the discharge of hydrogen ions. ($\text{ClO}_4^-$ ions are shown in this equation since the nature of the passivating layer-oxide or -perchlorate is uncertain). The presence of metallic lead on the surface of electrodes polarized beyond the point A was readily identifiable by the ease with which it amalgamated with a mercury drop.

Figure 9 shows the passivation time-current density data correlated in the form

$$(i - i_1) \frac{t^\frac{1}{2}}{p} = \frac{k}{p} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
FIG 8

Overpotential - time trace

$\beta$-PbO$_2$ electrode; electrolyte $6.65 \, \text{M H}^+$; total $[\text{ClO}_4^-]$ $6.85 \, \text{M (with NaClO}_4)$; $23 \, ^\circ \text{C}$; current density, $0.3 \, \text{A cm}^{-2}$
FIG 9 Relationship between current density and passivation time

$\beta$-PbO$_2$ ELECTRODE; ELECTROLYTE: (A) 0.5 M H$^+$ (B) 3.0 M H$^+$
(C) 6.65 M H$^+$; TOTAL [ClO$_4$] 6.85 M (WITH NaClO$_4$); 23°C
The passivation time depends on hydrogen ion concentration, and both $k_p$ (Figure 10) and $i_l$ (Figure 11) increase with increase in $[H^+]$.

Experiments in which polarization was interrupted before passivation and the electrode allowed to remain on open circuit for sufficient time for cathodic products to leave the vicinity of the electrode, indicate that subsequent passivation time was almost unaffected by the initial part of the polarization, as shown in Table 1.

**Discussion of Results**

It is clear from the interrupted polarization experiments that the electrode remains free of substantial films of cathodic product during the prepassivation period. Measurements at "active" $\beta$-PbO$_2$ electrodes in perchlorate solution will therefore be uncomplicated by the intrusion of thick films. The presence however of adsorption layers of the type discussed by Randles (54) could be inferred only by analysis of kinetic measurements.

Passivation of the cathode for the process represented by equation $[2.1]$ indicates that the capacity for Pb(II) has been exceeded in the layers of electrolyte immediately surrounding the cathode.

The concept of a diffusion layer (boundary layer), introduced by Nernst and Brunner (55), has been of
FIG 10  The variation of $k_p$ with acid concentration

$\beta$-PbO$_2$ electrode; total [ClO$_4$], 6.85 M, 23°C

Acid concentration, M
Variation of limiting current density with acid concentration

$\beta$-PbO$_2$ Electrode; Electrolyte, 6.85 M ClO$_4^-$ (with NaClO$_4$)

23°C
The results of current interruption experiments on β-PbO₂ electrode in acid perchlorate electrolytes at 23°C.

Total concentration of ClO₄⁻, 6.85 M with added NaClO₄.

<table>
<thead>
<tr>
<th>[H⁺] M</th>
<th>Current density A cm⁻²</th>
<th>Time of initial polarization t₁, sec</th>
<th>Rest time t₂, sec</th>
<th>Time to 1st transition (t₂ − t₁), sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.39</td>
<td>0</td>
<td>0</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>10</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>10</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>10</td>
<td>0.60</td>
</tr>
<tr>
<td>3.0</td>
<td>0.234</td>
<td>0</td>
<td>0</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>10</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>10</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.0</td>
<td>10</td>
<td>4.9</td>
</tr>
<tr>
<td>0.01</td>
<td>0.060</td>
<td>0</td>
<td>0</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>10</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.5</td>
<td>10</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.0</td>
<td>10</td>
<td>2.6</td>
</tr>
</tbody>
</table>
considerable use in the treatment of mass transfer processes at electrodes. These workers assumed that the electrode layer adheres sufficiently strongly to the electrode to prevent slipping, but at a definite distance $\delta$ from the electrode, termed the thickness of the diffusion layer, the average composition of this electrode layer is maintained. More recently, largely due to the work of Levich (56) and Agar (57), this physical concept has been replaced by the idea of a "mass transfer boundary layer" in which fluid motion is extended to the interphase. The diffusion layer is thus regarded as a hypothetical layer of electrolyte in which the flow of ions entering the layer is identical with that leaving it. The combined rate of all mechanisms acting over this mass transfer path may be expressed by a single rate equivalent to pure diffusion (58). The point of passivation of an electrode for an electrolytic process is reached when the concentration in the diffusion layer of any species participating in the electrode reaction reaches its critical value (e.g. attainment of the solubility limit).

When the electrode is polarized at a constant current density, the change in concentration ($\Delta C$) of the reacting species in the layer of solution very near the electrode may be derived as follows from the laws of non-steady-state diffusion (56).
\[ \Delta C = \frac{i}{2F} \times \sqrt{\frac{4t}{\pi D}} \quad \ldots \quad [2.4] \]

Where \( i \) is the current density

\( D \) is the diffusion coefficient

\( t \) is the time of polarization

\( Z, F \) and \( \pi \) have their usual significance.

This equation applies to an electrolyte presumed free from convection which would tend to suppress changes in concentration. According to [2.4] passivation may occur at every current density unless some mode of mass transfer other than diffusion applies, since

\[ i = k_p t^{-\frac{1}{2}} \quad \ldots \quad [2.5] \]

where

\[ k_p = \frac{ZF \sqrt{\pi D}}{2} \cdot \Delta C_i \quad \ldots \quad [2.6] \]

and \( \Delta C_i \) is the critical value of \( \Delta C \). Taking \( D \) as \( 9.0 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \) (the value at infinite dilution at \( 23^\circ \text{C} \) for lead perchlorate electrolytes), we obtain

\[ k_p = 513 \Delta C_i \quad \ldots \quad [2.7] \]

where \( \Delta C_i \) is measured in mole cm\(^{-3}\).

As suggested by Eisenberg, Bauman and Brettner (59), a certain current density requisite to establish and maintain the diffusion layer can be calculated; in this case the effective diffusion layer would differ in average concentration and thickness from that to be
expected under conditions of free convection. The
current required to maintain a concentration difference
\( \Delta C \) across the diffusion layer is given by

\[
i = ZF \frac{D}{\delta} \Delta C = 1.74 \frac{\Delta C}{\delta} \quad ........................[2.8]
\]

where \( \Delta C \) is in mole cm\(^{-3}\).

For the current to become limiting \((i_\text{l})\), \(\Delta C\) becomes
\(\Delta C_\text{i}\).

For diffusion controlled practical systems, by
combining equations \([2.5]\) and \([2.8]\) we obtain

\[
i - \frac{ZFD}{\delta} \Delta C_\text{i} = \frac{ZF \sqrt{\pi D}}{2} \Delta C_\text{i} \cdot t^{-\frac{1}{2}} \quad ........................[2.9]
\]

There is thus justification for an equation of the
form \([2.3]\), provided that diffusion dominates the mass
transfer and the value of \(\delta\) is reasonably constant in
the experimental current range. For most electro-
chemical systems the first condition is only fulfilled
when the duration of the polarization is sufficiently
short to prevent the development of free convection.
This duration is estimated to be about 20 sec (59).
The experiments reported in the present work are for
durations less than this limit.

Figure 9 shows that within the experimental range
of current densities the experimental results conform
accurately to equation \([2.3]\). Thus, the value of the
hypothetical \(\delta\) is reasonably constant. The extrapola-
tion to \(t^{-\frac{1}{2}} \frac{1}{p} = 0\) (infinite duration of polarization)
gives the minimum current density required to cause

28.
passivation; that is, the current density equivalent to mass transfer other than by diffusion when this latter is the controlling mechanism.

Figure 10 correlates \( k_p \) with \([H^+]\) and conforms to the following equation (method of least squares - IBM 1620 computer),

\[
k_p = 0.193[H^+] + 0.038 \text{ [2.10]}
\]

The value of \( \Delta C_i \) for the systems used in our experiments at constant ionic strength (added Na\(^+\)) would be expected to vary with the \([H^+]\). We may therefore compare equations \([2.3]\) and \([2.9]\) with equation \([2.10]\) and so obtain (in molar units)

\[
\Delta C_i = 0.38[H^+] + 0.074 \text{ [2.11]}
\]

Using equations \([2.8]\) and \([2.11]\), \( \delta \) can be calculated for each observed value of \( i_l \). The results are shown in Table 2. The values of \( \delta \), estimated for conditions where free convection is absent (i.e. in this case, for experiments within 0.05 to 20 sec of closing the circuit) may be compared with values of \( \delta \) obtained by other workers for systems subject to free convection. Although it is now well established (59) that \( \delta \) varies with electrolyte composition, current density, viscosity, diffusion coefficient, density, electrode size and shape, Glasstone (60) and Agar and Bowden (61) suggests on the basis of experiment that \( \delta \) should have the value of 0.05 cm; Brunner (55) found \( \delta \) to be
### Table 2

**Calculated Distance (δ cm) for Observed \( i_{\text{1-}} \)**

\( \beta\)-PbO\(_2\) electrode in acid-perchlorate electrolyte at 23°C.

Total concentration of Cl\(_4^-\) 6.85 M (with added NaClO\(_4\)).

<table>
<thead>
<tr>
<th>([H^+]) M</th>
<th>( i_{\text{1-}} ) A cm(^{-2})</th>
<th>( \delta ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.007</td>
<td>0.023</td>
</tr>
<tr>
<td>0.20</td>
<td>0.008</td>
<td>0.032</td>
</tr>
<tr>
<td>3.00</td>
<td>0.050</td>
<td>0.043</td>
</tr>
<tr>
<td>5.38</td>
<td>0.086</td>
<td>0.043</td>
</tr>
<tr>
<td>6.65</td>
<td>0.156</td>
<td>0.030</td>
</tr>
</tbody>
</table>
0.03 - 0.05 cm, whilst Laitinen and Kolthoff (62) quote \( \delta \) as 0.025 cm.

The excellent correlation of our \( \delta \) values with these accepted values suggests that the high viscosity of the electrolyte and the electrode orientation both tend to compensate in our experiments for the non-establishment of free convection.

However, the reasons for the change in \( \delta \) with \([H^+]\) although interesting, remain obscure due to uncertainty in the value of \( D \) in concentrated solution and also of the values of \( \Delta C_i \).

Thus, providing a measure of control over convection can be exercised, the assumption of a hypothetical diffusion layer in conjunction with non-steady-state diffusion enables the general features of the passivation-time current density relationships for \( \beta\text{-PbO}_2 \) in \( \text{HC}_{104} \) to be described semiquantitatively.
Experimental Results

A series of galvanostatic polarizations in perchloric acid electrolytes (NaClO₄ added to maintain a constant \([\text{ClO}_4^-]\)) were made. Overpotential-time traces recording the electrode reactions were similar to those obtained for \(\beta\)-PbO₂ and corresponded to transitions between the reactions \([2.1]\) and \([2.2]\) and the discharge of hydrogen ions. Examination of the electrode, at the point of hydrogen evolution, showed only a reddish-brown film, with no evidence of metallic lead (no amalgamation with mercury).

The time, \(t_p\), to the first transition, measured by the time taken for the potential to fall abruptly from the instant of closing the circuit, was studied as a function of current density and \([H^+]\).

Straight lines were obtained on plotting \(t_p^{-\frac{1}{2}}\) versus current density, \(i\), (Figure 12) confirming the relationship given by equation \([2.3]\). Both the constant \(k_p\) and the limiting current density \(i_l\) vary with \([H^+]\) as shown in Figures 13 & 14.

The dependence of \(k_p\) on \([H^+]\) calculated using the method of least squares (ICT 1905 computer) is

\[
k_p = 0.197 \ [H^+] + 0.015 \quad \ldots \ldots \ldots \ldots \ [2.12]
\]
Relationship between current density and passivation time

\( \alpha \text{PbO}_2 \) electrode; electrolyte:

- (A) 0.5M H\(^+\)
- (B) 1.0M H\(^+\)
- (C) 6.65M H\(^+\); total [ClO\(_2\)] 0.85M (with NaClO\(_4\)); 23°C

![Graph showing the relationship between current density and passivation time](image)
FIG 13  The variation of $k_p$ with acid concentration.

$\alpha$-PbO$_2$ electrode; total $[\text{ClO}_4^-]$, 6.85M, 23°C
FIG 14  Variation of limiting current density
with acid concentration

α-PbO₂ ELECTRODE: ELECTROLYTE, 6.85M ClO₄⁻ (WITH NaClO₄)

23°C

Limiting current density, A cm⁻²

Acid concentration, M
Discussion of Results

As with $\beta$-PbO$_2$, the passivation results indicate that the electrode remains active and free of films throughout a region sufficiently great for satisfactory electrode kinetic data to be obtained.

From the passivation time-current density data the following dependence of $\Delta C_i$ (the limiting concentration difference, in molar units, across the diffusion layer maintained by $i_1$) on $[H^+]$ at constant temperature is obtained.

$$\Delta C_i = 0.39 \left[ H^+ \right] + 0.030 \text{ at } T = 23^\circ \text{C} \quad \ldots \quad [2.13]$$

The diffusion layer thickness, $\delta$, calculated in a similar manner to that used for $\beta$-PbO$_2$ experiments leads to the results shown in Table 3. The similarity of $\delta$ for both $\alpha$- and $\beta$- lead dioxide suggest that for the diffusion controlled, first transition process, $\text{PbO}_2 \rightarrow \text{Pb}^{11}$, the effective surface area of each modification is approximately the same. This is to be expected as the diffusion layer being thick reflects the superficial area rather than the true surface area (63).

When the electrode, polarized to the point of hydrogen evolution was removed from the electrolyte, the absence of detectable lead on the electrode was a significant difference from the cathodic behaviour.
**TABLE 3.**

**CALCULATED DISTANCE (δ cm) FOR OBSERVED \( i_1 \).**

α-PbO₂ electrode in acid - perchlorate electrolytes at 23°C. Total concentration of Cl⁻, 6.85 M (with added NaClO₄).

<table>
<thead>
<tr>
<th>([\text{H}^+])</th>
<th>( i_1 )</th>
<th>( δ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>A cm⁻²</td>
<td>cm</td>
</tr>
<tr>
<td>0.027</td>
<td>0.002</td>
<td>0.035</td>
</tr>
<tr>
<td>0.24</td>
<td>0.006</td>
<td>0.035</td>
</tr>
<tr>
<td>0.94</td>
<td>0.015</td>
<td>0.046</td>
</tr>
<tr>
<td>3.00</td>
<td>0.050</td>
<td>0.042</td>
</tr>
</tbody>
</table>
of the α- material. This difference might be attributed to the greater oxidizing power of α-PbO₂ as indicated by the more positive E° and hence a greater free energy in the reaction.

\[ \text{PbO}_2 + \text{Pb} + 4 \text{HCIO}_4 = 2 \text{Pb(CIO}_4)_2 + 2 \text{H}_2\text{O} \quad [2.14] \]

In other words, in the case of the α- material, the redox reaction

\[ \text{Pb(IV)} + \text{Pb(0)} \rightarrow \text{Pb(II)} \quad [2.15] \]

occurs readily so removing any metallic lead that might be produced. This behaviour finds a parallel in the discharge reaction of α- and β-PbO₂ in dilute H₂SO₄ as reported by Mark (42), who found that the final PbSO₄ product in the case of α-PbO₂ remains as a tightly adherent film on the surface of the undischarged PbO₂ whereas the film on the β- material is much less coherent. It seems likely in the present experiments that the α- material becomes covered with an adherent film which is ultimately reduced to lead, with the latter simultaneously reacting with the underlying α-PbO₂ (64) to form PbO or some corresponding salt of perchloric acid. The final product in the case of β-PbO₂, however, is in less perfect physical contact with the underlying electrode and so reacts at a much slower rate, if indeed it reacts at all.
CHAPTER 3. THE LEAD DIOXIDE - SOLUTION EXCHANGE REACTION IN THE LOW OVERPOTENTIAL REGION

Introduction

The mechanism of exchange between simple ions in solution and atoms in a metal lattice has been the object of study for many years [see e.g. (65)]. Until recently, little informative work has been possible on the kinetics of electrode reactions mainly due to limitations in the experimental techniques. These arise because electrode surfaces are very sensitive to impurities and hence readily adsorb impurities at their active centres which are important for the exchange reaction. A further intrinsic difficulty is that of carrying out significant measurements if the electrode surface does not retain its original crystallographic configuration.

The introduction of modern purification methods (1) and development of improved electronic measuring techniques (2) have made study of kinetics of electrolytic deposition and dissolution more meaningful.

At lead dioxide electrodes, Fleischmann and co-workers (39) have observed the current-overpotential relationships expected for a rate determining charge transfer reaction. Their results corroborated the conclusions of other workers (20), namely, that the exchange reaction is slow.
The object of these studies is to determine first, the general path by which the ions pass from their initial state of hydration in the solution to their final state in the lattice and vice-versa, and secondly, which step in the overall path is rate-determining under given sets of conditions.

**Method of Investigation**

A number of experimental methods, which differ only in their experimental arrangements, are available for investigating electrode reactions. For the comparatively slow electrode reaction under study, the galvanostatic (constant current) and potentiostatic (constant potential) methods were considered.

Both methods, however, possess limitations. The most serious problem in the potentiostatic method is the ohmic resistance, $R_{\Omega}$, which prevents the setting up of potentiostatic conditions. In addition, the internal resistance of the circuit remains larger than $R_{\Omega}$ and a time constant greater than $R_{\Omega} C_L$ is needed to reach the constant overpotential. Furthermore, the problems of stability, due to the fact that feedback is used, makes it difficult to obtain a sufficiently fast response.

With the galvanostatic arrangement the double layer capacitance limits the application of this method. The charging time for the electrical double layer is relatively long because the charging current is limited by...
the constant current applied to the system. However, the ohmic resistance can be corrected for easily when it remains constant during the transient. In addition a far superior response time can be obtained with this technique compared with the potentiostatic technique.

**Interpretation of overpotential - current data.** The ideal galvanostatic response of a system would be a vertical increase of overpotential at the starting point, followed by a more or less slow increase of the overpotential with time due to concentration polarization, as shown in Figure 15. In reality the double layer capacitance, \( C_L \), limits the slope of the potential increase during the first part of the transient and can be calculated from

\[
C_L = \lim_{t \to 0} i \frac{dt}{d\eta} \quad [3.1]
\]

The overpotential necessary to drive the charge transfer reaction at a rate equivalent to the applied current is reached some time later.

When faradaic current passes across the interphase, concentration changes, \( \Delta C \), occur. Initially the increase of \( \Delta C \) with time is approximately proportional to the integral of current with time. These changes are small during the first period of the transient and hence an extrapolation of overpotential-time transients to zero time (providing the double layer is charged

36.
FIG 15  Schematic representation of a galvanostatic transient

\[ \text{Real} \]

\[ \text{Ideal} \]
and concentration overpotential is small) should give a relationship between current and overpotential as required by equation \([1.2]\). This simple analysis, however, breaks down if the reaction is fast, e.g. \(k^0 > 1 \text{ cm sec}^{-1}\), for the simple reaction \(0 + Ze = R\), since significant faradaic current flowing during the process of double layer charging makes the determination of \(\eta_D\) impossible by this simplified technique (66, 67).

The pseudo-ohmic overpotential, \(\eta_O\), is established in about \(10^{-11}\) sec. and is therefore observed on the oscilloscope as a gap in the trace between the zero point and the beginning of the \(\eta_t\) transient. \(\eta_O\) is linear with current density and the error it introduces may be corrected relatively easily.

**Experimental**

**Electrolytic system.** The electrolytic cell, electrodes and purification techniques were similar to those described in Chapter 2. Electrolytes were maintained at high ionic strength in order to minimise the electrolytic resistance. A range of electrolytes (constant perchlorate ion concentration 6.85 M) of variable \([\text{Pb}^{++}]\) at constant \([\text{H}^+]\) and variable \([\text{H}^+]\) at constant \([\text{Pb}^{++}]\) were investigated. All experiments were carried out in thermostatted water baths (± 0.1°C).
Electrical circuit. The square shape pulse was obtained from a pulse generator (Solartron, type GO 1005) with a circuit identical to that described in Chapter 2.

Measurements. After allowing sufficient time for the electrode to attain equilibrium with the electrolyte, the electrode was subjected to a single pulse of current for about 80 msec. The associated overpotential-time transient for a fixed current was recorded photographically on Polaroid film (type 47). The maximum potential excursion was ± 10 mV about the equilibrium.

On completion of a series of measurements for both anodic and cathodic polarization, each reading was checked resulting in two complete sets of \( \eta - i \) data for each electrolyte.

Accuracy of measurements. Current measured by observing the potential developed across a standardised carbon resistor was only as accurate as the oscilloscope used for the potential measurement. Electrode potentials could be read to ± 0.01 mV in the range up to 2 mV and ± 0.05 mV in the range up to 10 mV. The maximum error in the determinations is estimated as ± 10%.

Evaluation of kinetic parameters. The exchange current can be calculated from the slope of the faradaic current
versus overpotential curves at the origin (equation [1.3]).

An iterative programme has been devised by Farr, Hampson and Williamson (68) who show that the charge transfer coefficient, $\alpha$, and exchange current, $i_o$, can be determined from a statistical analysis of $\eta_D - i$ data. This data is introduced into the charge transfer equation [1.2] and optimum values of $\alpha Z$ and $i_o$ were determined by minimising the root-mean-square deviation of arbitrarily chosen $i_o$ values. (This programme has since been extended for high overpotential data using an ICT 1905 computer and is shown in Appendix 5).

For the reaction represented by equation [2.1], by analogy with equation [1.6], the following rate equation applies

$$i_o = 2Fk_1 C_{Pb}^{++} C_H^4 (1-\alpha) C_{PbO_2}^{(1-\alpha)} \ldots \ldots \ldots \ldots \ldots [3.2]$$

where $k_1$ is a rate constant, $C_{PbO_2}$ is taken as unity, and $\alpha$ can be estimated from the dependence of $i_o$ on the concentration of the electroactive species.
3.1. EXCHANGE REACTION AT $\beta$-PbO$_2$ ELECTRODES IN THE LOW OVERPOTENTIAL REGION

Experimental Results

Relation between overpotential and time. Examples of $\eta$-t curves are shown in Figure 16. The gap represents the pseudo-ohmic overpotential which was linear with current density, Figure 17, and corresponded to an electrolyte resistance (accurately calculated by employing overpotentials >10 mV) of 1.0 $\Omega$. The transient shows a steep rise, representing the double layer charging process, followed by a steadily increasing linear region from which $\eta_D$ results by extrapolation to zero time. The double layer capacitances corresponding to experimental electrolytes are shown in Table 4.

Relation between activation overpotential and current density. Figure 18 shows typical current-overpotential relationships for a series of electrolytes. $i_o$ results from the slope through the origin (equation [1.3]) and was identical for cathodic and anodic processes. A satisfactory comparison of $i_o$ values estimated geometrically with those calculated using the iterative technique is recorded in Table 5.

40.
FIG 16  Typical overpotential-time curves

$\beta$-PbO$_2$ ELECTRODE; ELECTROLYTE: 0.1 M Pb$^{2+}$, 3.0 M H$^+$,
$[\text{ClO}_4^-]$ 6.85 M (WITH NaClO$_4$); 23°C

1. TIME BASE 10 msec cm$^{-1}$; SENSITIVITY 0.5 mV cm$^{-1}$;
CURRENT DENSITY 0.02 mA cm$^{-2}$

2. TIME BASE 10 msec cm$^{-1}$; SENSITIVITY 2 mV cm$^{-1}$;
CURRENT DENSITY 0.06 mA cm$^{-2}$
3. TIME BASE 10 msec cm\(^{-1}\); SENSITIVITY 20 mV cm\(^{-1}\); CATHODIC CURRENT DENSITY 11.1 mA cm\(^{-2}\)
Dependence of pseudo-ohmic overpotential on current

- Cathodic polarization
- Anodic polarization

\[ R_n = 1 \Omega \]
MEAN DOUBLE LAYER CAPACITANCES AT 23°C.

β-PbO₂ electrodes in acid - lead perchlorate electrolytes.
Total concentration of ClO₄⁻, 6.85 M (with added NaClO₄).

<table>
<thead>
<tr>
<th>[Pb²⁺]</th>
<th>[H⁺]</th>
<th>C_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M</td>
<td>µF cm⁻²</td>
</tr>
<tr>
<td>0.045</td>
<td>3.0</td>
<td>82.0</td>
</tr>
<tr>
<td>0.090</td>
<td>3.0</td>
<td>78.0</td>
</tr>
<tr>
<td>0.47</td>
<td>3.0</td>
<td>80.6</td>
</tr>
<tr>
<td>1.39</td>
<td>3.0</td>
<td>79.0</td>
</tr>
<tr>
<td>0.098</td>
<td>6.85</td>
<td>82.2</td>
</tr>
<tr>
<td>0.096</td>
<td>0.20</td>
<td>72.2</td>
</tr>
</tbody>
</table>
FIG 18  Faradaic current overpotential curves

$\beta$-PbO$_2$ Electrode  23°C

$\eta_D$, mV

-40

-20

0

20

40

0.04

0.02

0.02

0.04

i, mA cm$^{-2}$

Anodic

Cathodic

ELECTROLYTE  6.85 M [ClO$_4$]

(WITH NaClO$_4$)

○ 1.5 M Pb$^{2+}$, 3.0 M H$^+$

Δ 0.1 M Pb$^{2+}$, 3.0 M H$^+$

• 0.1 M Pb$^{2+}$, 0.5 M H$^+$
TABLE 5.

EXCHANGE CURRENTS AND CHARGE TRANSFER COEFFICIENTS AT 23°C.

β-PbO₂ electrodes in acid - lead perchlorate electrolytes. Determined (a) Geometrically, and (b) Iteratively.
Total concentration of ClO₄⁻, 6.85 M (with added NaClO₄).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( i_0(a) ) mA cm⁻²</th>
<th>( i_0(b) ) mA cm⁻²</th>
<th>( \alpha(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.0 \text{ M H}^+ )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.045 M Pb²⁺</td>
<td>0.094</td>
<td>0.098</td>
<td>0.23</td>
</tr>
<tr>
<td>0.090 M Pb²⁺</td>
<td>0.110</td>
<td>0.113</td>
<td>0.20</td>
</tr>
<tr>
<td>0.470 M Pb²⁺</td>
<td>0.149</td>
<td>0.156</td>
<td>0.20</td>
</tr>
<tr>
<td>0.930 M Pb²⁺</td>
<td>0.169</td>
<td>0.177</td>
<td>0.19</td>
</tr>
<tr>
<td>0.09 M Pb²⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 6.65 \text{ M H}^+ )</td>
<td>0.158</td>
<td>0.160</td>
<td>0.18</td>
</tr>
<tr>
<td>0.50 M H⁺</td>
<td>0.086</td>
<td>0.093</td>
<td>0.22</td>
</tr>
<tr>
<td>0.05 M H⁺</td>
<td>0.042</td>
<td>0.048</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Dependence of exchange current on the concentration of electroactive species. The dependence of exchange current on $[\text{Pb}^{++}]$ is shown in Figure 19 and on $[\text{H}^+]$ in Figure 20. The dependence should follow a relationship given in equation [3.2] from which we obtain:

$$\left( \frac{\partial \log i_0}{\partial \log C_{\text{Pb}^{++}}} \right)_{C_{\text{H}^+}, C_{\text{C10}_4^-}} = \alpha = 0.2 \ldots \ldots \ [3.3]$$

$$\left( \frac{\partial \log i_0}{\partial \log C_{\text{H}^+}} \right)_{C_{\text{Pb}^{++}}, C_{\text{C10}_4^-}} = 4(1 - \alpha) = 0.2 \ [3.4]$$

Charge transfer coefficients obtained using the iterative method (similar for both anodic and cathodic processes) are given in Table 5 and agree with the value calculated from the lead ion dependence of $i_0$ (equation [3.3]) but not with the dependence of $i_0$ on hydrogen ion concentration, equation [3.4].

Temperature dependence of activation overpotential. Figure 21 shows the variation of overpotential with temperature. The slope of the lower plot, $\log_{10} i_0$ versus $1/T^\circ\text{K}$, corresponded to an enthalpy of activation of $7.4 \pm 0.6$ kcal mole$^{-1}$.

Discussion of Results.

Purity of the system. Satisfactory reproducibility
Variation of exchange current with $[\text{Pb}^{++}]$

$\beta$-PbO$_2$ ELECTRODE: ELECTROLYTE, 3.0 M H$^+$ + 6.85 M ClO$_4^-$ (WITH ADDED NaClO$_4$) 23 °C

$\eta_D < 10 \text{ mV}$

$\frac{\partial \log_{10} i_0}{\partial \log_{10} C_{\text{Pb}^{+}}} = 0.2$

$\log_{10} (\text{Lead concentration, M})$
FIG 20  Variation of exchange current with \([H^+]\)

\[ \beta-PbO_2 \text{ ELECTRODE; ELECTROLYTE}: 0.1 \text{ M Pb}^+; \text{TOTAL} [\text{ClO}_4^-] 6.85 \text{ M} 23^\circ\text{C} \]

\[ \eta_0 < 10 \text{ mV} \]

\[ \frac{\partial \log_{10} i_0}{\partial \log_{10} [H^+]} = 0.2 \]

\[ C_{\text{Pb}^{2+}}, 0.1 \text{ M} \]

\[ \log_{10} (\text{Acid concentration,M}) \]
FIG 21 Temperature dependence of current-overpotential curves for $\beta$-PbO$_2$

ELECTROLYTE: 0.09 M Pb$^{2+}$ + 0.5 M H$^+$; TOTAL [ClO$_4^-$] 0.85 M

![Graph showing temperature dependence of current-overpotential curves for $\beta$-PbO$_2$.](image)

Overpotential, mV vs Current, mA cm$^{-2}$

- Overpotential values are shown for different temperatures: 3°C, 20°C, 31°C, 42°C, and 53°C.

Below graph:

$\log_{10} i_o$, mA cm$^{-2}$ vs \(\frac{1}{T^\circ K \times 10^4}\)

$\Delta H = 7.4$ kcal mole$^{-1}$
confirmed that impurities were below the level required to interfere with the experimental results. Solutions which had not been well purified gave rise to spurious maxima, as shown in Figure 22, which developed at the leading edge of the pulse. Attempts to study this phenomenon with pulses of long duration proved unsuccessful because of its poor reproducibility. Mehl and Bockris (65) have observed similar phenomenon whilst studying the exchange at silver electrodes and concluded that it occurred almost exclusively in solutions which had not been adequately purified and suggested that it arose due to supersaturation of the surface with adspecies. Vermilyea (69) has discussed this phenomenon in terms of dislocation theory.

**Double layer capacitance.** The reasonably constant double layer capacitance measurements, are satisfactory, considering the accuracies with which current and overpotential could be measured and the difficulties associated with taking geometrical tangents from the transients. The mean value of $C_L$, 79 μF cm$^{-2}$, indicates a roughness factor of about 3 - 4, which seems reasonable for a polycrystalline material.

**Kinetic parameters.** The magnitude of the exchange current (0.17 mA cm$^{-2}$ in 1 M Pb$^{++}$, 3 M H$^+$, 6.85 M total ClO$_4^-$, at 23 °C) confirms that the reaction is slow, about three orders of magnitude smaller than the
FIG 22  Typical example of a spurious maxima produced on anodic polarization

$\beta$-PbO$_2$ ELECTRODE; ELECTROLYTE: 3.0 M H$^+$ + 2.0 M Pb$^{2+}$

TOTAL [ClO$_4$]$^-$ 6.85 M; CURRENT DENSITY 14 mA cm$^{-2}$
exchange current found for the solid Ag/Ag\(^+\) exchange in AgCl\(_{0.4}\) solution (65).

Mehl and Bockris (65) showed that the double layer charging time \(\tau\) is approximately given by:

\[
\left[\frac{RT}{2F\sigma}\right] \cdot C_L \quad \cdots \quad \cdots \quad \cdots \quad [3.5]
\]

and taking \(C_L\) to be 79 \(\mu\)F \(\text{cm}^{-2}\) and \(\sigma\) to be 0.1 \(\times\) \(10^{-3}\) A \(\text{cm}^{-2}\), we find \(\tau \approx 10\) msec.

Therefore the double layer is charged during the first few milliseconds of polarization. Further, since with this slow reaction, concentration polarization is relatively small during the time of our experiments (80 msec), the linear extrapolation of the \(\eta\)-t curve to zero time in order to separate \(\eta_D\) is justified (70). Recently, Kooyman and Sluyters (71) have considered this method as a general method for investigating electrode reactions, and it is clear from their paper that the method is adequate. For instance, the electrolysis time is longer than the relaxation time of the diffusing reactants.

The value of \(\alpha\), about 0.2, resulting from the arithmetical analysis of the overpotential-faradaic current data agrees with the concentration dependence of the exchange current in the case of Pb\(^{++}\). The value of 0.2 obtained for the dependence of \(i_o\) on \([H^+]\) (equation [3.4]) indicates a value of \(\alpha\) much higher than 0.2. Such results, however, can be
interpreted in terms of adsorption of hydrogen ions at the interphase when \( C_{H^+} \) becomes greater than the hydrogen ion concentration of the solution, i.e. \( C_{H^+} \) is not the value in solution but is related to the hydrogen ion concentration by some adsorption isotherm.

A simple treatment of this adsorption theory follows, assuming a Freundlich isotherm (on the basis that this isotherm is found to apply in similar cases of adsorption).

\[
C_{H^+} = k [H^+]^{1/n} \tag{3.6}
\]

where 'n' is a small whole number and \([H^+]\) is the bulk hydrogen ion concentration. Combining this Freundlich isotherm with the equilibrium equation \([3.2]\), we obtain

\[
i = k \alpha C_{Pb^{++}} [H^+]^{\frac{1}{n}(1-\alpha)/n} C_{PbO_2}^{1-\alpha} \tag{3.7}
\]

where \( k \) is a constant. Taking \( \alpha \) as 0.2, \( n \) becomes about 16, indicating strong adsorption of hydrogen ions. This conclusion is consistent with the work of Rüetschi and Cahan (48) who concluded that a condition for the formation of \( \beta-PbO_2 \) is the presence of adsorbed hydrogen ion. It is also interesting to note that often when very high or low values of the charge transfer coefficient have been reported there is evidence for adsorption (54).
Mechanism for the exchange reaction. Values of $\alpha$ obtained using the iterative technique are similar for both anodic and cathodic polarization and agreed with that value derived from the dependence of exchange current on lead ion concentration. The anodic and cathodic exchange currents are also identical for a given electrolyte. This suggests that the reaction involves a simultaneous two-electron charge transfer step.

A possible mechanism (written for the cathodic reaction) for the exchange reaction in the low overpotential region is as follows.

$$\text{PbO}_2 \cdot n \text{H}^+ = \text{PbO}_2 (\text{H}^+)_n \text{ads} \quad \ldots \ldots \ldots \quad [3.8a]$$

$$\text{PbO}_2 (\text{H}^+)_n \text{ads} + 2 \text{e} \rightarrow \text{Pb(II)} \quad \ldots \ldots \ldots \quad [3.8b]$$

$$\text{Pb(II)} + (4-n) \text{H}^+ \rightarrow \text{Pb}^{4+} + 2 \text{H}_2\text{O} \quad \ldots \ldots \ldots \quad [3.8c]$$

From the available thermodynamic data (72) it seems unlikely that Pb$^{4+}$ ions exist in solution. Consequently it seems probable that the overall reaction involves a Pb(IV) species, equation $[3.8a]$, at the surface either adsorbed or as part of the lattice. There is evidence for hydrogen ion adsorption (48). The proposed species PbO$_2$ (H$^+$)$_n$ may be considered to arise as a surface species formed as the product of adsorption of H$^+$ by lattice oxygen atoms on the surface. Such an adsorption would be expected to further weaken the bonds between surface lead atoms and the underlying fully coordinated
oxygen atoms of the PbO$_2$. It is not possible, on the evidence available, to differentiate between the possible intermediates with $n = 1, 2$ or $3$.

The addition of the two electrons, equation (3.8b), is the slow stage of the overall reaction and could lead to a variety of Pb(II) compounds (e.g. Pb(OH)$_2$, PbO, Pb(OH)$^+$) depending on the number of hydrogen ions involved in the initial step.

Anodically the reactions may be expected to occur in reverse order.

Generally, kinetic measurements around the equilibrium potential (i.e. $\eta < 10$ mV) do not provide sufficient information, in the absence of a knowledge of $\alpha$ and the extent of adsorption, to formulate the reaction mechanism. This arises since it is not possible to separate the anodic and cathodic processes occurring simultaneously. At high anodic and high cathodic overpotentials, however, the complementary reaction can be neglected, that is, $i$ approaches $i_A$ for high anodic overpotentials and $i_C$ for cathodic overpotentials. Consequently at a sufficiently high constant potential, $i$ depends on the concentration of the reactant electroactive species. A knowledge of the electrochemical reaction orders provides information which often allows the differentiation between possible mechanisms. The application of this technique is discussed in detail in Chapter 4.
Enthalpy of activation. Heats of activation have been reported for a number of processes, but their availability has not contributed very significantly to the understanding of electrode kinetics. The value of the enthalpy of activation for the charge transfer process is approximately that of other charge transfer reactions i.e. between 5 - 10 kcal mole$^{-1}$ (12).
Experimental Results

Relation between overpotential and time. Overpotential-time oscilloscopic transients obtained for \( \alpha\)-PbO\(_2\) were similar in shape to those obtained for \( \beta\)-PbO\(_2\); for corresponding current densities the overpotential at \( \alpha\)-PbO\(_2\) electrodes were significantly less than at \( \beta\)-PbO\(_2\) electrodes. The double layer capacitance, calculated from the initial rise of potential with time, is reasonably constant; mean values for a series of electrolytes are given in Table 6.

Relation between activation overpotential and current density. Current-overpotential plots (Figure 23) from which \( i_o \) was obtained were similar to those for the case of \( \beta\)-PbO\(_2\). Satisfactory agreement was again observed between values of \( i_o \) calculated geometrically, for both anodic and cathodic polarization, and values obtained using the iterative technique (68), as shown in Table 7.

Dependence of exchange current on the concentration of electroactive species. The dependence of \( i_o \) on \([\text{Pb}^{2+}]\) and \([\text{H}^+]\) are shown in Figure 24 and can be given as:-
**TABLE 6.**

**MEAN DOUBLE LAYER CAPACITANCES AT 23°C.**

α-FbO₂ electrode in acid-lead perchlorate electrolytes. Total concentration of ClO₄⁻, 6.85 M (with added NaClO₄).

<table>
<thead>
<tr>
<th>[Pb⁺⁺] M</th>
<th>[H⁺] M</th>
<th>C_L μF cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>3.0</td>
<td>137.3</td>
</tr>
<tr>
<td>0.0098</td>
<td>3.0</td>
<td>141.3</td>
</tr>
<tr>
<td>0.063</td>
<td>3.0</td>
<td>135.0</td>
</tr>
<tr>
<td>0.500</td>
<td>3.0</td>
<td>139.9</td>
</tr>
<tr>
<td>0.100</td>
<td>0.24</td>
<td>138.0</td>
</tr>
<tr>
<td>0.098</td>
<td>0.027</td>
<td>139.0</td>
</tr>
</tbody>
</table>
FIG 23 Faradaic current-overpotential curves

\[ \alpha - \text{PbO}_2 \text{ electrode} \quad 23^\circ \text{C} \]

\[ \eta_0, \text{mV} \]

\[ i, \text{mA cm}^{-2} \]

\[ -4.0 \quad -2.0 \quad 0 \quad 2.0 \quad 4.0 \]

\[ 0.02 \quad 0.04 \]

ELECTROLYTE 3.0 M H\(^+\) + 6.85 M Cl\(^-\) (WITH NaClO\(_4\))

\( \Delta \) 0.5 M Pb\(^{2+}\)

\( \Delta \) 0.25 M Pb\(^{2+}\)

\( \bigcirc \) 0.005 M Pb\(^{2+}\)

\( \bullet \) 0.0005 M Pb\(^{2+}\)


**TABLE 7.**

EXCHANGE CURRENTS AND CHARGE TRANSFER COEFFICIENTS AT 23°C.

\( \alpha\)-\( \text{PbO}_2 \) electrode in acid-lead perchlorate electrolytes. Determined (a) Geometrically, and (b) Iteratively.

Total concentration of \( \text{ClO}_4^- \), 6.85 M (with added Na\( \text{ClO}_4 \)).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( i_o(a) )</th>
<th>( i_o(b) )</th>
<th>( \alpha(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.0 \text{ M H}^+ )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.045 \text{ M Pb}^{++}</td>
<td>0.137</td>
<td>0.143</td>
<td>0.15</td>
</tr>
<tr>
<td>0.0098 \text{ M Pb}^{++}</td>
<td>0.156</td>
<td>0.163</td>
<td>0.17</td>
</tr>
<tr>
<td>0.063 \text{ M Pb}^{++}</td>
<td>0.194</td>
<td>0.197</td>
<td>0.20</td>
</tr>
<tr>
<td>0.500 \text{ M Pb}^{++}</td>
<td>0.266</td>
<td>0.276</td>
<td>0.20</td>
</tr>
<tr>
<td>0.1 \text{ M Pb}^{++}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.24 \text{ M H}^+</td>
<td>0.207</td>
<td>0.212</td>
<td>0.22</td>
</tr>
<tr>
<td>0.027 \text{ M H}^+</td>
<td>0.204</td>
<td>0.210</td>
<td>0.17</td>
</tr>
</tbody>
</table>
FIG 24 Variation of exchange current with Pb$^{2+}$ and H$^+$ concentration

α-PbO$_2$ electrode; total [ClO$_4^-$] 6.85M; 23°C

- τ$_0$ < 10 mV
- variable [Pb$^{2+}$], C$_{H^+}$ = 3.0M
- variable [H$^+$], C$_{Pb^{2+}}$ = 0.1M

\[ \frac{\partial \log_{10} I_0}{\partial \log_{10} C_{Pb^{2+}}} = 0.14 \]

\[ \frac{\partial \log_{10} I_0}{\partial \log_{10} C_{H^+}} = \text{zero} \]
\[
\left( \frac{\partial \log i_0}{\partial \log c_{\text{Pb}^{++}}} \right)_{c_{\text{H}^+}, c_{\text{ClO}_4^-}} = \alpha = 0.14 \quad \ldots \ \ [3.9]
\]

\[
\left( \frac{\partial \log i_0}{\partial \log c_{\text{H}^+}} \right)_{c_{\text{Pb}^{++}}, c_{\text{ClO}_4^-}} = 4(1 - \alpha) = 0 \quad \ldots \ \ [3.10]
\]

The charge transfer coefficients (Table 7) derived by the iterative method agree with the value obtained from the dependence of \(i_0\) on \([\text{Pb}^{++}]\) at constant \([\text{H}^+]\) but not with the dependence of \(i_0\) on \([\text{H}^+]\) at constant \([\text{Pb}^{++}]\).

**Temperature dependence of activation overpotential.**
The variation of overpotential versus current with temperature is shown in Figure 25; from the plot of \(\log_{10} i_0\) versus \(1/T^\circ\text{K}\), two approximately linear portions can be identified. These correspond to activation energies of \(\sim 3\) kcal mole\(^{-1}\) in the low temperature range and \(\sim 10\) kcal mole\(^{-1}\) in the higher temperature range.

**Discussion of Results**

The satisfactory reproducibility of results once again confirmed the purity of the system.

**Double layer capacitance.** As seen from Table 6 the
FIG 25  Temperature dependence of current
-overpotential curves for α-PbO₂

ELECTROLYTE: 0.025M Pb²⁺, 3.0M H⁺; TOTAL [ClO₄⁻] 5.85M
mean value of the double layer capacitance, 138 \( \mu \text{F} \) 
\( \text{cm}^{-2} \) is substantially higher than that exhibited by 
\( \beta\text{-PbO}_2 \) (78 \( \mu \text{F} \) \( \text{cm}^{-2} \)). This suggests that the ratio 
of the true to apparent surface area for \( \alpha\text{-PbO}_2 \) is 
almost twice that for \( \beta\text{-PbO}_2 \).

**Kinetic parameters.** The exchange reaction is slow.
For example, the magnitude of \( i_0 \) (0.30 mA cm\(^{-2} \) for 
a 1.0 M Pb\(^{++}\), 3.0 M H\(^{+}\), 6.85 M Cl\(^{-}\) electrolyte at 
23\(^0\)C) is comparable with that measured at \( \beta\text{-PbO}_2 \)
electrodes under comparable conditions (0.17 mA cm\(^{-2} \)).

The charge transfer coefficient calculated from 
the dependence of \( i_0 \) on \([\text{Pb}^{++}]\), Figure 24, is in agree­
ment with the iterative values shown in Table 7. The 
lack of experimental variation of \( i_0 \) values with \([\text{H}^{+}]\) 
at 23\(^0\)C, Figure 24, suggests a charge transfer coeffi­
cient of unity which can be interpreted in terms of 
hydrogen ion adsorption at the interphase.

**Mechanism.** The equality of the anodic and cathodic 
exchange currents and charge transfer coefficients, 
in the vicinity of the equilibrium potential, indicated 
that the rate controlling reaction is the same for 
both anodic and cathodic processes. The reaction is 
a simultaneous two-electron transfer process and a 
reaction mechanism similar to that postulated for 
\( \beta\text{-PbO}_2 \) would be expected to occur.
Enthalpy of activation. The observation that the enthalpy of activation increases with temperature (Figure 25) was confirmed for a number of electrolytes. Such changes were not observed with $\beta$-PbO$_2$ and have not, as yet, received a satisfactory explanation. It is interesting to note, however, that Angstadt, Venuto and Rüetshi (73) for PbO$_2$ in H$_2$SO$_4$ in the same temperature range as reported here, show a pronounced change in slope of the electrode potential versus temperature curve in the case of $\alpha$-PbO$_2$ which is absent in the case of $\beta$-PbO$_2$. On the other hand, the observation that the enthalpy of activation increases with temperature might indicate changes in double layer structure (e.g. adsorption or desorption), or changes in the concentration of transient intermediates.
CHAPTER 4.  THE LEAD DIOXIDE-PLUMBOUS ION EXCHANGE AT HIGH OVERPOTENTIAL

Introduction

The exchange mechanism of an electrode reaction may vary as the potential excursion at the electrode is increased from the equilibrium potential. Such a variation, for example, was observed by Gerischer (74), and Mehl and Bockris (10) while investigating the deposition of Ag from AgClO$_4$. They found that the reaction is controlled predominantly by surface diffusion around the equilibrium potential but at potentials remote from equilibrium the charge transfer process becomes rate determining.

This change of rate control from one to another process might be expected to occur for the following reasons. Firstly, the fraction of active growth sites increases with increasing overpotential, resulting in a decrease in the effective distance through which an adspecies has to migrate; i.e. the rate of surface diffusion for a given degree of supersaturation increases, and hence, the tendency for rate control by surface diffusion decreases. Secondly, at high cathodic overpotentials the rate of the anodic process decreases, and as a result of this the time a species spends on the surface after charge transfer and the probability of that species reaching a step and being incorporated at a growth site both increase.
This results in an increase in the rate constant for surface diffusion, and this latter eventually ceases to be rate controlling.

The possibility of the participation of adspecies in the rate controlling step is precluded because the data obeys the charge transfer equation, \[ \eta_d - i \] over the whole potential range investigated. There is, however, another possibility of a change in the rate controlling charge transfer process. A preliminary analysis of the high overpotential-current data, obtained from passivation experiments, indicated that the kinetic parameters obtained from the Tafel plots were different from those obtained using the iterative technique for \( \eta_d < 10 \text{ mV} \). This suggests that a process change occurs in the exchange reaction at lead dioxide as the potential excursion is increased from the equilibrium potential. In the low overpotential region the reaction mechanism appears as a simultaneous two-electron transfer. The probability of electrons exchanging in pairs has attracted considerable attention. Conway and Bockris (75) have shown that the heat of activation for a simultaneous two-electron transfer process exceeds 100 kcal mole\(^{-1}\), resulting in an exceedingly small rate constant. It seems more probable that the reaction occurs as a consecutive single-electron transfer over the whole overpotential region but with the time interval between the electron transfers becoming longer as the overpotential is increased. Hence, due to the limitations in the
experimental technique it may only be possible to
distinguish between the charge transfer steps at
high overpotential.

Theory

Exchange current and rate determining step. The
equations for a two-electron transfer between 0 and R
involving two consecutive transfer steps and an inter-
mediate, S, are as follows.

\[ \begin{align*}
0 + e &= S \quad \text{[4.1a]} \\
S + e &= R \quad \text{[4.1b]}
\end{align*} \]

Each step has its own characteristic exchange current
\((i_{oa} \text{ and } i_{ob})\) and cathodic transfer coefficient \((\alpha_a \text{ and } \alpha_b)\). The exchange currents are defined in terms
of concentrations \(C\), and corresponding standard rate
constants, \(k^0\), by (12)

\[ \begin{align*}
i_{oa} &= F k_a^0 c_0^{1-\alpha_a} c_s^{\alpha_a} \quad \text{[4.2a]} \\
i_{ob} &= F k_b^0 c_s^{1-\alpha_b} c_R^{\alpha_b} \quad \text{[4.2b]}
\end{align*} \]

By writing for each step a charge-transfer equation
(14) for the dependence of the charge-transfer over-
potential, \(\eta_p\), upon current density, \(i\), and then
eliminating terms connected with the concentration
of the intermediate species, Vetter (76) obtained the
equation (This equation is derived in Appendix 6)
\[
\frac{1}{2} = \frac{\exp(-\alpha_a + \alpha_b) \frac{F \eta_D}{RT} - \exp(2-\alpha_a - \alpha_b) \frac{F \eta_D}{RT}}{\frac{1}{\tau_{ob}} \exp(1-\alpha_a) \frac{F \eta_D}{RT} + \frac{1}{\tau_{oa}} \exp(-\alpha_b) \frac{F \eta_D}{RT}} \quad \ldots \quad [4.3]
\]

where \( F, R \) and \( T \) have their usual significance. At high overpotential this equation gives plots of \( \eta_D \) versus \( \log_{e} i \) (Tafel plots) having slopes \( -\frac{\alpha_a}{F} \frac{F}{RT} \) and \( (1-\alpha_b) \frac{F}{RT} \) for the cathodic and anodic branches respectively; corresponding intercepts of the rectilinear parts of these plots for \( \eta_D = 0 \) yield \( 2i_{oa} \) and \( 2i_{ob} \). Current-overpotential characteristics corresponding to equation \([4.3]\) have been computed by Hurd (77) for a number of \( i_{oa}/i_{ob} \) ratios. It was confirmed that the curves passed through the origin (\( \eta_D = 0, i = 0 \)) with the slope predicted by equation \([4.4]\)

\[
-\left( \frac{\partial \eta_D}{\partial i} \right)_{\eta_D = 0} = \frac{RT}{4F} \left( \frac{1}{\tau_{oa}} + \frac{1}{\tau_{ob}} \right) \quad \ldots \quad [4.4]
\]

obtained by differentiating equation \([4.3]\) with respect to \( i \) and setting \( \eta_D = 0 \). Vetter and Thiemke (78), investigating the Ti(III)/Ti(I) reaction, calculated \( i_{oa} \) and \( i_{ob} \) from intercepts of the cathodic and anodic branches of the Tafel plots and showed that the slope calculated from equation \([4.4]\) agreed with that observed at \( \eta_D = 0 \). This evidence confirmed the view that the Ti(III)/Ti(I) exchange involves two consecutive one-electron transfer stages within the potential range investigated.
For the case of a two-electron transfer involving consecutive single-electron transfer steps in which one step is slow and rate determining, Lovreček (78) in a somewhat more general treatment than Vetter's (76) showed that the slopes of the cathodic and anodic branches of the linear-logarithmic regions are given respectively by,

\[ \frac{d \log e^{iC}}{d \eta_D} = \frac{-F}{RT} (n^*_C - 1 + \alpha_i) \quad [4.5] \]

and

\[ \frac{d \log e^{iA}}{d \eta_D} = \frac{F}{RT} (n^*_A - \alpha_i) \quad [4.6] \]

where \( n^*_C \) (and \( n^*_A \)) is the ordinal number of the slowest step in a multistep cathodic (or anodic) reaction, and \( \alpha_i \) is \( \alpha_a \) or \( \alpha_b \) (equation [4.1a] and [4.1b]). For the two-step reaction [4.1], \( n_C \) may be 1 (or 2) with \( \alpha_i \) equal to \( \alpha_a \) (or \( \alpha_b \)); similarly when \( n^*_A \) is 1 (or 2), \( \alpha_i \) is \( \alpha_b \) (or \( \alpha_a \)). Equations [4.5] and [4.6] are derived in Appendix 7.

Expressions equivalent to equations [4.5] and [4.6] can each be obtained from equation [4.3] 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 equations [4.1a] and [4.1b] for \( i_{oa} = \infty \), \( i_{ob} \) is finite and reaction [4.1b] controls). Four \( \frac{d \log e^{i}}{d \eta_D} \)
values (Two anodic and two cathodic) are obtained corresponding to $n_A^* = 1$ or 2 and $n_C^* = 1$ or 2 using, in each case, the appropriate value of the transfer coefficient.

The usefulness of Lovreček's treatment lies in the possibility of choosing values of $n_A^*$ and $n_C^*$ consistent with the experimental data and hence identifying the slow step in the multistep process. Lovreček and Marinčič (80) for example applied the method to the Cd(II)/Cd(Hg) exchange.

The electrochemical reaction order. The determination of reaction order by observing the dependence of the rate of the reaction on concentration is well established. It has not, however, been much applied to the study of reactions at electrodes, with the exception of work done by Vetter, Gerischer and their collaborators who have used the method exclusively for elucidating electrochemical reactions at mercury and amalgam electrodes (see for example ref. 81). The basis of this method is that at sufficiently high cathodic overpotentials the cathodic current flowing at any fixed potential is a function of the concentration of those electroactive species directly involved in the cathodic current flow. Conversely, at high anodic overpotentials the reaction rate (measured by $i$) is a function of the concentration of the reduced species. For comparison of these reaction rates (current densities), potentials
must be referred to some standard and in this case the reference potential chosen was that corresponding to arbitrarily selected solutions of fixed composition.

This particular procedure is only possible if either the anodic or cathodic exchange reactions can be suppressed by the application of high overpotentials. In some cases such overpotential measurements are not feasible but reaction orders may still be deduced, however, from the dependence of the exchange currents on concentration, using relationships of the type given by equation [4.2].

**Experimental**

The electrolytic cell, electrical circuit and electrode geometry were identical to those described in Chapter 2.

A range of electrolytes (constant perchlorate ion concentration 6.85 M) of variable \([\text{Pb}^{++}]\) at constant \([\text{H}^+]\) and variable \([\text{H}^+]\) at constant \([\text{Pb}^{++}]\) were prepared and purified using the technique described in Chapter 2.

Both \(\alpha\)- and \(\beta\)-PbO\(_2\) electrodes were prepared as described in Appendix 2.
4.1. **EXCHANGE REACTION AT \( \beta\)-PbO\(_2\) ELECTRODES**

**AT HIGH OVERPOTENTIAL**

**Experimental Results**

Overpotential-time curves were similar in shape to those observed in the low overpotential region (see Figure 16) and results in a value for the double layer capacitance, of \(78^\pm6\ \mu\text{F cm}^{-2}\).

Using the iterative technique, described in Chapter 3, optimum values of \(\alpha Z\) and \(i_o\) were determined from experimental \(\eta_D\) versus \(i\) data.

Calculations were made over a progressively increasing range of \(\eta_D\) values, each successive increase (with the associated \(i\)) being incorporated with the previous \(\eta_D\) versus \(i\) values. For example, 10 sets of \(\eta_D\) versus \(i\) readings at 1 mV intervals were used to cover the range up to 10 mV (point A, Figure 26). The range of experimental readings was then increased to 15 mV and so on to cover the whole potential range (point B, Figure 26).

The results show that in the lower \(\eta_D\) ranges, \(\alpha Z\) and \(i_o\) remained constant for both anodic and cathodic polarization, but as the magnitude of \(\eta_D\) was increased in the higher range, these optimum values of \(\alpha Z\) and \(i_o\) changed. In Figure 26 these optimum \(\alpha Z\) values are plotted for a particular electrolyte concentration, as a function of the highest value of \(\eta_D\), \(\eta_D^{\text{max}}\). Table 8 shows the limits within which \(\alpha Z\) is constant. The changes in
FIG 26  Variation of transfer coefficient with overpotential
β-PbO₂ electrode in 0.1M Pb²⁺ + 0.2M H⁺, [ClO₄⁻] 6.85M

Anodic polarization

Cathodic polarization

Transfer coefficient, αz

| Overpotential |, mV

0 80 160 240

0.5 1.0 1.5
TABLE 8.

POTENTIAL LIMITS OF CONSTANT $a_2$ FOR $\beta$-PbO$_2^-$

Potential region (about the equilibrium) in which the reaction conforms to a two-electron transfer process.

<table>
<thead>
<tr>
<th>Concentration, M</th>
<th>Potential Region (±5 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead concentration at</td>
<td></td>
</tr>
<tr>
<td>constant $[H^+]$, 3.0 M; $[ClO_4^-]$, 6.85 M</td>
<td></td>
</tr>
<tr>
<td>1.47</td>
<td>- 28 mV to + 12 mV</td>
</tr>
<tr>
<td>0.47</td>
<td>- 30 mV to + 16 mV</td>
</tr>
<tr>
<td>0.093</td>
<td>- 41 mV to + 19 mV</td>
</tr>
<tr>
<td>$H^+$ concentration at</td>
<td></td>
</tr>
<tr>
<td>constant $[Pb^{++}]$, 0.1 M; $[ClO_4^-]$, 6.85 M</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>- 30 mV to + 13 mV</td>
</tr>
<tr>
<td>0.48</td>
<td>- 32 mV to + 15 mV</td>
</tr>
<tr>
<td>0.20</td>
<td>- 28 mV to + 13 mV</td>
</tr>
</tbody>
</table>
AZ from the constant value at low anodic and cathodic

\( \eta_D \) indicates a change in the charge transfer process.

Figure 27 shows a typical current-overpotential characteristic, for anodic and cathodic polarization, presented as a \( \log_{10} i \) versus \( \eta_D \) (Tafel) plot. The kinetic parameters, transfer coefficient and exchange current, were obtained from the slope and intercept respectively and are summarized for a series of electrolytes in Table 9.

Figures 28 and 29 show a family of Tafel plots for a series of electrolytes. Figure 28 refers to electrolytes of varying Pb\(^{++}\) and constant H\(^+\) concentration, relative to the reference system \( \beta\)-PbO\(_2\), 3.0 M H\(^+\), 1.0 M Pb\(^{++}\) (6.85M Cl\(_4\) with added NaClO\(_4\)) at equilibrium. On this scale, potentials (represented by \( E_{3M} \)) are given by:

\[
E_{3M} = \eta_D - 0.029 \log_{10} \left[ \text{Pb}^{++} \right] \text{ at } 25^\circ\text{C} \quad [4.7]
\]

Potentials for the complementary system (varying H\(^+\) and constant Pb\(^{++}\) concentrations) shown in Figure 29 are relative to the equilibrium potential for the reference system 0.1 M Pb\(^{++}\) and 1.0 M H\(^+\). On this scale, potentials (represented by \( E'_{1M} \)) are given by:

\[
E'_{1M} = \eta_D + 0.118 \log_{10} \left[ \text{H}^+ \right] \text{ at } 25^\circ\text{C} \quad [4.8]
\]

The validity of both equations \[4.7\] and \[4.8\] was confirmed for the above systems by potentiometric measurements at equilibrium as described in Appendix 3.
FIG 27  Typical overpotential - current plots for $\eta_d>50$ mV

$\beta$-PbO$_2$ ELECTRODE : ELECTROLYTE : 0.1 M Pb$^{2+}$ + 0.2 M H$^+$

TOTAL [ClO$_4^-$], 6.85 M (WITH ADDED NaClO$_4$) 23°C

FROM THE SLOPE:

$$
\frac{2.3RT}{F} \frac{\Delta \text{Log}_{10} i_a}{\Delta \eta_d} = 0.20
$$

INTERCEPT $= 2i_{ob} = 0.35$ mA cm$^{-2}$

ANODIC

FROM THE SLOPE:

$$
\frac{2.3RT}{F} \frac{\Delta \text{Log}_{10} i_c}{\Delta \eta_d} = 0.95
$$

INTERCEPT $= 2i_{ba} = 0.084$ mA cm$^{-2}$

CATHODIC

$\log_{10}$ (current density), mA cm$^{-2}$
**TABLE 9.**

**CHARACTERISTICS OF TAFEL PLOTS.**

β-PbO₂ electrode in acid perchlorate electrolytes at 23°C. Total concentration of ClO₄⁻, 6.85 M with added NaClO₄.

<table>
<thead>
<tr>
<th>Concentration molarity (M)</th>
<th>Cathodic coeff.</th>
<th>Anodic coeff.</th>
<th>Intercepts at ( \eta_D = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( -\frac{2.3RT \log I_C}{F \delta \eta_D} )</td>
<td>( \frac{2.3RT \log I_A}{F \delta \eta_D} )</td>
<td>( I_{ob2} ) (mA cm⁻²)</td>
</tr>
<tr>
<td>Pb²⁺ H⁺</td>
<td>0.93 3.0 0.84</td>
<td>0.21</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>0.47 3.0 0.88</td>
<td>0.22</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>0.093 3.0 0.82</td>
<td>0.22</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>0.45 3.0 0.90</td>
<td>0.22</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>0.089 0.48 0.84</td>
<td>0.22</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>0.092 0.20 0.86</td>
<td>0.22</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>0.093 0.0032 0.82</td>
<td>0.24</td>
<td>0.042</td>
</tr>
</tbody>
</table>
FIG 28 Anodic and cathodic current density-potential curves for $\beta$-PbO$_2$ at various Pb(II) concentrations in 3.0M HClO$_4$ at 23°C.
FIG 29 Anodic and cathodic current density-potential curves for $\beta$-PbO$_2$ at variable acid concentration in 0.1M Pb$^{2+}$ at 23°C.
The inserted diagram in Figure 28, and Figure 30 shows the dependence of anodic current on \([\text{Pb}^{++}]\) at constant potential. Figures 31 and 32 show the dependence of anodic and cathodic currents on \([\text{H}^+]\) for polarization within the Tafel region.

The dependence of exchange currents \((i_{oa} \text{ and } i_{ob})\) on \([\text{Pb}^{++}]\) at constant \([\text{H}^+]\) is shown in Figure 33 and on \([\text{H}^+]\) at constant \([\text{Pb}^{++}]\) in Figure 34.

**Discussion of Results**

**Process Change.** In Chapter 3 it was shown that the computed transfer coefficient for the low overpotential region is the same for both anodic and cathodic polarization and that this value agreed with that derived from the dependence of exchange current on lead ion concentration. It was also shown that the exchange currents were identical for both anodic and cathodic polarization for a given electrolyte.

As the potential excursion from the equilibrium potential is increased sufficiently, a pronounced change is observed in the kinetic parameters, as indicated by significant variations in \(\alpha z\). (Figure 26, Table 8). The constancy of \(\alpha z\) in the lower overpotential regions extends further into the cathodic than into the anodic region. It should be noted that attempts to force \(\eta_D\) versus \(i\) data of the form given by equation \([4.3]\) into an expression of the type equation \([1.2]\) would result, for small \(\left|\eta_D\right|_{\text{max}}\), in the computed \(\alpha z\) values being
FIG 30  Dependence of anodic current density on lead concentration

$\beta$-PbO$_2$ electrode

$\log_{10}(\text{Anodic current density}, \text{mA cm}^{-2})$ vs $\log_{10}(\text{Lead concentration}, \text{M})$

- $E_{3M} = 0.25 \text{ V}$
- $E_{3M} = 0.20 \text{ V}$
- $E_{3M} = 0.15 \text{ V}$

---

$\log_{10}(\text{Anodic current density}, \text{mA cm}^{-2})$

$\log_{10}(\text{Lead concentration}, \text{M})$
FIG 31  Dependence of anodic current density on [H+] 

β-PbO₂ ELECTRODE; ELECTROLYTE; 0.1 M Pb²⁺ + 6.85 M ClO₄⁻  23°C
FIG 32  Dependence of cathodic current density on $[H^+]$

$\beta$PbO$_2$ ELECTRODE: ELECTROLYTE: 0.1 M Pb$^+$, 0.85 M ClO$_4^-$, 23°C

![Graph showing the dependence of cathodic current density on $[H^+]$. The graph includes data points and lines for different potentials: $E'_M = -0.20V$, $E'_M = -0.25V$, $E'_M = -0.1V$, and $E'_M = -0.15V$. The x-axis represents $\log_{10}(H^+ \text{concentration}), M$, and the y-axis represents $\log_{10}(\text{Cathodic current density}), \text{mA cm}^{-2}$.]}
FIG 33  Variation of exchange current with [Pb$^{2+}$]

$\beta$-PbO$_2$ ELECTRODE; ELECTROLYTE 3.0 M H$^+$ + 6.85 M ClO$_4^-$ (WITH NaClO$_4$)

$\eta_D > 50$ mV

- Cathodic polarization
- Anodic polarization

$\frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [Pb^{2+}]} = 0.62$

$\frac{\partial \log_{10} i_{ob}}{\partial \log_{10} [Pb^{2+}]} = 0.11$

$\log_{10}(\text{Lead concentration, M})$
FIG 34  Variation of exchange current with $[H^+]$

$\beta$-PbO$_2$ ELECTRODE; ELECTROLYTE 0.1 M Pb$^{2+}$ 6.85 M ClO$_4^-$ (WITH NaClO$_4$)

$\eta_D > 50$ mV

$\frac{\Delta \log_{10} I_{ob}}{\Delta \log_{10} [H^+]} = 0.08$

- Cathodic polarization
- Anodic polarization

$\log_{10} I_{ob}$, mA cm$^{-2}$

$\log_{10}$ (Acid concentration, M)
strongly dependent upon \( \eta_D \max \) with this dependence becoming negligible as \( \eta_D \max \) increased to high values, results which are in variance with the above observations.

Table 9 shows the characteristics \([i_0 \text{ and } (RT/F) \frac{\partial \log e i_i}{\partial \eta D}]\) calculated from the linear high overpotential Tafel plots. These results suggest that in this high overpotential region the reaction involves two consecutive single-electron charge transfer steps. Thus, i) the sum of the cathodic and anodic coefficients \([-\frac{(RT/F) \partial \log e i_c}{\partial \eta D} \text{ and } \frac{(RT/F) \partial \log e i_A}{\partial \eta D}, \text{ respectively} \] is significantly less than two.

ii) the anodic and cathodic exchange currents, obtained by extrapolation of Tafel plots to \( \eta_D \) equal zero, are appreciably different.

iii) these exchange currents differ from those obtained for the low overpotential region.

That these consecutive single-electron charge-transfer processes do not, however, occur in the low overpotential region is seen from an analysis of the results in Table 10. This follows from a comparison of the experimental charge-transfer resistances, (calculated for \( \eta_D < 10 \text{ mV} \)), with those obtained from the theoretical slope of the appropriate equation\([4.4]\) for the two-consecutive single-electron transfer steps; the differences in magnitude indicate a change in the reaction mechanism from that applying in the high overpotential region.

62.
TABLE 10.

CHARGE TRANSFER RESISTANCES.

Comparison of experimental charge transfer resistances (for $\eta_D < 10 \text{ mV}$) with those calculated from equation [4.4] for $\eta_D > 50 \text{ mV}$.

$\beta$-PbO$_2$ electrode in acid perchlorate electrolytes at 23°C.

<table>
<thead>
<tr>
<th>Concentration molarity (M)</th>
<th>Charge transfer resistance (ohms cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>0.93</td>
<td>3.0</td>
</tr>
<tr>
<td>0.47</td>
<td>3.0</td>
</tr>
<tr>
<td>0.093</td>
<td>3.0</td>
</tr>
<tr>
<td>0.045</td>
<td>3.0</td>
</tr>
<tr>
<td>0.095</td>
<td>6.65</td>
</tr>
<tr>
<td>0.089</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Rate determining step. The slopes of Tafel plots for a series of electrolyte compositions are fairly constant (Table 9). For cathodic polarization the average coefficient is $0.86 \pm 0.1$, and for anodic polarization the average coefficient is $0.24 \pm 0.02$. Interpretation of this data using Lovreček's theory only gives rational values for the charge transfer coefficients, corresponding to the 1st and 2nd charge transfer reactions, if $n^*_c$ and $n^*_a$ are each equal to one. Hence, the first charge transfer step in both the anodic and cathodic directions emerges as the rate determining step.

On this basis we calculate the charge transfer coefficients $\alpha_a$ and $\alpha_b$ using equations [4.5] and [4.6] and the mean Tafel slopes as follows:

\[ n^*_c = 1 + \alpha_i = 0.86 \pm 0.1 \] \hspace{1cm} [4.9] 
when $n^*_c = 1$, $\alpha_i = \alpha_a = 0.86 \pm 0.1$

\[ n^*_a - \alpha_i = 0.24 \pm 0.02 \] \hspace{1cm} [4.10] 
when $n^*_a = 1$, $\alpha_i = \alpha_b = 0.24 \pm 0.02$

Reaction Order. The dependence of faradaic current on $[\text{Pb}^{++}]$ at anodic and cathodic overpotentials is shown in Figures 28 and 30. Referring to the cathodic plot, it will be seen that in the higher overpotential region the experimental results fall on the same straight (Tafel) line. This is to be expected from the fact that the
activity of $\beta$-PbO$_2$ is constant. \( \frac{\partial i_C}{\partial [\text{Pb}^{++}]} \) at constant \([H^+], [\text{C}10_4^-], T \text{ and } E\), is therefore zero.

For the anodic side of Figure 28, a family of parallel linear (Tafel) plots is obtained in the higher overpotential region, and further examination of these plots (inserted plot of Figure 28) shows that \( \frac{\partial i_A}{\partial [\text{Pb}^{++}]} \) at constant \([H^+], [\text{C}10_4^-], T \text{ and } E\) is constant over a wide concentration range. This suggests that the rate of the reaction is first order with respect to \([\text{Pb}^{++}]\) over this concentration range. However, plots of \(\log i_A \text{ vs } \log [\text{Pb}^{++}]\) (Figure 30) at constant potential show a decrease in reaction order in the lower \([\text{Pb}^{++}]\) regions, tending from \(\approx 1\) to \(\approx 0.3\). Various explanations of this low reaction order may be offered. Fleischmann and Liler (38) have observed similar apparently low reaction orders (0.26), in the case of deposition of PbO$_2$ from acetate solutions, and explained these in terms of the adsorption of Pb$^{++}$ at the electrode; there is, however, no discernible evidence for Pb$^{++}$ adsorption in this system. Alternatively, self discharge might occur especially at low \([\text{Pb}^{++}]\). Since at least one Pb$^{++}$ ion must however be concerned in the electrode reaction, it seems very probable therefore that the reaction is first order with respect to Pb$^{++}$.

From the above observations and the following derived information (see Figures 29, 31 and 32)

\[
\left( \frac{\partial \log i_C}{\partial \log C_{H^+}} \right)^{C_{\text{Pb}^{++}}, C_{\text{C}10_4^-}, T, E} = 1.5 \quad (4.11)
\]
we may now write, for cathodic polarization:

\[ i_C = k_C \cdot F \cdot C_{H^+}^{1.5} \] \[ 4.13 \]

and for anodic polarization:

\[ i_A = k_A \cdot F \cdot C_{\text{Pb}^{++}} \cdot C_{H^+}^{-0.4} \] \[ 4.14 \]

where \( k_C \) and \( k_A \) are the potential-dependent rate constants.

**Mechanism for the exchange reaction.** A mechanism (written for the cathodic direction) for the exchange reaction in the high overpotential may possibly comprise the following steps.

(i) Addition of hydrogen ions to the lead dioxide lattice.

\[ \beta-\text{Pb}_2O_2 + n H^+ = \text{Pb}_2O_2(H^+)_{n \text{ ads}} \] \[ 4.15 \]

The feasibility of the proposed species, \( \text{Pb}_2O_2(H^+)_{n} \), has already been considered in Chapter 3. It is probably formed as a surface species as the product of hydrogen ion adsorption by the lattice oxygen atoms on the surface. 'n' can assume three possible values i.e. \( n = 1, 2 \) or 3. The value of \( n = 4 \) is precluded because at least one \( H^+ \) ion is required in the
final step of the reaction.

(ii) Transfer of an electron to form a transient Pb(III) compound.

\[
\begin{align*}
PbO_2(H^+) + e^- & = [OPbOH] \quad \text{[4.16a]} \\
PbO_2(H^+)_2 + e^- & = [HOPbOH]^+ \quad \text{[4.16b]} \\
PbO_2(H^+)_3 + e^- & = [HOPbOH_2]^{2+} \quad \text{[4.16c]}
\end{align*}
\]

This is the slow step of the cathodic reaction and involves the first electron transfer. The formation of a Pb(III) intermediate as the slow step was proposed by Varypaev and Fedot'ev (82) while studying the electrodeposition of PbO_2 from Pb(NO_3)_2 solution. However, schemes based on a Pb^{3+}, as suggested by the Russian workers, are more open to objection than those based on a transitory low charged intermediate. In this step the formation of a hydroxy intermediate is suggested and may take the form \([PbO.OH]^{-}\), \([HOPbOH]^+\) or \([PbOH.H_2O]^{2+}\) depending on whether \(n\) is 1, 2 or 3 in the initial step. A difficulty with this theory is that compounds of the above type have not been observed. Of the three possibilities the uncharged \([PbO.OH]^{-}\) and symmetrical uni-charged \([HOPbOH]^+\) are probably most favoured.

(iii) Transfer of a second electron to form a Pb(II) compound.
The transfer of the second electron is a fast step. Of the possible products Pb(OH)$_2$, being a neutral molecule, might be expected to transfer across the double layer more readily than a charged ion.

$\left[\text{PbOH}\right]^+$ has been shown by Olin (23) to exist in acid-lead perchlorate electrolytes while the probability of a biplumbite ion, HPbO$_2^-$ existing in acid solution has also been considered (72).

(iv) The transformation of the Pb(II) compound to lead perchlorate.

\[
Pb(II) + (4 - n) \text{H}^+ \rightarrow Pb^{++} + 2 \text{H}_2\text{O} \quad [4.18]
\]

The rate equation for the cathodic reaction (rate control by step (ii)) at sufficiently high overpotential is

\[
i_C = k_F c_{\beta-PbO_2}^{n} \quad [4.19]
\]

where $k_C$ is the rate constant. From the equilibrium given in equation [4.15], and assuming the activity of $\beta$-PbO$_2$ is constant, it then follows, in the absence of H$^+$ ion adsorption that:

\[
i_C = k'_F (c_H^+)^n \quad [4.20]
\]
where \( k'_C \) is the appropriate rate constant. The effect of 
\( H^+ \) ion adsorption would be to reduce the exponent of the 
\( C_{H^+} \) term. The experimentally observed exponent of 1.5 
is thus evidence for \( H^+ \) ion adsorption if \( n \) is 2 or 3.

When the process is carried out anodically, the above 
reactions may either occur in the reverse order, or pro-
ceed via a completely different intermediate. The rate 
determining step now becomes step (iii), i.e. the transfer 
of the first electron, leading to the formation of the 
\( \text{Pb(III)} \) intermediate.

The rate equation for the anodic reaction at 
sufficiently high overpotential is:

\[
i_A = k_AF \frac{C_{\text{Pb(II)}}}{C_{\text{Pb}^{++}}} \quad \text{[4.21]}\]

From the equilibrium given in step (iv)

\[
K_S = \frac{[\text{Pb(II)}][H^+]^{4-n}}{[\text{Pb}^{++}]} \quad \text{[4.22]}
\]

(where \( K_S \) is the equilibrium constant), it follows that

\[
i_A = k'_A F \frac{C_{\text{Pb}^{++}}}{C_{H^+}^{4-n}} \quad \text{[4.23]}
\]

where \( k'_A \) is the appropriate rate constant.

In this case \( H^+ \) adsorption would increase the value 
of the \( C_{H^+} \) exponent, equation \([4.23]\). The experimentally 
observed reaction order, \(-0.4\), indicates the presence of 
such adsorption. This further supports the conclusions 
drawn from the cathodic experiments and previous observ-
ations in the low overpotential region (Chapter 3). This 
value is consistent with \('n'\) equal to 1, 2 or 3. There
seems no reason to suggest, however, that the same amount of adsorption occurs for both anodic and cathodic processes. Adsorption is likely to be potential dependent, and therefore different for anodic and cathodic polarization.

Alternative reaction schemes have been tentatively suggested by other workers. Thirsk and Wynne-Jones (36) investigating the reaction in an acid-lead sulphate electrolyte considered sulphate ion discharge followed by the formation of a persulphate ion, and hydroxyl ion discharge but concluded that of the two alternatives the latter appeared more attractive. No perchlorate anion complexes are formed with lead and thus, such anionic involvement in the reaction mechanism would not be expected.

Fleischmann and Liler (38), studying the formation of O-PbO$_2$ in acetate electrolytes, considered hydroxyl radical participation, produced by the discharge of hydroxyl ions. Hydroxyl radical formation, however, might be expected to occur preferably in electrolytes of high pH and in the presence of strong acid electrolytes would be expected to reach infinitesimal proportions.

In conclusion, it is not possible with any absolute degree of certainty to decide which of the proposed reaction schemes is the most probable. For the cathodic reaction, the mechanisms written with 'n' equal to 2 or 3 and for the anodic reaction, n equal to 1, 2 or 3 appear, on the experimental evidence, equally likely.
Apparent exchange current. The calculation of exchange current by extrapolation of linear-logarithmic $\eta_D - i$ data to $\eta_D = 0$ assumes that no mechanistic change occurs in the region over which the extrapolation is made. Since such a change does occur, $i_o$ values calculated this way can only be interpreted hypothetically. These apparent exchange currents, however, depend on the concentration of the electroactive species and from Figure 33 and 34 we obtain:

\[ \frac{\partial \log i_{oa}}{\partial \log C_{Pb^{++}}} = 0.6 \quad \ldots \ldots \ldots \quad [4.24] \]

\[ \frac{\partial \log i_{oa}}{\partial \log C_{H^+}} = 0.08 \quad \ldots \ldots \ldots \quad [4.25] \]

\[ \frac{\partial \log i_{ob}}{\partial \log C_{Pb^{++}}} = 0.11 \quad \ldots \ldots \ldots \quad [4.26] \]

\[ \frac{\partial \log i_{ob}}{\partial \log C_{H^+}} = 0.11 \quad \ldots \ldots \ldots \quad [4.27] \]

From equations \([4.16] - [4.18]\), in terms of equations \([4.2a]\) and \([4.2b]\) for a single electron cathodic transfer:

\[ i_{oa} = k_o C_{PbO_2(H^+)_n}^{1-a} C_{Pb(III)}^a \quad \ldots \ldots \ldots \quad [4.28] \]

From the equilibrium, equation \([4.15]\)

\[ K = \frac{[PbO_2(H^+)_n]}{[H^+]^n} \quad \ldots \ldots \ldots \quad [4.29] \]

it follows that

70.
\[ i_{oa} = k'_a c_{Pb(III)}^n c_{H}^{1-a} \] \[4.30\]

Similarly for the anodic reaction
\[ i_{ob} = k'_b c_{Pb(III)}^{1-a} c_{Pb(II)} \] \[4.31\]

which with equation \[4.22\] gives
\[ i_{ob} = k'_b c_{Pb(III)}^{1-a} c_{Pb}^{n-(4-n)a} \] \[4.32\]

Both equations \[4.30\] and \[4.32\] contain a term involving the intermediate Pb(III) species. Since the concentration of this latter is unlikely to be independent of potential (because of its ionic nature), the apparent exchange may only be discussed semi-qualitatively.

From equation \[4.30\] the following two equations for the cathodic reaction are obtained.

\[ \left( \frac{\partial \log i_{oa}}{\partial \log c_{Pb}^{++}} \right) = a_a \left( \frac{\partial \log c_{Pb(III)}}{\partial \log c_{Pb}^{++}} \right) \] \[4.33\]

\[ \left( \frac{\partial \log i_{oa}}{\partial \log c_{H}^{+}} \right) = n (1-a_a) + a_a \left( \frac{\partial \log c_{Pb(III)}}{\partial \log c_{H}^{+}} \right) \] \[4.34\]

The L.H.S. of equation \[4.33\] has the numerical value ~ 0.6, and combining this value with the previously determined value of 0.86 for \( a_a \) (equation \[4.9\]), we obtain

\[ \left( \frac{\partial \log c_{Pb(III)}}{\partial \log c_{Pb}^{++}} \right) = 0.7 \] \[4.35\]
Similarly the L.H.S. of equation \([4.34]\) has the value 0.08, leading to

\[
* \left( \frac{\partial \log C_{\text{Pb}(\text{III})}}{\partial \log C_{\text{H}^+}} \right) = -0.3 \text{ for } n=2; \text{ and } -0.4 \text{ for } n = 3. \quad [4.36]
\]

In the same way, equation \([4.32]\) gives the following two equations for the anodic reaction

\[
* \left( \frac{\partial \log i_{\text{ob}}}{\partial \log C_{\text{Pb}^{2+}}} \right) = \alpha_b + (1-\alpha_b) \left( \frac{\partial \log C_{\text{Pb}(\text{III})}}{\partial \log C_{\text{Pb}^{2+}}} \right) \quad [4.37]
\]

\[
* \left( \frac{\partial \log i_{\text{ob}}}{\partial \log C_{\text{H}^+}} \right) = -(4-n)\alpha_b + (1-\alpha_b) \left( \frac{\partial \log C_{\text{Pb}(\text{III})}}{\partial \log C_{\text{H}^+}} \right) \quad [4.38]
\]

The corresponding numerical values for the L.H.S., from equations \([4.26]\) and \([4.27]\), are 0.11 and 0.11 and these combined with the previously determined \(\alpha_b\) value of 0.78 (equation \([4.10]\) ) give

\[
* \left( \frac{\partial \log C_{\text{Pb}(\text{III})}}{\partial \log C_{\text{Pb}^{2+}}} \right) = -3.0 \quad [4.39]
\]

\[
* \left( \frac{\partial \log C_{\text{Pb}(\text{III})}}{\partial \log C_{\text{H}^+}} \right) = \begin{cases} 11.8 \text{ for } n = 1 \\ 7.1 \text{ for } n = 2 \\ 4.0 \text{ for } n = 3 \end{cases} \quad [4.40]
\]

The two cathodic results (equations \([4.35]\) and \([4.36]\) ) could be interpreted as indicating an increase in the effective concentration of the Pb(III) intermediate with

---

*FOOTNOTE* In equations \([4.24]\) to \([4.27]\) and equations \([4.33]\) to \([4.40]\) the appropriate intensity factors are maintained constant. i.e. in equation \([4.24]\), \([H^+]\), \([ClO_4^-]\), \(T\) are constant.
decrease in $[H^+]$ or increase in $[\text{Pb}^{++}]$. These latter changes would, in effect, alter the electrode potential to more negative values and so (as illustrated below) favour the participation of the Pb(III) in the overall reaction. Similarly, in the anodic process (equations [4.39] and [4.40]), increasing the $[H^+]$ or decreasing the $[\text{Pb}^{++}]$ will raise the electrode potential and again favour the Pb(III) participation. This is in line with the results of the $|\eta_D| - \alpha Z$ correlation, Figure 26. Thus at high positive and at high negative potentials the reaction becomes consecutive electron transfer involving an intermediate.

The above evidence for two consecutive single-electron stages at high overpotential must, however, be considered in conjunction with the earlier evidence for a single two-electron stage at low overpotential. Figures 35a and 35b relate to the lower overpotential and high overpotential conditions respectively. In Figure 35a the reaction path (dotted line) does not cross the energy curve for the Pb(III); there is no transitory intermediate and the two-electron reaction occurs in one step. In 35b, however, the cathodic polarization raises curve A to curve C; in this case, the Pb(III) energy curve is intersected so producing a "stable" region (E in Figure 35b) of existence of this intermediate in the overall path from C to D, with the result that the overall charge transfer process now occurs in two consecutive single-electron transfer steps.
FIG 35  Potential energy diagrams

(a) Reaction coordinate

Potential energy

Pb(III)  Pb(IV)  Pb(II)

(b) Reaction coordinate

Potential energy

Pb(III)  Pb(IV)  Pb(II)
4.2. EXCHANGE REACTION AT \( \alpha\)-PbO\(_2\) ELECTRODES AT HIGH OVERPOTENTIAL

Experimental Results

The experimental overpotential versus current density data was examined as described for \( \beta\)-PbO\(_2\). The behaviour of \( \eta \) with progressive increase in \( \eta_{D\ max} \) (Figure 36) was very similar to that reported for the experimental results obtained for \( \beta\)-PbO\(_2\), Figure 26. ' \( \eta \)Z' remained constant only within a narrow region enclosing the equilibrium potential; Table 11 shows the potential limits of this region.

Figure 37 shows a typical anodic and cathodic Tafel plot (\( \log_{10} i \) versus \( \eta_{D} \)), from which the transfer coefficient and exchange current can be calculated.

Figure 38 shows a family of Tafel plots for variable \( [\text{Pb}^{\text{++}}] \) at constant \( [\text{H}^{+}] \). Potentials are relative to the reference system 3.0 M \( \text{H}^{+} \), 1.0 M \( \text{Pb}^{\text{++}} \) (6.85 M \( \text{ClO}_4^- \) with added \( \text{NaClO}_4 \)) for an \( \alpha\)-PbO\(_2\) electrode at equilibrium.

Figure 39 shows a similar plot for electrolytes of variable \( [\text{H}^+] \) at constant \( [\text{Pb}^{\text{++}}] \). Potentials for the complementary system are relative to the equilibrium potential for the reference system \( \alpha\)-PbO\(_2\), 0.1 M \( \text{Pb}^{\text{++}} \), 1.0 M \( \text{H}^+ \) (6.85 M \( \text{ClO}_4^- \)).

The dependence of net faradaic current on concentration at constant anodic and cathodic potentials is
FIG 36 Variation of transfer coefficient with $\eta_{D\text{max}}$

$\alpha$-PbO$_2$ electrode; electrolyte: 0.1 M Pb$^{2+}$ + 0.1 M H$^+$
TOTAL [ClO$_4^-$] 6.85 M (with NaClO$_4$); 23 °C

Anodic polarization

Cathodic polarization

Transfer coefficient, $a^2$

Overpotential, mV

0.2 0.6 1.0 1.4

0 80 160 240
TABLE 11.

POTENTIAL LIMITS OF CONSTANT $\alpha$ FOR $\alpha$-$\text{PbO}_2^-$

Potential region (about the equilibrium) in which the reaction conforms to a two-electron transfer process.

<table>
<thead>
<tr>
<th>Concentration, M</th>
<th>Potential Region ($\pm$ 5 mV)</th>
</tr>
</thead>
</table>

**Lead concentration at**

constant $[H^+]$, 3.0 M,

$[\text{ClO}_4^-]$, 6.85 M.

<table>
<thead>
<tr>
<th>Concentration, M</th>
<th>Potential Region ($\pm$ 5 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>- 22 mV to + 13 mV</td>
</tr>
<tr>
<td>0.0098</td>
<td>- 32 mV to + 12 mV</td>
</tr>
<tr>
<td>0.0050</td>
<td>- 38 mV to + 14 mV</td>
</tr>
</tbody>
</table>

**$H^+$ concentration at**

constant $[\text{Pb}^{2+}]$, 0.1 M,

$[\text{ClO}_4^-]$, 6.85 M.

<table>
<thead>
<tr>
<th>Concentration, M</th>
<th>Potential Region ($\pm$ 5 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94</td>
<td>- 35 mV to + 9 mV</td>
</tr>
<tr>
<td>0.24</td>
<td>- 39 mV to + 13 mV</td>
</tr>
<tr>
<td>0.027</td>
<td>- 25 mV to + 10 mV</td>
</tr>
</tbody>
</table>
Typical overpotential-current density plots

$\alpha$-PbO$_2$ electrode; electrolyte: 0.1 M Pb$^{2+}$, 3.0 M H$^+$

Total [ClO$_4^-$] 6.85 M (with added NaClO$_4$) 23°C

From the slope, $\frac{2.3RT}{F} \log_{10} \frac{\Delta \delta}{\Delta \varphi}$ = 0.22

Intercept = $2i_{ob} = 0.63$ mA cm$^{-2}$

From the slope, $-2.3RT \frac{\delta \log_{10} \delta}{\delta \varphi}$ = 0.96

Intercept = $2i_{oa} = 0.126$ mA cm$^{-2}$
shown in Figures 38, 40 and 41 for variable \([\text{Pb}^{++}]\) and Figures 42 and 43 for variable \([\text{H}^+]\).

Anodic and cathodic exchange current dependencies on \([\text{Pb}^{++}]\) at constant \([\text{H}^+]\), and \([\text{H}^+]\) at constant \([\text{Pb}^{++}]\) are shown in Figures 44 and 45 respectively.

**Discussion of Results**

A detailed discussion of the evidence for a change of mechanism in the charge transfer process, from a simultaneous two-electron transfer to two consecutive single-electron transfer steps, has been presented for \(\beta\)-\(\text{PbO}_2\). Similar evidence has been observed for the case of \(\alpha\)-\(\text{PbO}_2\). This can be summarized as:-

i) the sum of the cathodic and anodic transfer coefficients is significantly less than two (Table 12) and changes with \(|\eta D|\) (Figure 36).

ii) the anodic and cathodic exchange currents, obtained by extrapolating Tafel plots to \(\eta D\) equal zero, are both appreciably different from each other (Table 12) and also from the value obtained in the low overpotential region.

iii) the charge transfer resistance, \(R_D\), observed in the low overpotential region differs from that calculated from high overpotential measurements (Table 13).

Confirmation that a process change occurs as the overpotential is increased is observed directly at low \([\text{Pb}^{++}]\). Figure 46 shows a typical cathodic Tafel plot.
Cathodic and anodic current density-potential curves for
\( \alpha\text{-PbO}_2 \) at various \( \text{Pb}(\text{II}) \) concentrations in 3.0M \( \text{HClO}_4 \) at 23°C.

Electrolyte: 3.0M\([\text{H}^+]\); total \([\text{ClO}_4^-]\), 6.85M

- \([\text{Pb}^{2+}]\)
  - 0.50M
  - 0.15M
  - 0.063M
  - 0.030M
  - 0.0098M
  - 0.0051M
  - 0.00099M
  - 0.00050M
  - 0.00025M

\( \text{Log}_a i, \text{ mACm}^{-2} \) vs. \( E_{3\text{M}, \text{vol}t}^a \) for cathodic and anodic processes.
Cathodic and anodic current density-potential curves for α-PbO₂ at variable H⁺ concentration in 0.1 M Pb⁺⁺ at 23°C.

Electrolyte: 0.1 M Pb⁺⁺; total [ClO₄⁻] 6.85 M

- [H⁺] 3.0 M
- 1.0 M
- 0.24 M
- 0.097 M
- 0.027 M

Log₁₀ i, mA/cm²

-0.3 -0.2 -0.1 0 0.1 0.2 0.3

Eₚ, volt

Cathodic Anodic
FIG 40 Dependence of cathodic current density on [Pb$^{2+}$]

α-PbO$_2$ electrode. Electrolyte 3.0M H$^+$; total [ClO$_4^-$] 6.85M. 23°C

- $E^\alpha_{3M} = -0.15$V
  - $\frac{\partial \log_{10} i}{\partial \log_{10} [Pb^{2+}]} = -0.06$

- $E^\alpha_{3M} = -0.10$V
  - $\frac{\partial \log_{10} i}{\partial \log_{10} [Pb^{2+}]} = -0.14$

- $E^\alpha_{3M} = -0.05$V
  - $\frac{\partial \log_{10} i}{\partial \log_{10} [Pb^{2+}]} = -0.18$

Log$_{10}$ (Cathodic current density) mA cm$^{-2}$

Log$_{10}$ (Lead concentration), M
FIG 41 Dependence of anodic current density on lead concentration. $\alpha$-PbO$_2$ electrode

\[ \log_{10}(\text{Anodic current density}, \text{mA cm}^{-2}) \]

\[ \log_{10}(\text{Lead concentration}, \text{M}) \]
FIG 42 Dependence of cathodic current density on $[H^+]$

$\alpha$-PbO$_2$ ELECTRODE: ELECTROLYTE 0.1 MPb$^{2+}$ 6.85 M ClO$_4^-$ 23°C

Log$_{10}$ (Cathodic current density), mA cm$^{-2}$

Log$_{10}$ ($H^+$ concentration), M

$E_M = -12$ V  $E_M^\alpha = -18$ V  $E_M^\alpha = -24$ V
FIG 43 Dependence of anodic current density on $[H^+]$

$\alpha$-PbO$_2$ ELECTRODE : ELECTROLYTE; 0.1 M Pb$^{2+}$ 6.85 M ClO$_4^-$ 23°C

$\log_{10}(\text{H}^+ \text{concentration}), \text{M}$
Variation of exchange current with lead concentration for α-PbO$_2$ at 23°C

$\eta_D > 50$ mV

- Anodic polarization
- Cathodic polarization

$[H^+] = 3.0$ M

$\frac{\partial \log_{10} i_{oa}}{\partial \log_{10} [Pb^{++}]} = 0.3$

$\frac{\partial \log_{10} i_{ob}}{\partial \log_{10} [Pb^{++}]} = 0.1$

Log$_{10} (\text{Lead concentration})$, M
FIG 45  Variation of exchange current with $[H^+]$

$\alpha$PbO$_2$ ELECTRODE. ELECTROLYTE: 0.1M Pb$^{2+}$, 6.85M$[\text{ClO}_4^-]$}

$\eta_D > 50 \text{ mV}$

23°C

$\log_{10} 2i_e, \text{ mAcm}^{-2}$

-1.1

-0.9

-0.7

-0.5

-0.3

-2.0

-4.0

$\log_{10} (\text{Acid concentration, M})$

O  Cathodic polarization

●  Anodic polarization
TABLE 12.

CHARACTERISTICS OF TAFEL PLOTS.

α-PbO₂ electrode in acid perchlorate electrolytes at 23°C.
Total concentration of ClO₄⁻, 6.85 M with added NaClO₄.

<table>
<thead>
<tr>
<th>Concentration molarity (M)</th>
<th>Cathodic coeff.</th>
<th>Anodic coeff.</th>
<th>Intercepts at η_D=0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb⁺⁺ H⁺</td>
<td>-2.3RT \frac{\partial \log i_C}{\partial \eta_D}</td>
<td>2.3RT \frac{\partial \log i_A}{\partial \eta_D}</td>
<td>2i_{ob} (mA/cm²)</td>
</tr>
<tr>
<td>0.25 3.0</td>
<td>0.94</td>
<td>0.22</td>
<td>0.117</td>
</tr>
<tr>
<td>0.0098 3.0</td>
<td>0.90</td>
<td>0.20</td>
<td>0.0690</td>
</tr>
<tr>
<td>0.0050 3.0</td>
<td>0.94</td>
<td>0.18</td>
<td>0.0417</td>
</tr>
<tr>
<td>0.0010 3.0</td>
<td>0.92</td>
<td>0.18</td>
<td>0.0141</td>
</tr>
<tr>
<td>0.098 0.24</td>
<td>0.98</td>
<td>0.20</td>
<td>0.0955</td>
</tr>
<tr>
<td>0.10 0.027</td>
<td>1.00</td>
<td>0.18</td>
<td>0.100</td>
</tr>
<tr>
<td>0.10 0.0001</td>
<td>0.84</td>
<td>0.18</td>
<td>0.123</td>
</tr>
</tbody>
</table>
TABLE 13.

**CHARGE TRANSFER RESISTANCES.**

Comparison of experimental charge transfer resistances (for $\eta_p < 10 \text{ mV}$) with those calculated from equation [4.4] for $\eta_p > 50 \text{ mV}$. 

$\alpha$-PbO$_2$ electrode in acid perchlorate electrolytes at $23^\circ\text{C}$. 

<table>
<thead>
<tr>
<th>Concentration molarity (M)</th>
<th>Charge transfer resistance ohms cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{++}$  H$^+$</td>
<td>Experimental</td>
</tr>
<tr>
<td>0.005          3.0</td>
<td>93.3</td>
</tr>
<tr>
<td>0.0098         3.0</td>
<td>80.0</td>
</tr>
<tr>
<td>0.063          3.0</td>
<td>65.8</td>
</tr>
<tr>
<td>0.50           3.0</td>
<td>48.0</td>
</tr>
<tr>
<td>0.098          0.24</td>
<td>61.8</td>
</tr>
<tr>
<td>0.100          0.027</td>
<td>61.0</td>
</tr>
</tbody>
</table>
FIG 46

Cathodic Tafel plot for $\alpha$-PbO$_2$

Electrolyte: 0.005 M Pb$^{2+}$, 3.0 M H$^+$, [ClO$_4^-$] 6.85 M : 23°C

From $-2.3RT\log_{10}J - \frac{\alpha\eta_0}{F}$
Slope = $-0.94$ F/mV
Intercept = $2\eta_0 = 0.042$ mA cm$^{-2}$

cf. $\alpha = 0.18$ and $\eta_0 = 0.137$ mA cm$^{-2}$ for $\eta_0 < 10$ mV

From $-23RT\log_{10}J - \frac{\alpha\eta_0}{2F}$
Slope = $-0.25$ F/mV
Intercept = $\eta_0 = 0.126$ mA cm$^{-2}$
at low $[\text{Pb}^{++}]$. Two distinct rectilinear regions are identifiable. At low overpotential the transfer coefficient and exchange current obtained from the slope and intercept of the plot are identical with values obtained using the iterative treatment of $\eta_B$ versus $i$ data.

**Rate determining step.** Using the Lovreček treatment the rate determining step in an electrode process involving two consecutive single-electron transfer steps can be determined from the Tafel slopes using equations [4.5] and [4.6]. Since the transfer coefficients must lie between 0 and 1 it follows that:

$$n^*_C - 1 + \alpha_i = 0.95 \pm 0.05 \quad \ldots \ldots \ldots \ldots \ldots \ldots [4.41]$$

when $n^*_C = 1$, $\alpha_i = \alpha_a = 0.95 \pm 0.05$

$$n^*_A - \alpha_i = 0.20 \pm 0.02 \quad \ldots \ldots \ldots \ldots \ldots \ldots [4.42]$$

when $n^*_A = 1$, $\alpha_i = \alpha_b = 0.80 \pm 0.02$

As observed with $\beta$-PbO$_2$ the first charge transfer step must be the slow step in both anodic and cathodic directions, that is, the step that leads to the formation of a Pb(III) intermediate. The difference between the magnitude of the charge transfer coefficients in the case of $\alpha$- and $\beta$-PbO$_2$ is barely significant.

**Reaction order.** Figure 40 shows that the rate of the cathodic reaction decreases with $[\text{Pb}^{++}]$. Since the
Pb\(^{++}\) ion is not a formal participant in the cathodic polarization of PbO\(_2\), it is expected that at high over-potential values, the Tafel curves for a series of electrolytes in which only [Pb\(^{++}\)] is varied would be expected to be collinear (as found in the case of \(\beta\)-PbO\(_2\)). At constant \([H^+]\) the rate of the reaction at sufficiently high fixed potential is equivalent to \(\frac{\partial \log i_C}{\partial \log [\text{Pb}^{++}]} \sim -0.1\), giving a closely-spaced approximately parallel set of Tafel lines. (The apparent variation of \(\frac{\partial \log i_C}{\partial \log [\text{Pb}^{++}]}\) with change in \(E_{3M}^\alpha\), Figure 4, probably arises from inaccuracies in the experimental results). This reaction order suggests that the activity of the electrode decreases with increase in [Pb\(^{++}\)] and that this is a real change in electrode activity.

It has already been pointed out (Chapter 1) that \(\beta\)-PbO\(_2\) is the favoured product of the anodic oxidation of Pb\(^{++}\) in acid solution. Consequently, under conditions of exchange and equilibrium the proportion of (the less reactive) \(\beta\)-PbO\(_2\) in the electrode surface is increased with increase in the exchange reaction (measured by \(i_o\)). At low [Pb\(^{++}\)] the exchange current is small and consequently the \(\alpha\)-PbO\(_2\) electrode remains substantially free of \(\beta\)-PbO\(_2\). As [Pb\(^{++}\)] is increased, \(i_o\) and the proportion of \(\beta\)-PbO\(_2\) in the electrode surface is increased. (\(\alpha\)-PbO\(_2\) has a higher positive \(E^0\) value than \(\beta\)-PbO\(_2\) (see Appendix 3) and hence the modification of \(\alpha\)-PbO\(_2\) electrodes to contain \(\beta\)-PbO\(_2\) in the surface must represent a decrease in electrode activity).

Comparison of Tafel plots (Figure 38) for \(\alpha\)-PbO\(_2\) with Tafel plots (Figure 28) for \(\beta\)-PbO\(_2\) shows that the
cathodic portion of the $\alpha$- is forced towards the $\beta$- line as $[\text{Pb}^{++}]$ is increased in the electrolyte. $\beta$-$\text{PbO}_2$ cannot be so modified in acid solution and cathodic curves are collinear as observed (Figure 28).

The remaining reaction orders calculated from Figures 38, 40, 42 and 43 are:

\[
\left( \frac{\partial \log i_C}{\partial \log C_{H^+}} \right) = 2.0 \quad \text{[4.43]}
\]

\[
\left( \frac{\partial \log i_A}{\partial \log C_{\text{Pb}^{++}}} \right) = 0.3 \text{ to } 1.0 \quad \text{[4.44]}
\]

\[
\left( \frac{\partial \log i_A}{\partial \log C_{H^+}} \right) = -0.4 \quad \text{[4.45]}
\]

The change of reaction order, equation [4.44] in electrolytes of low $[\text{Pb}^{++}]$ was observed for the case of $\beta$-$\text{PbO}_2$ and has already been discussed.

Since at the equilibrium potential $\partial \log i_0 / \partial \log C_{H^+}$ was in the region of zero (equation [3.10]), the numerical values of the equations [4.43] and [4.45] would not be subject to changes in the structure of the electrode as discussed for the case of reaction orders with respect to $\text{Pb}^{++}$.

\* \* \* \* \* \* \*

FOOTNOTE In equations [4.43] to [4.45] the appropriate intensity factors are maintained constant.
We may write for cathodic polarization

\[ i_c = \alpha_c^k F C_{H^+}^{2+0} \] \[ 4.46 \]

where \( \alpha_c^k \) is a potential-dependent rate constant. Because of the dependence of the cathodic current on \( [\text{Pb}^{++}] \), Figure 41, \( \alpha_c^k \) is also dependent on the constitution of the \( \alpha\text{-PbO}_2 \) electrode and varies between its value for \( \alpha\text{-PbO}_2 \) in acid electrolytes free of \( \text{Pb}^{++} \) (\( \alpha \)-electrode) and the value obtained from the \( \beta\text{-PbO}_2 \).

For anodic polarization we have

\[ i_A = \alpha_A^k F C_{\text{Pb}^{++}} C_{H^+}^{0.4} \] \[ 4.47 \]

where \( \alpha_A^k \) is a potential-dependent rate constant.

**Mechanism.** On the basis of the previous discussion for the exchange mechanism at \( \beta\text{-PbO}_2 \), and the above reaction orders which suggest that at least two \( H^+ \) ions are involved in the cathodic rate determining step, the following mechanism (written for the cathodic direction) probably describes the reaction.

\[
\begin{align*}
\alpha\text{-PbO}_2 + 3 \text{H}^+ &\rightleftharpoons \alpha\text{-PbO}_2(H^+)_{3 \text{ads}} \quad [4.48a] \\
\alpha\text{-PbO}_2(H^+)_{3 \text{ads}} + e &\rightarrow [\text{PbOH}]^{++} + \text{H}_2\text{O} \quad [4.48b] \\
[\text{PbOH}]^{++} + e &\rightarrow [\text{PbOH}]^{+} \quad [4.48c] \\
[\text{PbOH}]^{+} + \text{H}^+ &\rightarrow \text{Pb}^{++} + \text{H}_2\text{O} \quad [4.48d]
\end{align*}
\]
The rate equation for the cathodic reaction (rate control by equation [4.48b]) is

\[ i_C = \alpha_C^k F C_{PbO_2} C_H^{3+} \] \[ [4.49] \]

and for the anodic reaction (rate control by equation [4.48a])

\[ i_A = \alpha_A^k F C_{Pb^{++}} C_H^{-1} \] \[ [4.50] \]

where \( \alpha_C^k \) and \( \alpha_A^k \) are the appropriate rate constants.

If only two \( H^+ \) ions were involved in the initial step (equation [4.8a]), as suggested by the appearance of a cathodic reaction order of 2, the possibility of \( H^+ \) adsorption at the electrode surface would be precluded. This is somewhat anomalous since the numerical low reaction order on the anodic side for the \( H^+ \) ion indicates that it is adsorbed. Hence only the above reaction scheme, with the participation of three \( H^+ \) ions explains both the evidence for \( H^+ \) ion adsorption and the observed reaction orders. A further point in favour of this mechanism is that Olin (23) has observed \( [PbOH]^+ \) in acid-lead perchlorate electrolytes.

**Apparent exchange current.** The dependence of the exchange current on the concentration of the electroactive species can be obtained from Figures 44 and 45.

\[ \left( \frac{0 \log i_{oa}}{0 \log C_{Pb^{++}}} \right) = 0.3 \] \[ [4.51] \]
With the $\beta$-modification it was possible to discuss
semiquantitatively the exchange current dependencies.
For $\alpha$-$\text{PbO}_2$ calculations of the dependence of $\text{Pb(III)}$
with the concentration of electroactive species are
similar in sign but different in magnitude from that
observed with $\beta$-$\text{PbO}_2$ in the case of all postulated
mechanisms.

Using the relationships \([4.33], [4.34] \text{ and } [4.37], [4.38]\),
taking values for $\alpha_h = 0.95$ and $\alpha_b = 0.80$ and
using equations \([4.51] \text{ to } [4.54]\) the following dependencies
are obtained.

\[
\left( \frac{\partial \log i_{\text{oa}}}{\partial \log C_{\text{H}^+}} \right) = 0 \quad \ldots \quad [4.52]
\]

\[
\left( \frac{\partial \log i_{\text{ob}}}{\partial \log C_{\text{Pb}^{++}}} \right) = 0.11 \quad \ldots \quad [4.53]
\]

\[
\left( \frac{\partial \log i_{\text{ob}}}{\partial \log C_{\text{H}^+}} \right) = 0 \quad \ldots \quad [4.54]
\]

\[
\left( \frac{\partial \log C_{\text{Pb(III)}}}{\partial \log C_{\text{Pb}^{++}}} \right) = 0.3 \quad \ldots \quad [4.55]
\]

cf 0.7 for $\beta$-$\text{PbO}_2$.

\[
\left( \frac{\partial \log C_{\text{Pb(III)}}}{\partial \log C_{\text{H}^+}} \right) = -0.1 \text{ for } n = 2 \quad \ldots \quad [4.56]
\]

cf -0.3 and -0.4 for $\beta$-$\text{PbO}_2$.

For the anodic reaction
\[ \frac{d \log C_{\text{Pb}^{(\text{III})}}}{d \log C_{\text{Pb}^{++}}} = -3.5 \quad \text{[4.57]} \]

cf -3.0 for \(\beta\)-PbO

\[ \frac{d \log C_{\text{Pb}^{(\text{III})}}}{d \log C_{H^+}} = \begin{cases} 12.0 & \text{for } n = 1 \\ 8.0 & \text{for } n = 2 \\ 4.0 & \text{for } n = 3 \end{cases} \quad \text{[4.58]} \]

cf 11.8 and 8.0 and 4.0 for \(\beta\)-PbO

At the equilibrium the current flowing involves both anodic and cathodic directions. Figure 46 clearly indicates that an equilibrium is established between \(\alpha\)- and \(\beta\)-PbO in the electrode surface via the agency of the Pb\(^{++}\) ion in the electrolyte. Exchange current dependencies would be expected to be more complicated in the \(\alpha\)-material than in the \(\beta\)-material in acid electrolytes. Examination of the dependence of \(i_{oa}\) with \([\text{Pb}^{++}]\) in the case of initially \(\alpha\)-PbO\(_2\) electrodes in acid electrolytes (Figure 44) indicates the \(\alpha\)-PbO\(_2\) exchange current is greater than that exhibited by \(\beta\)-PbO\(_2\) at low \([\text{Pb}^{++}]\) but approaches that of \(\beta\)-PbO\(_2\) at high \([\text{Pb}^{++}]\), Figure 33. This once again indicates that a process of transformation has occurred in the electrolyte via the Pb\(^{++}\) ion. The extent of this change in electrode constitution depends upon the \([\text{Pb}^{++}]\) in solution i.e., on the extent of the exchange current; a high exchange current engendering a sensible complete transformation of the \(\alpha\)-PbO\(_2\) (less stable) into the \(\beta\)-PbO\(_2\) (more stable).
CHAPTER 5.  A STUDY OF THE DIFFERENTIAL CAPACITANCE OF LEAD DIOXIDE IN AQUEOUS ELECTROLYTES

Introduction

Many studies of the electrical double layer capacitance of solid electrodes in aqueous electrolytes have been made [see e.g. (83)]. Such information allows, in the absence of adsorption, the determination of the point of zero charge, $E_Z$, i.e. the potential at which the charge of the ionic double layer is equal to zero. $E_Z$ is characteristic of the metal or oxide electrode and differences in $E_Z$ would be expected to be proportional to differences in their work functions (12). In addition, double layer capacitance measurements might be expected to shed light on the double layer structure of solid metal or oxide electrodes and so enable an extension of the theory for the ideally polarizable electrode to such systems.

The double layer capacitance of lead dioxide electrodes has been investigated by Kabanov, Kiseleva and Leikis (84) in sulphuric and perchloric acid electrolytes using the a.c. technique of Vorsina and Frumkin (85). They found that the polarizable region extends from $\sim 1.5$ V to $\sim 1.85$ V (NHE). The minimum in the differential capacitance curves occurred at $\sim 1.78$ V (NHE), and was assumed to be the point of zero charge.
This minimum compared favourably with the value obtained by Leikis and Venstrem (86) for the maximum of the plot of surface hardness as a function of potential.

In the present investigation the differential capacitance of \( \alpha \)- and \( \beta \)-PbO\(_2\) have been studied in order to determine:

i) the general shape of the capacitance curve, and how it is affected by ions in the solution, by adsorbed species at the interphase, and by the structure of the oxide lattice,

ii) the potential of the capacitance minimum in dilute solutions and its relation to the capacitance curve generally,

iii) the effective surface area of both PbO\(_2\) modifications, and,

iv) the degree to which the double layer of the oxide electrode, having metallic conductivity, possesses properties similar to those of a metallic electrode.

**Experimental**

Electrolytic cell. The electrolytic cell, shown in Figure 47, was constructed of borosilicate glass and had a capacity of 200 ml. The purification limb contained active charcoal through which the electrolyte was circulated by means of a nitrogen-activated lift pump. Details of charcoal and nitrogen purification are given in Appendix 4.
FIG 47  Electrolytic cell

A Test electrode
B Counter electrode
C Purification limb containing activated charcoal
D Reference electrode
E Nitrogen lift pump
Counter electrode. The counter electrode was made from platinum gauze of large surface area ($\sim 20 \text{ cm}^{-2}$), sealed in lead-free soda glass and connected to the electrical circuit via the usual mercury-iron contact. Before use, the electrode was thoroughly burned-off and cleaned with 50-50 concentrated sulphuric and nitric acid.

Reference electrode. Saturated and normal calomel electrodes were used in sodium perchlorate electrolytes. In perchloric acid, calomel electrodes were used in conjunction with a sodium perchlorate salt bridge. The most convenient electrode for use in alkaline electrolytes was a mercury-mercurous oxide electrode, introduced into the reference limb. All reference electrodes were standardised before and after use against saturated calomel electrodes.

Test electrode. The test electrodes were identical in geometry and construction to those described in Chapter 2.

Electrolytes. All solutions were prepared from A.R. grade chemicals using water twice distilled from deionized stock (conductivity $< 1 \mu$ohm cm$^{-1}$). Each solution was standardised before and after use.

Purification procedure. The stringent purification procedure was identical to that described in Chapter 2.
Each electrolyte was allowed to circulate for at least two weeks before results were taken.

**Electrical circuit.** The electrical circuit is shown in Figure 48.

For zero out-of-balance current

\[
\frac{Z_1}{Z_{\text{cell}}} = \frac{Z_2}{Z_4} \quad \cdots \quad [5.1]
\]

\[
C_{\text{xs}} = \frac{C_4}{R_1} \cdot R_2 \quad \text{and} \quad R_{\text{xs}} = \frac{R_1}{C_4} \cdot C_2 \quad \cdots \quad [5.2]
\]

The use of the Schering bridge had the following advantages:

i) the cell impedance was measured as a series combination which was advantageous in interpreting results,

ii) experimental capacitance was balanced with a resistance and vice versa. Large bridge resistances were more readily available than large bridge capacitors so that large pseudocapacitances were easily dealt with. The bridge components were Muirhead (0.05 or 0.1% grade).

**a.c. generator.** a.c. from an audiofrequency generator (Advance type H1) was applied to the bridge through a screened 65:1 isolating transformer. The amplitude of the sinusoidal voltage was 5 mV peak-to-peak.

**Detector.** The out of balance signal was passed through the filter, (Muirhead, type D-925-B, set to reject
FIG 48  Electrical circuit for impedance measurements

For Wave Analyzer operation (Hewlett Packard type 302A) in B.F. mode, output connects across O-O, input connects across i-i

\[ C_{xs} = \frac{C_4 R_2}{R_1} \quad \text{and} \quad R_{xs} = \frac{R_1 C_2}{C_4} \]
50 c/sec) to a tuned amplifier (General Radio, type 1232A).

**Potential measurements.** The potential measurements were made with a potentiometric pH meter (Pye 11088). The input impedance was effectively infinite ($>10^{12}\Omega$) and consequently could be left connected, monitoring the electrode potential, as impedance measurements were taken.

**Bridge polarizing circuit.** The potential was changed by polarizing the bridge symmetrically; this arrangement produced less interference than the usual method of applying the potential across the cell. The test electrode was connected directly to earth because of the difficulty of screening it.

**Frequency response of the a.c. bridge.** The response of the a.c. bridge was checked, at various frequencies, by measuring the impedance of an analog comprising of a standard capacitance (1μF) in series with a high stability carbon resistance (225Ω). Attempts to screen all connections using co-axial leads to minimise interference and consequently increase the scope of the bridge, had very little or no effect on the response of the bridge over the frequency range 30 c/sec to 5 kc/sec (Table 14).

**Experimental procedure.** All experiments were made in air thermostats at temperatures $23 \pm 1^\circ C$. A freshly prepared electrode was removed from the electrodeposition circuit, washed with twice distilled water, and introduced into the electrolytic cell.
**TABLE 14.**

**BRIDGE IMPEDANCE RESPONSE OVER DIFFERENT FREQUENCY RANGES.**

Determined using (a) unscreened a.c. bridge (b) screened a.c. bridge.

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>Error (a)</th>
<th>Error (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30c/sec-500c/sec</td>
<td>±1%</td>
<td>±1%</td>
</tr>
<tr>
<td>500c/sec-1kc/sec</td>
<td>±1%</td>
<td>±1%</td>
</tr>
<tr>
<td>5kc/sec-10kc/sec</td>
<td>±5%</td>
<td>±5%</td>
</tr>
<tr>
<td>10kc/sec-20kc/sec</td>
<td>±5%</td>
<td>±7%</td>
</tr>
<tr>
<td>20kc/sec-50kc/sec</td>
<td>±100%</td>
<td>±70%</td>
</tr>
</tbody>
</table>
The potential of the test electrode was adjusted to the potential of zero current flow, \( E_{i=0} \). The time dependence of the electrode capacitance, \( C_e \), was measured and equilibrium was considered achieved when \( C_e \) became stable with time. The electrode remained on an open circuit until the reading was taken. Reproducible constant values of \( C_e \) provided a criterion of the purity of the system.

On reaching equilibrium the potential was changed from \( E_{i=0} \) to potentials more positive and then to potentials more negative than \( E_{i=0} \). The test electrode was allowed to reach equilibrium at each new potential before the measurements were made. In the region of the capacitance minimum the measurements in some cases were extended up to one hour.

The capacitance, resistance and faradaic current were measured as a function of the applied potential for a given frequency; the bridge was balanced at frequencies in the range 1 kc/sec to 30 c/sec.
5.1. DIFFERENTIAL CAPACITANCE OF $\beta$-PbO$_2$

IN AQUEOUS ELECTROLYTES

Experimental Results

Time dependence of the electrode capacitance. The $\beta$-PbO$_2$ electrode achieved almost instantaneous equilibrium in perchloric acid electrolytes. In sodium perchlorate electrolytes $C_e$ increased somewhat with time and the time to reach equilibrium was concentration dependent, decreasing with increase of solution conductivity. $C_e$ in sodium hydroxide electrolytes reached equilibrium within 24 hours for all concentrations investigated.

Comparison of equilibrium $C_e$ values, on similar electrodes for a given electrolyte, indicated that the electrode surface was reproducible to within $\pm$ 10%.

Differential capacitance curves. Figures 49, 50 and 51 show $C_e$ versus $E_h$ for a variety of aqueous electrolytes.

The results indicate the following polarizable regions, $\sim$1.38 V to $\sim$1.67 V for HClO$_4$; $\sim$1.1 V to $\sim$1.65 V for NaClO$_4$; and $\sim$0.3 V to $\sim$1.05 V for NaOH, all potentials referring to the normal hydrogen electrode (NHE). Outside these regions considerable faradaic current flowed, particularly at more positive potentials, and was eventually accompanied by oxygen evolution. The minimum in the differential capacitance curves, $E_{\text{min}}$, occurred at 1.65 $\pm$ 0.05 V, 1.58 $\pm$ 0.05 V, 1.00 $\pm$ 0.05 V, respectively in the above electrolytes.
FIG 49  Differential capacitance for $\beta$-PbO$_2$ in HClO$_4$ electrolytes

(A) 1.0 M; (B) 0.01 M; (C) 0.001 M; AT 1 kc/sec.  23°C
FIG 50  Differential capacitance curves for $\beta$-PbO$_2$

in aqueous NaClO$_4$ electrolytes

(A) 0.2 M NaClO$_4$;  (B) 0.02 M NaClO$_4$ ;  (C) 0.008 M NaClO$_4$;  AT 1 kc/sec

Differential capacitance, $\mu$F cm$^2$

$E_h$ V
FIG 51 Differential capacitance curves for β-PbO₂ in NaOH electrolytes

(A) 0.1 M; (B) 0.01 M; (C) 0.001 M; AT 1 kc/sec; 23°C
As the electrolyte concentration was decreased the value of $C_e$ fell sharply, not only in the region of the minimum but also on either side of the minimum without any significant variation of the potential of the capacitance minimum, although the latter became more pronounced.

There was no significant variation in the resistance component, $R_e$, in the polarizable region at constant frequency.

No appreciable hysteresis effects were observed in the polarizable region when the faradiac current did not exceed 0.03 mA cm$^{-2}$.

**Frequency dependence of the differential capacitance.**

Figures 52, 53 and 54 show the relatively small effect of frequency on the differential capacitance curves (Figure 52 also includes the differential capacitance curves obtained by Kabanov et al (84)). $C_e$ decreases with increasing frequency, the dispersion is potential dependent and appears to increase as the conductivity of the particular electrolyte decreases.

**Discussion of Results**

**Time dependence of the electrode capacitance.** The initial decrease of electrode capacitance with time in NaClO$_4$ and NaOH electrolytes probably results from surface rearrangement (87). This initial decrease was followed
FIG 52  Differential capacitance curves for $\beta$-PbO$_2$

in 0.01 M HClO$_4$ electrolyte

(A) 110 c/sec ; (B) 300 c/sec ; (C) 1 kc/sec  23°C

(D) & (E) CURVES OBTAINED BY KABANOV et al AT 500 c/sec & 5 kc/sec
FIG 53 Differential capacitance curves for $\beta$-PbO$_2$

in 0.02 M NaClO$_4$ electrolyte

(A) 70 c/sec ; (B) 110 c/sec ; (C) 300 c/sec ; (D) 1 kc/sec ; 23°C

Differential capacitance, $\mu$F cm$^{-2}$

$E_h, V$

1.1 1.3 1.5 1.7
FIG 54 Differential capacitance curves for $\beta$-PbO$_2$

in 0.001 M NaOH electrolyte

(A) 110 c/sec; (B) 300 c/sec; (C) 1 kc/sec; 23°C
by an increase of \( C_e \) with time in NaCl\( _4 \) electrolytes until a constant value was obtained. Kabanov et al observed this phenomenon in HC\( _4 \) electrolytes and suggested that it is associated with the swelling of the lead dioxide, resulting in a change of the crystal structure with an increase in the true surface area. The constancy of \( C_e \) with time for \( \beta \)-Pb\( \text{O}_2 \) in HC\( _4 \) electrolytes, however, appears to contradict this suggestion of the swelling of the lead dioxide. \( C_e \) for \( \alpha \)-Pb\( \text{O}_2 \), moreover, has a pronounced time dependence and as Kabanov et al did not differentiate between the two Pb\( \text{O}_2 \) modifications their electrodes may have consisted of mixtures. Alternatively, the stringent purification procedure carried out in the present investigation may have proved more successful than that used by Kabanov et al.

On the other hand, the relatively slow approach to equilibrium in NaCl\( _4 \) and NaOH electrolytes may indicate some form of surface adsorption e.g. of H\( ^+ \) ions. This, however, appears to be inconsistent with the insignificant variation of \( E_{\text{min}} \) with electrolyte concentration (Figure 50), the small frequency dispersion effect observed (Figure 53) and similarity of the magnitude of \( C_e \) for the different electrolytes investigated.

**Differential capacitance curves.** Values for the potential minimum for HC\( _4 \) electrolytes were approximately 0.1 V more negative than those previously
reported (84) although the general shape of the curves is very similar.

The capacitance measurements in the present work were only made when the electrode had attained equilibrium at the applied potential. In contrast, Kabanov et al (84) recorded the differential capacitance measurements with comparative rapidity and found that the minimum is shifted towards negative potentials by tens of millivolts if the electrode was allowed to achieve equilibrium at each potential. These workers concluded that this change resulted due to adsorption of anions. On the other hand, this small variation in $E_{\text{min}}$ may be attributed to changes in surface characteristics resulting from different methods of $\text{PbO}_2$ preparation. $E_{\text{min}}$ in NaClO$_4$ electrolytes ($1.58$ V) is some $70$ mV more negative than that observed in HCIO$_4$ electrolytes. The shift in $E_{\text{min}}$ probably results from hydrogen ion adsorption, evidence for which has already been discussed in Chapter 3.

$E_{\text{min}}$ for NaOH electrolytes is $1.00$ V. The change in $E_{\text{min}}$ from that observed in neutral electrolytes is probably too large to be accounted for purely in terms of adsorption of OH$^-$ ions. A possible explanation is a change in the electrode activity of $\beta$-$\text{PbO}_2$ resulting in a change in the electrode surface to an equilibrium mixture of both modifications.

$E_{\text{min}}$ need not correspond to the point of zero charge if potential dependent adsorption of hydrogen or oxygen is present. The minimum in HCIO$_4$ and NaClO$_4$ electrolytes
is very close to the point of oxygen discharge so increasing the possibility of hydroxyl ion adsorption. However, the small frequency dispersion effect, and the absence of hysteresis effects in the polarizable region in the case of NaClO₄, suggests that the adsorption of these species are not a serious complication in this case.

The shape of the differential capacitance curves are affected by [H⁺]. At negative potentials H⁺ adsorption occurs and results in an increase in the slope of Cₑ versus Eₕ on going from NaOH to NaClO₄ i.e. increase in [H⁺]. At anodic potentials oxygen evolution is enhanced by decrease in [H⁺].

**Frequency dependence of electrode capacitance.** Several models attempting to explain the variation of capacitance with frequency have been proposed. McMullen and Hackerman (88) suggest that it is caused by a faradaic current due to the presence of small amounts of impurities. However, the increase in the frequency dispersion with dilution appears to contradict this. Bockris and Conway (89) have proposed that, due to strong adsorption forces, the water molecules in the inner Helmholtz layer are unable to follow the applied field, resulting in capacitance dispersion. Frumkin (90) has associated this phenomena with the presence in the electrode surface of irregularities and cracks which would create paths of different resistance to different areas of the electrode. These
different areas would have different time constants and a frequency dispersion would result. Evidence in support of this suggestion has been given by Ramaley and Enke (91) and Tsa and Jofa (92). The presence of micropores and crevices in the electrolytic semi-crystalline deposit of $\beta$-PbO$_2$ is entirely probable. The uneven surface may also account for the observed decrease of capacitance with dilution in regions other than the minimum.
5.2. DIFFERENTIAL CAPACITANCE OF Α-ПbO₂ IN AQUEOUS ELECTROLYTES

Experimental Results

Time dependence of the electrode capacitance. A time dependence of \( C_e \) was observed in perchloric acid and in sodium perchlorate electrolytes if the electrode was held at \( E_i = 0 \). Equilibrium \( C_e \) values, however, were obtained at potentials more positive than \( E_i = 0 \).

In sodium hydroxide electrolytes equilibrium was readily achieved at \( E_i = 0 \).

Differential capacitance curves. Electrometric measurements, Figures 55 and 56, indicated that the polarizable regions extend from \(~1.4\) V to \(~1.7\) V for \( \text{HClO}_4 \), \(~0.3\) V to \(~1.0\) V for \( \text{NaClO}_4 \) and \(~0.35\) V to \(~1.0\) V for \( \text{NaOH} \). \( E_{\text{min}} \) occurred at \( 1.65 \pm 0.05 \) V, \( 0.65 \pm 0.1 \) V and \( 0.59 \pm 0.05 \) V respectively in the above electrolytes.

At potentials more positive than \(~1.5\) V the characteristics of the \( C_e \) versus \( E_h \) curves, for Α-ПbO₂ in \( \text{HClO}_4 \) electrolytes, were identical to those observed for Β-ПbO₂ (Figure 49). \( C_e \), however, appeared slightly higher for the Α- modification and there was some variation in \( R_e \) with \( E_h \) (Figure 55). The polarizable regions for \( \text{NaClO}_4 \) and \( \text{NaOH} \) electrolytes are displaced to more negative potentials compared with the corresponding polarizable regions for Β-ПbO₂.
FIG 55  Differential capacitance curves for 
\( \alpha\)-PbO\(_2\) in HClO\(_4\) electrolytes

(A) 0.1 M; (B) 0.01 M; (C) 0.001 M; AT 1 kc/sec. 23°C

![Graph showing differential capacitance curves for \( \alpha\)-PbO\(_2\) in HClO\(_4\) electrolytes.](image)
Differential capacitance curves for $\alpha$-PbO$_2$ in aqueous NaOH electrolytes

(A) 0.01 M; (B) 0.001 M AT 1 kc/sec.  23 °C
As the electrolyte concentration was lowered \( C_e \) decreased but there appeared to be no significant variation in \( E_{\text{min}} \).

**Frequency dependence of the differential capacitance.**

In \( \text{HCIO}_4 \) and \( \text{NaOH} \) electrolytes, \( C_e \) decreases with increasing frequency as shown in Figures 57 and 58. An unusual frequency effect was observed in \( \text{NaClO}_4 \) electrolytes. Initially the capacitance decreases on increasing the frequency up to \( \approx 300 \) c/s but then increases with increasing frequency.

**Discussion of Results**

**Time Dependence of the electrode capacitance.** The time dependence of \( C_e \) and \( R_e \) in inert electrolytes of pH 7 is interesting as no significant time dependence was observed in the presence of a potential determining \( \text{Pb}^{++} \) ion. It may be attributed to a reaction occurring at the electrode surface, such as \( \text{H}^+ \) ion adsorption. A further possibility is a change in activity of the unstable \( \alpha\)-\( \text{PbO}_2 \) electrode in electrolytes of low pH until an equilibrium mixture of the two modifications is obtained; the presence of a \( \text{Pb}^{++} \) ion may have the effect of hastening such an equilibrium process. This could account for the pronounced time dependence of \( C_e \) observed by Kabanov et al but not observed in the case of pure \( \beta\)-\( \text{PbO}_2 \) because of its stability in solutions of low pH.

96.
Differential capacitance curves for $\alpha$-PbO$_2$ in 0.01 M HClO$_4$ electrolyte

(A) 70 c/sec; (B) 300 c/sec; (C) 1 kc/sec. 23°C
FIG 58  Differential capacitance curves for $\alpha$-PbO$_2$

in 0.001 M NaOH electrolyte

(A) 110 c/sec ; (B) 300 c/sec ; (C) 1 kc/sec  

$23^\circ$C

Differential capacitance, $\mu$F cm$^{-2}$

$E_h$, V
Differential capacitance curves. The minimum and shape of the \( C_e \) versus \( E_n \) curves in \( \text{HClO}_4 \) electrolytes, are very similar to \( \beta\text{-PbO}_2 \) and completely different from the behaviour of \( \alpha\text{-PbO}_2 \) in \( \text{NaClO}_4 \) and \( \text{NaOH} \) electrolytes. This further substantiates the conclusions drawn in Chapter 4, namely that the activity of \( \beta\text{-PbO}_2 \) in a "\( \alpha\)-electrode" increases in acid electrolytes.

In \( \text{NaClO}_4 \) and \( \text{NaOH} \) electrolytes the position of \( E_{\text{min}} \) is approximately 1 V more negative than that observed for \( \beta\text{-PbO}_2 \). Such a change is difficult to explain because the physical and chemical properties of \( \alpha\- \) and \( \beta\text{-PbO}_2 \) are very similar. However, anion adsorption (such as \( \text{OH}^- \)) would be expected to shift the potentials to more negative values.

Frequency dependence of the differential capacitance.

The variation of \( C_e \) with frequency in \( \text{HClO}_4 \) and \( \text{NaOH} \) electrolytes is of the same order as that observed for \( \beta\text{-PbO}_2 \) electrodes and probably arises from the presence of micropores and crevices in the \( \alpha\text{-PbO}_2 \) electrode surface.

No satisfactory explanation can be offered for the unusual frequency effect in \( \text{NaClO}_4 \) electrolytes. The electrolytes were the same as those previously used for the measurement of capacitance of \( \beta\text{-PbO}_2 \), hence the possibility of impurities in the system can be discounted. As a further check for faults arising from the a.c. bridge, measurements were made using several different a.c. bridges. The semiconductor properties of \( \alpha\text{-PbO}_2 \) may be increased on application of an a.c. current but the magnitude of the
observed electrode capacitance appears to contradict this possibility. An exchange reaction occurring at the electrode surface is a further possibility.

**Conclusions**

i) The variation of $E_{\text{min}}$ for different electrolytes suggests that $E_{\text{min}}$ does not correspond to the point of zero charge.

ii) The values of $C_e$ at $E_{\text{min}}$ in 1 M NaClO$_4$, 70 μF cm$^{-2}$ for β-PbO$_2$, and in 1 M HClO$_4$, 90 μF cm$^{-2}$ for β-PbO$_2$ and 140 μF cm$^{-2}$ for α-PbO$_2$ compare favourably with the values obtained for the double layer capacitance from $\eta$-t transients (Chapter 3). These values also suggest that the effective surface area of α-PbO$_2$ is greater than that of β-PbO$_2$.

iii) The differential capacitance data confirms that the properties of the electrical double layer, formed at the surface of the lead dioxide electrode, are basically the same as those prevailing on metallic electrodes.
CHAPTER 6. SURVEY AND COMPARISON OF THE REPORTED DATA CONCERNING THE ELECTROCHEMISTRY OF $\alpha$- AND $\beta$-PbO$_2$

Thermodynamic Data

A survey of the most important thermodynamic data for $\alpha$- and $\beta$-PbO$_2$ is given in Table 15.

The potentiometric results of the present work (Appendix 3) show that the reversible potentials for $\alpha$-PbO$_2$ lie approximately 7-11 mV above the reversible potentials for the $\beta$- modification. This is in close agreement with results reported by other workers, see for e.g. Rüetschi et al (45). The difference in electrode potentials between $\alpha$- and $\beta$-PbO$_2$, in the same electrolyte, indicates that the former modification is the better oxidising agent. Also it may be concluded that the $\alpha$- modification having the greater free formation enthalpy, $\Delta G^0$, is the more stable.

A number of workers [see e.g. (73)] have reported different temperature coefficients for the electrode potentials of $\alpha$- and $\beta$-PbO$_2$. These temperature dependencies lead to an enthalpy difference, $\Delta H$, of -2.6 kcal at 25°C between the two modifications.

Surface Area

Table 16 shows the conclusions drawn by various

99.
<table>
<thead>
<tr>
<th>Thermodynamic Property</th>
<th>( \alpha\text{-PbO}_2 )</th>
<th>( \beta\text{-PbO}_2 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Electrode potential</td>
<td>+1.708 V</td>
<td>+1.715 V</td>
<td>(45)</td>
</tr>
<tr>
<td>E, in 4.4 M H(_2)SO(_4), 25°C, vs NHE.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii) Electrode potential</td>
<td>+1.657 V</td>
<td>+1.668 V</td>
<td>(Present Work)</td>
</tr>
<tr>
<td>E, in 3.0 M H(^+), 0.1 M Pb(^{2+}), Cl(_{10}^-), 6.35 M, 23°C, vs NHE.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii) Standard potential, ( E_0 )</td>
<td>+1.697 V</td>
<td>+1.687 V</td>
<td>(93) (94)</td>
</tr>
<tr>
<td>( +1.691 \text{ V} )</td>
<td>( +1.682 \text{ V} )</td>
<td>(95)</td>
<td></td>
</tr>
<tr>
<td>iv) Temperature coeff. of E in 4.62 M H(_2)SO(_4).</td>
<td>-0.36 mV/°C</td>
<td>-0.20 mV/°C</td>
<td>(73)</td>
</tr>
<tr>
<td>v) Free formation enthalpy, ( \Delta G^\circ ) per mol.</td>
<td>-51.94 kcal</td>
<td>-52.34 kcal</td>
<td>(73)</td>
</tr>
<tr>
<td>vi) Formation enthalpy, ( \Delta H^\circ ) per mol.</td>
<td>-63.52 kcal</td>
<td>-66.12 kcal</td>
<td>(95)</td>
</tr>
<tr>
<td>Method</td>
<td>System</td>
<td>Result</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>----------------------</td>
<td>--------</td>
<td>------------------</td>
</tr>
<tr>
<td>i) Differential capacitance</td>
<td>Inert electrolytes</td>
<td>α &gt; β</td>
<td>(Present Work)</td>
</tr>
<tr>
<td>using a.c. bridge.</td>
<td>HClO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii) Double layer capacitance</td>
<td>Pb⁺⁺, H⁺, ClO₄⁻</td>
<td>α &gt; β</td>
<td>(Present Work)</td>
</tr>
<tr>
<td>from galvanostatic pulse experiments.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii) Discharge expts.</td>
<td>H₂SO₄</td>
<td>β &gt; α</td>
<td>Angstadt (75)</td>
</tr>
<tr>
<td>iv) Passivation expts.</td>
<td>Pb⁺⁺, H⁺, ClO₄⁻</td>
<td>α = β</td>
<td>(Present Work)</td>
</tr>
<tr>
<td>v) Appearance.</td>
<td>In absence of oxide-solution interphase</td>
<td>β &gt; α</td>
<td>Mark (42)</td>
</tr>
<tr>
<td>vi) Crystal size.</td>
<td>see (v)</td>
<td>β &gt; α</td>
<td>Astachov (96)</td>
</tr>
</tbody>
</table>
workers from a study of the relative surface areas of the \( \alpha \)- and \( \beta \)- modifications.

In the present work double layer capacitance measurements, obtained from the initial rise of potential with time (Chapter 3), and differential capacitance data obtained from aqueous inert electrolytes (Chapter 5), both indicate that the apparent surface area of \( \alpha \)-PbO\(_2\) is greater than that of \( \beta \)-PbO\(_2\). These measurements suggest roughness factors (i.e. the ratio of the apparent to the true surface area) of 5 and 3 respectively.

In contrast, Angstadt and co-workers (75) have observed a shorter discharge time for the \( \alpha \)- material in \( \text{H}_2\text{SO}_4 \) compared with \( \beta \)-PbO\(_2\) and they attribute this difference to a larger surface area of the \( \beta \)- material. Mark (42) from an examination of the appearance of electrodeposited \( \alpha \)- and \( \beta \)-PbO\(_2\) concluded that the latter had the rougher surface. This is supported by earlier Russian evidence that \( \alpha \)-PbO\(_2\) tends to form larger crystals than \( \beta \)-PbO\(_2\) (96).

The discrepancies between the above observations may be due to:-

i) the use of different conditions for the preparation of experimental electrodes,

ii) difficulties involved in the comparison of the true surface area of any oxide in the presence and absence of an oxide-solution interphase. These difficulties arise because of complications (e.g. adsorption) which can occur to different extents in different electrolytes,
iii) discharge experiments on the time scale involved for the passivation experiments (Chapter 2), may only reflect the apparent surface area of the diffusion layer and not the true surface area of the electrodeposited material as discussed by de Levie (63).

**Kinetic Parameters**

**Exchange current.** Table 17 compares exchange currents obtained for α- and β-PbO₂ with those calculated from experimental η-i data of other workers. The observed exchange currents for the α-modification are generally higher than those obtained for β-PbO₂. This is in broad agreement with the conclusions drawn by Mark and Vosburgh (40).

It is possible to make a general comparison of the exchange currents for α- and β-PbO₂ (Table 17) but because of the uncertainty in the true surface area and the variation in the dependence of i₀ on the concentration of the electroactive species comparison in the absolute sense is difficult.

**Transfer coefficient.** The significance of the transfer coefficient has recently been discussed in detail by Bauer (97). This author has pointed out that there is no adequate justification for the introduction of the transfer coefficient as an implicitly potential independent parameter. Marcus (98) however has shown that the
### TABLE 17.

**COMPARISON OF THE EXCHANGE CURRENTS FOR α- AND β-PbO₂**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Exchange Current</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-PbO₂</td>
<td>β-PbO₂</td>
<td></td>
</tr>
<tr>
<td>mA cm⁻²</td>
<td>mA cm⁻²</td>
<td></td>
</tr>
</tbody>
</table>

#### a. Low overpotential region (\(\eta_p < 10 \text{ mV}\))

- 0.01 M Pb⁺⁺, 3.0 M H⁺ + 6.85 M ClO₄⁻
- 0.1 M H₂SO₄ saturated with PbSO₄
- 0.10 M HNO₃ + 0.05 M Pb⁺⁺
- 0.15 M HClO₄ + 0.1 M Pb⁺⁺
- 1.0 M HClO₄ + 0.1 M Pb⁺⁺

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Exchange Current</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.159</td>
<td>0.074</td>
<td>(Present work)</td>
</tr>
<tr>
<td>0.06-0.11</td>
<td>0.06-0.11</td>
<td>(40)</td>
</tr>
<tr>
<td>0.006-0.01</td>
<td>~0.4</td>
<td>(40)</td>
</tr>
</tbody>
</table>

#### b. High overpotential region (\(\eta_p > 50 \text{ mV}\))

- 0.5 M Pb⁺⁺, 3.0 M H⁺ + 6.85 M ClO₄⁻
- 0.5 M Pb⁺⁺, 3.0 M H⁺ (\(2i_{oα}\))
- 0.5 M Pb⁺⁺, 3.0 M H⁺ (\(2i_{ob}\))

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Exchange Current</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.126</td>
<td>0.118</td>
<td>(Present work)</td>
</tr>
<tr>
<td>0.670</td>
<td>0.330</td>
<td>(Present work)</td>
</tr>
</tbody>
</table>
transfer coefficient is a function of several terms which are not independent of the electrode potential but becomes independent of electrode potential if the double layer effects are small and the potential is not far removed (say \( \pm 250 \text{ mV} \)) from the equilibrium potential. In the present work the potential excursion from the equilibrium potential does not exceed this limit and the double layer effects can be considered constant in the presence of the large concentration of supporting electrolyte. The transfer coefficient is constant in the region of the equilibrium potential (Table 8 and 11) but changes abruptly over a small potential region (corresponding, it is suggested, to a change in the rate determining process) but becomes potential independent at high overpotentials (shown by linear Tafel plots).

Table 18 summarizes the transfer coefficients obtained for \( \alpha \)- and \( \beta \)-Pb\(_2\) in the present work. Fleishmann et al (39) have reported transfer coefficients for a number of processes concerned with the deposition of lead dioxide on to a platinum substrate. However, comparison of results from both investigations is difficult. In the present work deposition and dissolution occur at a uniform surface whereas in the latter investigation the production of a reproducible area is uncertain and deposition may be potential dependent. In addition complications may arise from specific anion effects e.g. sulphate adsorption on the deposited Pb\(_2\) (42) and acetate adsorption on the platinum substrate (38).
TABLE 18.

COMPARISON OF OBSERVED TRANSFER COEFFICIENTS FOR $\alpha$- AND $\beta$-PbO$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Cathodic Coeff.</th>
<th>Anodic Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Low overpotential region, $Z=2$</td>
<td>(a)</td>
<td>(1-a)</td>
</tr>
<tr>
<td>$\alpha$-PbO$_2$</td>
<td>0.18 ±0.05</td>
<td>0.8 ±0.05</td>
</tr>
<tr>
<td>$\beta$-PbO$_2$</td>
<td>0.20 ±0.05</td>
<td>0.8 ±0.05</td>
</tr>
<tr>
<td>b) High overpotential region, $Z=1$</td>
<td>($\alpha_a$)</td>
<td>($\alpha_b$)</td>
</tr>
<tr>
<td>$\alpha$-PbO$_2$</td>
<td>0.95 ±0.05</td>
<td>0.78 ±0.02</td>
</tr>
<tr>
<td>$\beta$-PbO$_2$</td>
<td>0.86 ±0.10</td>
<td>0.78 ±0.02</td>
</tr>
</tbody>
</table>
CHAPTER 7. CONCLUSIONS AND FURTHER WORK

i) Preliminary polarization studies indicate that electrode kinetic measurements can be made on both $\alpha$- and $\beta$-PbO$_2$ without the intrusion of solid films.

ii) Kinetic measurements around the equilibrium potential confirmed that the exchange reaction between either $\alpha$- or $\beta$-PbO$_2$ and plumbous ions in solution is slow, and charge transfer is the rate determining step. There is some evidence that both electrons are transferred in one stage.

iii) As the potential excursion from the equilibrium potential is increased there is evidence for a process change from a simultaneous two-electron transfer at low overpotentials to two consecutive single-electron transfer steps at high overpotential. On the basis of the observed reaction orders, possible reaction mechanisms can be formulated.

iv) In some respects the investigation of the kinetics of exchange at $\alpha$-PbO$_2$ electrodes in H$^+$ electrolytes is not as satisfactory as the investigation with the $\beta$- modification. This is because the anodic reaction leads to the formation of a certain amount of $\beta$- material so that an initially $\beta$- free electrode surface becomes modified to contain some $\beta$- material.
Further Work

i) Investigation of the exchange reaction in a different electrolyte, e.g. NaOH, where the dissimilar behaviour of the two modifications, observed while making differential capacitance measurements, suggests that a comparison of the electrochemical properties of each modification unaffected by the other might be made.

ii) Further study of the non-linear temperature dependence of the exchange current (obtained when $\eta_D < 5 \text{ mV}$) and its possible relationship to the intersection of the electrode potential versus temperature curves (at $\eta_D = 0$) reported by Angstadt et al (73).
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APPENDIX 1

Alphabetical list of symbols.

Throughout this work the symbols conform to the recommendations of the Symbols Committee of the Royal Society, 1951. The following list describes additional symbols commonly used throughout the text.

\[ C_L \] double layer capacitance
\[ C_e \] electrode capacitance
\[ C_{Pb^{++}} \] concentration of plumbous ion at the interphase
\[ C_{xs} \] experimental capacitive component of the cell impedance
\[ \Delta c \] increase in concentration required for attainment of critical concentration at the electrode (equation \([2.4]\))
\[ oC_R \] concentration of species R at the electrode at equilibrium
\[ D \] diffusion coefficient (equation \([2.4]\))
\[ E_Z \] potential of zero charge
\[ E_h \] applied potential
\[ E_{i=0} \] potential of zero current
\[ E^o \] equilibrium potential
\[ E_{\text{min}} \] potential of capacitance minimum
\[ E_{3M} \] equilibrium potential for the system \(\beta\)-PbO\(_2\), 3.0 M H\(^+\), 1.0 M Pb\(^{++}\)
\[ E_M' \] equilibrium potential for the system \(\beta\)-PbO\(_2\), 0.1 M Pb\(^{++}\), 1.0 M H\(^+\)
\( E_{\text{eq}} \) for the system \( \alpha-\text{PbO}_2 \),
\[ 3.0 \text{ M } \text{H}^+, 1.0 \text{ M } \text{Pb}^{++} \]
\( E_{\text{eq}}' \) for the system \( \alpha-\text{PbO}_2 \),
\[ 0.1 \text{ M } \text{Pb}^{++}, 1.0 \text{ M } \text{H}^+ \]
\( \Delta H \) enthalpy of activation
\( K \) equilibrium constant in equation [4.29]
\( K_S \) equilibrium constant in equation [4.23]
\( R_D \) charge transfer resistance
\( R_e \) cell resistance
\( R_P \) polarization resistance
\( R_\Omega \) ohmic resistance
\( R_{xS} \) experimental resistive component of the cell impedance
\( a \) constant in Tafel equation [1.4]
\( b \) constant in Tafel equation [1.4]
\( i \) current density
\( i_A \) anodic current density
\( i_C \) cathodic current density
\( i_l \) limiting current density below which passivation will not occur (equation [2.3])
\( i_o \) exchange current density
\( i_{oa} \) exchange current density for step [4.1a]
\( i_{ob} \) exchange current density for step [4.1b]
\( k_A \) potential dependent rate constant in equation [4.13]
\( k_C \) potential dependent rate constant in equation [4.14]
\( k_p \) passivation constant (equation [2.3])
\( k^0 \) standard rate constant
\( k^0_a \) standard rate constant in equation [4.2a]

(ii)
standard rate constant in equation \([4.2b]\)  
rate constant in equation \([3.2]\)  
potential dependent rate constant in equation \([4.23]\)  
potential dependent rate constant in equation \([4.20]\)  
potential dependent rate constant in equation \([4.46]\)  
potential dependent rate constant in equation \([4.47]\)  
ordinal number of slowest step in a multistep anodic reaction  
ordinal number of slowest step in a multistep cathodic reaction  
time for electrode to passivate  
successive polarization times in current interruption  
cathodic transfer coefficient  
cathodic transfer coefficient for reaction \([4.1a]\)  
cathodic transfer coefficient for reaction \([4.1b]\)  
equal to \(\alpha_a\) or \(\alpha_b\)  
overpotential  
overpotential due to charge transfer  
highest value of \(\eta_D\)  
ohmic overpotential  
diffusion layer thickness  
double layer charging time, equation \([3.5]\)
Electrodeposition of $\alpha$- and $\beta$-lead dioxide.

Although the electrochemical preparation of lead dioxide has attracted considerable attention [see e.g. (1)], difficulties involved in the preparation of either form, free of the other, have recently been discussed (2). Preliminary experiments have shown that pH is not the only controlling factor; electrolyte composition, current density and temperature of electroformation also have to be considered. Because of these difficulties it was found necessary to systematically investigate the conditions under which well crystallized samples of $\alpha$- and $\beta$-PbO$_2$, containing no preferred orientation, may be prepared substantially free of each other.

For the electrodeposition of $\beta$-PbO$_2$, acid-lead perchlorate and acid-lead nitrate electrolytes appear to give the most consistent results. Perchlorate electrolyte has been chosen, in preference to nitrate, in view of a) the stability of the ClO$_4^-$ ion (not easily reduced) and b) the subsequent use of ClO$_4^-$ electrolytes for the kinetic study.

The electrodeposition of $\alpha$-PbO$_2$ is relatively simple since $\alpha$-PbO$_2$ has been prepared from sodium plumbite electrolytes (3).

Various supporting electrodes have been used for the electrodeposition of lead dioxide. These include platinum, gold, nickel and tantalum at low pH and platinum and lead
at high pH. In view of its ready availability and inert nature, platinum was chosen for the present investigation.

**Experimental**

**Materials.** All chemicals were of analytical reagent quality.

Supporting electrodes (anodes) were prepared from platinum (99.9999% pure) supplied by Johnson Matthey. Cathodes for the deposition of PbO$_2$ were made from lead (99.9995% pure) supplied by Société de la Vielle Montagne, electrodes being mounted in lead-free soda glass with polyethylene. (N.B. The use of normal Pyrex glass to soda glass seals is not possible with acid-perchlorate electrolytes).

**Electrolytes.** Acid-lead perchlorates electrolytes were prepared from yellow lead monoxide added to perchloric acid. Sodium plumbite electrolyte was prepared from sodium hydroxide (2 M) saturated with PbO.

**Deposition circuit.** The platinum anode and lead cathodes were suspended in a single compartment cell. Current was supplied from a power pack (Solartron, type A.S. 759.2) and measured using a Cambridge unipivot galvanometer. The temperature was controlled to ± 0.1°C using a thermostatted water bath.

**Procedure.** The following conditions were found to be

(ii)
satisfactory for the electrodeposition of $\alpha$- and $\beta$-PbO$_2$.

$\alpha$-PbO$_2$: Electrolysis of a sodium plumbite electrolyte at a current density of 0.8 mA cm$^{-2}$ at 30°C. This method is similar to that described by Dodson (3).

$\beta$-PbO$_2$: Electrolysis of a lead perchlorate (2.25 M), perchloric acid (0.1 M) electrolyte at a rate of 0.8 - 1.0 mA cm$^{-2}$ at 30°C.

Analysis

The X-ray diffraction patterns obtained for $\alpha$-PbO$_2$, using a Philips diffractometer (type PW 1051) with copper $K_\alpha$ radiation and scanning speed of 1°/min, were in good agreement with that reported in the American Standard Testing Materials Index (A.S.T.M.), as shown in Table A.

For the examination of $\beta$-PbO$_2$ deposits standard mixtures of $\alpha$- and $\beta$-PbO$_2$ were prepared. $\alpha$-PbO$_2$ was electrodeposited as described above; pure $\beta$-PbO$_2$ was obtained from Messrs Hopkin and Williams (Micro-Analytical Reagent).

For the analysis, three lines were chosen from the diffraction patterns obtained for the standard mixtures viz, the $\alpha$-modification interplanar spacing 2.63 Å, the $\beta$-modification 2.46 Å and 1.85 Å. As proposed by Dodson (3), a plot of the intensities of the $\alpha$-, 2.63 Å line relative to the intensities of the $\beta$-, 2.46 Å and 1.85 Å lines against the % $\alpha$-modification in the mixture yield two approximately straight lines on a semilog scale (Figure I). This method gave reproducible results within 5% in repeated analysis of the standard mixtures.
TABLE A.

COMPARISON OF OBSERVED AND STANDARD DIFFRACTION PATTERNS FOR $\beta$-FeO$_2$.

<table>
<thead>
<tr>
<th>Interplanar Spacing</th>
<th>Relative Intensity</th>
<th>Interplanar Spacing</th>
<th>Relative Intensity</th>
<th>Indices</th>
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<td></td>
<td>$\AA$</td>
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<td></td>
</tr>
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<td>80</td>
<td>101</td>
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FIG 1 Calibration curves for standard mixtures of $\alpha + \beta$ lead dioxide obtained from diffraction patterns

- Ratio of 2.46 Å $\beta$ line to 2.63 Å $\alpha$ line
- Ratio of 1.85 Å $\beta$ line to 2.63 Å $\alpha$ line
Table B gives the X-ray diffraction pattern obtained for $\beta$-PbO$_2$ prepared under the optimum conditions.

References

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<th>Interplanar Spacing</th>
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<th>Observed</th>
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<th>Relative Intensity</th>
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<td>113</td>
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<td>40</td>
<td>204, 313</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 3.

Electrode potential measurements.

Potential measurements were made against a saturated calomel electrode with a bridge of saturated ammonium nitrate solution, the liquid junction being formed in a three-way capillary tap. The system was equilibrated at 25 ± 1°C for sufficient time before measuring its potential (Pye Potentiometric pH Meter, type 11088).

Figure II shows the dependence of electrode potential on concentration. The reversible potential of α-PbO₂ differs from that of β-PbO₂ by 11 mV positive at pH 0 and 7 mV positive at pH 2.5.
FIG II  Dependence of electrode potential on [H+] and [Pb++]

TOTAL [ClO₄⁻] = 6.85 M WITH ADDED NaClO₄; 23°C

\[ E, \text{V vs NHE} \]

- \( \alpha\text{-PbO}_2 \)
- \( \beta\text{-PbO}_2 \)

\[ \log_{10}[\text{Pb}^{++}] \]

\[ \log_{10}[\text{H}^+] \]
APPENDIX 4.

The preparation of pure nitrogen for electrolyte circulation.

Commercial oxygen free nitrogen was passed over copper wire heated to 400°C. Periodically the copper was reduced by hydrogen at 400°C. Before entering the cell the nitrogen was saturated with water by passage through cell electrolyte contained in a presaturation vessel.

The preparation of the purified charcoal.

Activated charcoal (B.D.H., special for gas adsorption) was extracted in a Soxhlet apparatus with constant boiling hydrochloric acid. Extraction was continuous for two months the solvent being changed weekly. The charcoal was freed from chloride and hydrogen ion by extracting with water in the Soxhlet apparatus. Freedom from chloride was judged by testing with silver nitrate. The washing process took approximately two months. Charcoal was stored under conductivity water in Pyrex flasks fitted with ground glass stoppers. Before introduction into the electrolytic cell the purified charcoal was shaken with a small quantity of cell electrolyte, and the solution containing very fine material decanted. This was repeated a few times over 24 hours so that the residual material was free from fines which might pass or block the frit. Charcoal was transferred to the purification limb with a spatula and packed with a glass rod.
APPENDIX 5.

Programme for the determination of exchange current and charge transfer coefficient from overpotential-current data.

The programme is based on the technique introduced by Farr, Hampson and Williamson. J. Electroanal. Chem., 13, 1967.

The programme is written in fortran II-D for the I.B.M. 1620 computer. It has also been converted to fortran IV to run on the I.C.T.1905.

The programme consists of a main programme, a subroutine subprogramme PXMEW2 and a Function subprogramme PXMEW3.

The Main Programme. This reads in the data, forms the arguments for PXMEW2 and punches the results. It also controls the "dropping off" of successive values of $i$ and $\eta$ allowing $\alpha$ to be calculated as a function of overpotential range.

The function subprogramme PXMEW3. This function computes $i_o$ (see equation (1)) and the root mean square deviation of the calculated exchange currents from the values of supplied by the subroutine PXMEW2.

The subroutine PXMEW2. This is a programme to find the maximum value of a function of a single variable without using derivatives.
Method
This programme performs a step by step search to find the maximum value of function $F$ of a single variable $X$, given initial values for $X$ and a step length $A$. If a step improves the value of $F$, the step length is multiplied by a scale factor $S > 1$ and the process is repeated. When a step fails to improve the value, the current step length is reduced by a half and search recommences from the best point found so far but in the opposite direction. The whole process is iterated until the change in the step length is less than a specified quantity.

The variable $X$ may be constrained to lie in a certain range. The subroutine comes to an end if the search reaches the boundary twice.

Use
The subroutine is called by an instruction

```fortran
CALL PXMFW2 (F,X,A,B,EPS,N,K,G,H,S)
```

The arguments are:-

- **F** - The function to be investigated. On return to the main programme this has the value of the maximum (or minimum).
- **X** - The argument of the function, which must be set to an initial value on entry and on returning to the main programme contains the value at which the maximum or minimum occurs.
- **A** - The initial step length (is changed by the routine and needs to be set for each entry).
- **B** - Set to +1 for a maximum or -1 for a minimum.
- **EPS** - The accuracy to which the $X$ value is required.
N - Set to 0 for no constraints or +1 if constraints are present.
K - Set to +1 for normal output or 0 if results required at every function evaluation.
G,H - The lower and upper bounds on X.
S - The scale factor. (The value of S in the range 1 ≤ S ≤ 2 is recommended).

This subroutine calls the function PXMEWJ(X) to evaluate the function for a given value of the argument X.

Input Data

ALFO = initial value of α.
DALI = initial step length for α.
ACC  = scale factor (1 ≤ ACC ≤ 2).
EPS  = accuracy to which α is required.
COUNT = number of current readings.
FINIS = point at which to stop "dropping off" current values.
TEMP = temperature (°C).
XLOW) = lower and upper bounds for α (0.0 and 1.0 suggested values).
XUP )
KPRINT = 1 or 0 to control output (See PXMEW2).
KREST = 1 or 0 for constraints or no constraints in α.
DIMENSION XI(100),FTA(100)
COMMON XI,ETA,N,Z,AVEXO
F=23091.648
READ 44,NCASES
DO 23 ICASE=1,NCASES
51 READ 40,ALFO,DAL,ACC,EPS,COUNT,FNIS,TEMP,XLOW,XUP,
M=COUNT
READ 41,(XI(I),I=1,M)
T2=TEMP+273.
READ 41,(ETA(I),I=1,M)
DO 21 I=1,M
21 ETA(I)=ETA(I)/(1000.*T2)**F
A=0.*
24 Z=COUNT-A
N=Z
PUNCH 44*N
ALPHA=ALFO
STEP=DAL
KR=KREST
CALL PXMEW2(ISDEV1,ALPHA,STEP,-1.,EPS,KP
*PRINT,XLOW,
XUP,IND)
IF(KPRINT)25 .. 26 9 25
26 PUNCH 150
150 FORMAT(79X,H-)
TEST=COUNT-A
IF(TST=FINIS)23,23,24
40 FORMAT(9F6.0,211)
41 FORMAT(10F8.0)
44 FORMAT(13)
45 FORMAT(F4.0,3X3(E12.6,3X))
23 CONTINUE
100 FORMAT(13)
CALL EXIT
END

FUNCTION PXMEW3(ALPHA)
DIMENSION XI(100),FTA(100)
COMMON XI,ETA,N,Z,AVEXO
4 SUMX=0.
SUMXX=0.
T3=ALPHA-1.
DO 5 I=1,N
W=ETA(I)
T4=EXPF(W*ALPHA)-EXPF(T3*W)
AZ=XI(I)/T4
SUMX=SUMX+AZ
5 SUMXX=SUMXX+AZ*AZ
AVEXO=SUMX/Z
AVEXX=SUMXX/Z
PXMEW3=(AVEXX-AVEXO*AVEXO)/AVEXO**.5
RETURN
END
SUBROUTINE PXMEW2(FX,X,ICS,EPS,JK,G,H,S)
  ICO=0
  FP=PXMEW3(X)
PUNCH 200,ICO,FP,X
  J=2
  F=B*FP
17 FK=F
  1 X=X+A
      IF(N)3,2,3
  2 ICO=ICO+1
      F1=B*PXMEW3(X)
      GO TO 9
  3 IF(G-X)4,4,5
  4 IF(X-H)2,2,6
  5 X=G
      PUNCH 201
201 FORMAT(17HAT LOWER BOUNDARY)
      GO TO 7
  6 X=H
      PUNCH 202
202 FORMAT(17HAT UPPER BOUNDARY)
  7 IF(N)18,8,8
  8 N=-1
      GO TO 2
  9 IF(K)11,10,11
10 FP=B*F1
      PUNCH 200,ICO,FP,X
11 IF(N+1)12,20,12
12 F=(F1-F)14,13,13
13 F=F1
      A=S*A
      J=2
      GO TO 1
14 X=X-A
15 A=-S*A
      J=J-1
      IF(J)11,16,1
16 FP=R*F
      PUNCH 200,ICO,FP,X
      J=2
      GO TO 23
18 FP=PXMEW3(X)
      PUNCH 200,ICO,FP,X
      GO TO 21
23 IF(ABS(F)1-EPS)21,21,17
21 F=FP
      RETURN
200 FORMAT(15,2E20,8)
20 N=-2
      F=F1
      GO TO 15
END
APPENDIX 6.

Derivation of the charge transfer equation for a consecutive single-electron charge transfer reaction.

Consider two consecutive single-electron charge transfer reactions

\[ 0 + e = S \] \[ 1a \]
\[ S + e = R \] \[ 1b \]

Using equation \[1,2\], and including all the double layer effects in the apparent exchange currents \(i_{oa}\) and \(i_{ob}\) for steps \[1a\] and \[1b\] we have

\[
\frac{i}{2} = i_{oa} \left[ \exp(-\alpha_a) \frac{F \eta_D}{RT} - \frac{a_x}{a_x^e} \exp(1-\alpha_a) \frac{F \eta_D}{RT} \right] \quad \text{[2a]}
\]

\[
\frac{i}{2} = i_{ob} \left[ \frac{a_x}{a_x^e} \exp(-\alpha_b) \frac{F \eta_D}{RT} - \exp(1-\alpha_b) \frac{F \eta_D}{RT} \right] \quad \text{[2b]}
\]

where \(a_x\) is the activity of the intermediate \(S\) at the overpotential \(\eta_D\) and \(a_x^e\) is the activity of \(S\) at the equilibrium potential.

Eliminating \(a_x/a_x^e\) from equations \[2a\] and \[2b\] yields

\[
\frac{i}{2} = \frac{1}{2} \frac{\exp(-\alpha_a) \eta_D}{RT} \frac{F}{RT} - \frac{1}{2} \frac{\exp(1-\alpha_a) \eta_D}{RT} \frac{F}{RT}
\]

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

\[
\frac{i}{2} = \frac{1}{2} \frac{\exp(-\alpha_a) \eta_D}{RT} \frac{F}{RT} - \frac{1}{2} \frac{\exp(1-\alpha_a) \eta_D}{RT} \frac{F}{RT}
\]

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

\[
\frac{i}{2} = \frac{1}{2} \frac{\exp(-\alpha_a) \eta_D}{RT} \frac{F}{RT} - \frac{1}{2} \frac{\exp(1-\alpha_a) \eta_D}{RT} \frac{F}{RT}
\]

\[
\frac{i_{ob}}{2} \frac{\exp(-\alpha_b) \eta_D}{RT} + \frac{1}{2} \frac{i_{oa}}{2} \frac{\exp(-\alpha_b) \eta_D}{RT} \frac{F}{RT}
\]
APPENDIX 7.

Derivation of the equation for the determination of the rate determining step.


An overall electrode process

\[ 0 + Ze = R \] \[ 1 \]

may involve more than one step i.e.

\[ 0 + Z_1e = P \] \[ 2a \]
\[ P + Z_2e = Q \] \[ 2b \]
\[ Q + Z_3e = R \] \[ 2c \]

Assuming that one of the steps becomes rate determining when a net current flows, then the change in potential produces a change in the ratio of activities for every step which can be considered reversible.

If the activity of \( O \), \( a_0 \), is assumed constant, for cathodic polarization the activities of the ions preceding the rate determining step will change depending on the potential change \( \eta \).

\[ a_P' = a_P \exp(\eta \frac{ZF}{RT}) \] \[ 3 \]
\[ a_Q' = a_Q \exp(2 \eta \frac{ZF}{RT}) \] \[ 3a \]

(where \( a \) and \( a' \) are the activities before and after the potential change)
Hence the activity ratios corresponding to the change in potential

\[
\frac{a_0}{a_0'} = \frac{a_0}{a_p} \exp(-\eta ZF/RT) \quad \ldots \quad [4]
\]

and \[
\frac{a_p'}{a_Q} = \frac{a_p}{a_Q} \exp(-\eta ZF/RT) \quad \ldots \quad [4a]
\]

The change in activity ratio for each reversible step is \(
\exp(-\eta ZF/RT).
\)

Hence for a general case

\[
a_{nC}' = \exp(-\eta ZF/RT)^{nC-1} \cdot a_{nC} \quad \ldots \quad [5]
\]

\((n_C)\) is the number of the step in which the respective ion will be reduced

If the \(n_C\) step is the rate determining step then

\[
a_{nC}' = \exp(-\eta ZF/RT)^{nC-1} \cdot a_{nC} \quad \ldots \quad [6]
\]

Similarly the activity of any ion involved in reduction after the rate determining step can be calculated.

\[
a_{\tilde{n}C}' = \exp(-\eta ZF/RT)^{-\tilde{n}C-1} \cdot a_{\tilde{n}C} \quad \ldots \quad [7]
\]

\((\tilde{n})\) is the number of the step starting from \(R\)

For an ion produced in the rate determining step

\[
a_{\tilde{n}C}' = \exp(-\eta ZF/RT)^{-\tilde{n}C-1} \cdot a_{\tilde{n}C} \quad \ldots \quad [8]
\]

\((\tilde{n}_C)\) is the number of the rate determining step

(ii)
From equation \[5\]
\[
\log a_{nC}' = -(n_{C} - 1)ZF \eta /2.3 \text{ RT} + \log a_{nC} \quad \cdots \quad [9]
\]
and from equation \[7\]
\[
\log a_{nC}^{-} = (\bar{n}_{C} - 1)ZF \eta /2.3 \text{ RT} + \log a_{nC}^{-} \quad \cdots \quad [10]
\]
and for the ions involved in the slow step
\[
\log a_{nC}' = -(\bar{n}_{C} - 1)ZF \eta /2.3 \text{ RT} + \log a_{nC}' \quad \cdots \quad [11]
\]
and \( \log a_{nC}^{-} = (\bar{n}_{C}' - 1)ZF \eta /2.3 \text{ RT} + \log a_{nC}^{-} \quad \cdots \quad [11a]\)

Applying the general electrode kinetic equation for the cathodic rate determining step.
\[
i_{C} = k_{C} \cdot a_{nC}' \exp{\frac{-\alpha FZ}{RT}} \quad \cdots \quad [12]
\]
and, with \( Z = 1 \)
\[
\frac{\partial \log i_{C}}{\partial \eta} = \frac{\partial \log a_{nC}}{\partial \eta} - \frac{\alpha F}{2.3RT} \quad \cdots \quad [13]
\]
From equation \[11\]
\[
\frac{\Delta \log a_{nC}'}{\Delta \eta} = \frac{-(n_{C} - 1)F}{2.3 \text{ RT}} \quad \cdots \quad [14]
\]
combining equations \[13\] and \[14\]
\[
\frac{\partial \log i_{C}}{\partial \eta} = \frac{-F(n_{C} - 1 + \alpha)}{2.3RT} \quad \cdots \quad [15]
\]
Similarly for the anodic reaction the following equation can be derived

(iii)
\[ \frac{d \log i_A}{d \eta} = \frac{F}{2.3RT} (n_A^* - Q) \]