Some aspects of the electrochemical behaviour of zinc

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SOME ASPECTS OF THE ELECTROCHEMICAL BEHAVIOUR
OF ZINC

by

Alan Marshall

Supervisor: Dr. N.A. Hampson

Submitted for the Degree of Doctor of Philosophy
of Loughborough University of Technology.

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The work described in this thesis has not been submitted, in full or in part, to this or any other institution for a higher award.
SUMMARY

The active region of the dissolution of zinc in flowing electrolyte has been examined. In certain circumstances the active dissolution is extended indefinitely when silicate ion is present.

Double layer capacitance measurements have been made and the results confirm earlier observations that it is possible to study the electrode/electrolyte solution interphase free from the intrusion of adsorbed anions. It is also shown that the silicate ion is adsorbed at the electrode at potentials close to the dissolution potential.

The exchange reaction has been studied and improvements made to earlier reported data. A proposed mechanism consistent with the new kinetic data appears to be satisfactory.

From Faradaic impedance, linear sweep potential and R.D.E. measurements it appears that the adsorption of silicate at the electrode/electrolyte interphase retards the charge transfer reaction and hinders the dissolution.

The constitution of alkaline solutions of high Zn(II) concentration have been studied using laser Raman, n.m.r. and infra red spectroscopy and potentiometry. Solutions are relatively complex, the complexity depending upon the age. It is concluded that the initial product consists of quasi-colloidal particles (micelles), based on Zn(OH)$_2$ and molecules of hydration. The micelles do not appear to be electro-active for the Zn(II)/Zn exchange. A first order decay yielding ultimately the solution species (Zn(OH)$_2$.2H$_2$O), Zn(OH)$_3$.H$_2$O$^-$ and Zn(OH)$_4$$^2$$^-$ is postulated.
Possible industrial applications of the above work have been explored and a number of tests with commercial zinc/air primary devices made. Although the initial results are promising it is clear that before full commercial exploitation can be made some adjustment to the thermo-dynamic properties of the electrolyte are required. Means of achieving this are discussed and some possibilities are explored.
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### APPENDIX 1

- ANALYSES OF ELECTROLYTES,
- PREPARATION OF CHARCOAL
CHAPTER 1
INTRODUCTION

In recent years particular attention has been focussed on electrochemical energy devices as a replacement for the diminishing fossil fuels. The Shell Research Group have been actively involved in the development of new electrochemical energy devices for possible uses in both private and commercial transport. Their investigations of the zinc/air cell and the zinc slurry/air cell (mechanically rechargeable devices) indicated that their capabilities were promising and warranted further research.

Preliminary optimisation studies had indicated that the silicate ion and the lithium ion behaved as capacity extenders and had profound effects on the discharge characteristics of the above devices. It appeared, therefore, that the use of these extenders was the next logical step in the development of high capacity zinc/air cells. It was realised that the investigation would have to be linked not only with a study of the mode of action of capacity extenders, but is was also desirable to re-examine some aspects of the electrochemistry of zinc in alkaline solution. These areas of zinc behaviour appeared to be not fully settled although a large number of very detailed examinations had outlined the general features of this complicated reaction. This thesis describes work undertaken to achieve these goals.

THE PRESENT STUDY

For the study of the zinc/air cells and behaviour optimisation of extenders a galvanostatic polarisation technique was selected, not only because of success obtained at Shell but also in view of the type of
performance expected from a successful electrochemical energy device. The mechanism and kinetics of the dissolution reaction were investigated using a rotating disc technique since the results are easily abstracted and minimal instrumentation problems are encountered. Considerable experience in the use of the a.c. impedance technique has been accumulated in this laboratory and, therefore, this method of study was also chosen to provide complimentary information. Studies of solid metal systems are complicated by the difficulties of reproducing clean electrode surfaces and the marked effect of trace impurities in solution\(^1\). Frumkin\(^2-4\) has discussed the importance of the studies of the double layer capacitance and the significance of the potential of the zero charge. Consequently the studies of the exchange reactions in this work were preceded by an investigation of the electrode/electrolyte interphase. The technique of potentiometry has been used previously to elucidate the constitution of potassium zincate solutions. In the present study concentrated potassium zincate solutions were examined using the techniques of laser Raman, nuclear magnetic resonance and infra-red spectroscopy in order to provide additional methods for determining the constitution.
2.1 The Electrode/Electrolyte Interphase

The local concentration of reacting species at the charged interphase is an important factor in the rates of electrochemical reactions. Therefore, it is essential that a description of the structure of the electrode/electrolyte interphase accompanies any discussion of electrode processes.

The simplest model of the distribution of charged species at the interphase was proposed by Helmholtz\(^5\) who regarded the interphase as a 'double layer' of charge; there being a layer of charge at the electrode that was equal in magnitude, but opposite in sign to a charged layer in the electrolyte. The two thin layers of charge were parallel and the system approximated to that of a parallel plate condenser having an electrical capacity \(C_{dl}\). This implies that the electrical behaviour of this double layer is purely capacitive and that there is no ohmic leakage resistance in parallel, corresponding to ion discharge. This is an idealised requirement since in practical situations the electrode/electrolyte interphase will have a small current passing corresponding to the occurrence of some net electrode reaction. A mercury electrode between the reversible hydrogen potential and 0.9V (n.h.e.) is the only practical system which approaches idealised conditions. This type of electrode system is termed "ideally polarisable".

Gouy\(^6\) and Chapman\(^7\) modified the theory of Helmholtz\(^5\) and developed the concept of a diffuse layer rather than a compact layer of ions in the electrolyte. This was necessary since the Helmholtz model neglected the thermal distribution of ions occurring at finite temperatures.
Comparisons of experimental results with values calculated from the Gouy-Chapman theory reveals discrepancies because they had considered ions as point charges which could approach to within infinitely small distances of the electrode surface.

By considering the finite size of the ions, Stern\textsuperscript{8} showed that the diffuse part of the double layer extended from the bulk of the solution up to within a finite distance of the electrode surface. The overall picture of the double layer was now of a diffuse layer and a compact layer close to the electrode surface. The compact layer was subdivided by Grahame\textsuperscript{9} into an inner and outer compact plane. The inner Helmholtz plane is governed by the plane of closest approach of solvent dipoles and specifically adsorbed ions. The outer Helmholtz plane is determined by the plane of closest approach of solvated cations.

Figure 2-1 shows a generally accepted model of the electrical double layer. Using this model of the double layer Grahame has shown that the double layer capacitance is given by:

\[
\frac{1}{C_{\text{d1}}} = \frac{1}{C_{\text{diff}}} + \frac{1}{C_{\text{comp}}}. \tag{2.1}
\]

where

- $C_{\text{d1}}$ = total double layer capacitance
- $C_{\text{diff}}$ = capacitance of the diffuse layer
- $C_{\text{comp}}$ = capacitance of the compact layer

The diffuse layer component becomes significantly larger than the capacitance associated with the compact layer as the electrolyte becomes more dilute, and $C_{\text{d1}}$ becomes virtually independent of $C_{\text{comp}}$. At very low concentrations a sharp minimum is obtained on a $C_{\text{d1}}$ versus electrode potential plot. This minimum is associated with the point of zero
FIG. 2-1  Model of the electrical double layer.

COMPACT LAYER

Solvent Molecules

DIFFUSE LAYER

Solvated Cations

Specifically Adsorbed Anions

Inner Helmholtz Plane

Outer Helmholtz Plane
charge (p.z.c.) on the electrode. Frumkin $^2,^3$ discussed the importance of the p.z.c. and indicated that it is not affected by the introduction of potential determining ions. The p.z.c. can, therefore, be used in the discussion of charge adsorption at a polarisable electrode in the presence of potential determining ions. The electrode potential, with respect to the p.z.c. is termed the "rational potential", $E_{\text{rat}}$. At positive $E_{\text{rat}}$ values adsorption of negative ions is favoured while at negative $E_{\text{rat}}$ values positive ions are attracted to the interphase. When there is little or no charge on the electrode the magnitude of $E_{\text{rat}}$ is small and the adsorption of neutral molecules compete favourably with ionic adsorption.

The adsorption of neutral molecules has a pronounced effect on the values of the double layer capacitance. Two sharp capacitance maxima occur at either side of the p.z.c. and there is a substantial decrease of capacitance in the potential region close to the p.z.c. The decrease in the values of the capacitance between the two maxima is connected with the lower polarisability of the organic molecules compared to the solvent. The capacitance maxima at potentials on either side of the p.z.c. result from the desorption of the organic molecules.

A study of the differential capacitance and a knowledge of the p.z.c. is an important preliminary to the study of reactions at an electrode/electrolyte interphase.
2.2 Mass Transport

Mass transport of reactants to and products away from the electrode occurs by three main processes: migration, diffusion and convection.

2.2.(i) Migration

Mass transport by migration is the result of the force exerted on charged particles by an electric field. However, in the presence of a large excess of background or supporting electrolyte, migration of electroactive material is minimised to an extent where it can be neglected.

2.2.(ii) Diffusion

Diffusion is perhaps the most widely studied means of mass transport and exists whenever concentrations differences are established. The extent of diffusion is measured by the diffusion co-efficient which is dependent on the dimensions of the diffusing species and the viscosity of the solvent.

Consider the linear diffusion of reacting species to a plane electrode in a static solution (no migration or convection) with respect to the reaction.

\[ O + ne^- \xrightarrow{} R \]  (2.2)

For electrolysis experiments carried out at constant potential three experimental facts are noticeable; namely that the current is proportional to \( C_o^b \) and to the electrode area, and that the current decreases with the time of electrolysis. These facts must be accounted for in any derived time/current relationship. Concentrations are denoted by \( C_o \) and \( C_R \), with the superscripts "s" and "b" to signify concentrations at the electrode surface and in the bulk of solution.
The number of moles of a substance diffusing across a given cross-sectional area ($Acm^2$) in a time $dt$ is proportional to the concentration gradient of the diffusing species

$$\frac{dN}{dt} = KA \frac{\partial C_0}{\partial x}$$

(2.3)

The proportionality constant $K$ is defined as the diffusion coefficient $D_o$ hence:

$$\frac{dN}{dt} = D_o A \frac{\partial C_0}{\partial x}$$

(2.4)

This equation relates the diffusion rates to concentration and is known as Fick's first law. A useful modification is obtained if the number of moles diffusing through unit area in unit time - the flux of material is considered. The flux is usually defined as, $q$, and is given by:

$$q = \frac{dN}{Adt} = D_o A \frac{\partial C_0}{\partial x}$$

(2.5)

If the electrolysis is considered over a period of time then $C_o$, and hence $\frac{\partial C_0}{\partial x}$ must vary and in fact $C_o$ will decrease since $O$ is being consumed at the electrode. It is, therefore, necessary to know $C_o$ both as a function of distance from the electrode and time. The change in $C_o$ with time between two planes at a distance $x$ and $x + dx$ from the electrode surface ($x = 0$) will be the difference between the number of moles of $O$ entering the plane at $x + dx$ and the number leaving at the plane $x$, thus

$$\frac{\partial C_o}{\partial t} = q(x + dx) - q(x)$$

(2.6)

$$\frac{\partial C_o}{\partial t} = \frac{\partial q}{\partial x} \text{ as } dx \rightarrow 0$$
therefore,
\[
\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2}
\]  
(2.7)

This is Fick's second law and the fundamental equation for linear diffusion in solution. The instantaneous current associated with this process for a step in potential will be directly proportional to the flux at \(x = 0\):
\[
i_t = nF \rho(0, t) = (nFAD_o \frac{\partial C_o}{\partial x})_0, t
\]  
(2.8)

The value of the concentration gradient at the electrode surface, \((\frac{\partial C_o}{\partial x})_0, t\), can be obtained from (2.7) by applying the appropriate conditions. This gives
\[
\frac{\partial C_o}{\partial x} = \frac{C_o^b}{\pi^{\frac{1}{2}} D_o^{\frac{1}{2}} t^{\frac{3}{2}}}
\]  
(2.9)

which, when substituted in (2.8) gives the expression for the instantaneous current at a plane electrode under semi-infinite linear diffusion control
\[
i_t = \frac{nFAD_o^{\frac{1}{2}} C_o^b}{\pi^{\frac{1}{2}} t^{\frac{3}{2}}}
\]  
(2.10)

This equation (2.10) satisfies all the experimental requirements; the current is proportional to the bulk concentration and the area of the electrode and that it decreases inversely with \(t^{\frac{3}{2}}\).

2.2.(iii) Convection

There are two types of convection, forced and natural. Forced convection is produced by agitating the molecules of the solution using paddles, rotating electrodes, flowing electrolytes or ultrasonic
vibration. Natural convection occurs when electrolysis takes place at an electrode because of density changes in the vicinity of the electrode. These density changes cause an influx of ions from the surrounding part of the solution towards the electrode, independently of that caused by diffusion.

2.3 Charge Transfer Process

The transference of charge across the double layer in a metal ion electrode reaction requires that the reacting ion passes through the electrode/electrolyte double layer and is discharged at the electrode.

Consider the redox reaction (2.2)

\[
0 + n e^- \xrightarrow{\frac{k_c}{k_a}} R
\]

At the equilibrium potential charge is simultaneously being donated and accepted by the electrode in a dynamic equilibrium. According to the generally accepted theory of Volmer and Erdey-Gruz\textsuperscript{10} both anodic and cathodic processes are controlled by the potential dependent activation energy barriers; this concept has been discussed elsewhere\textsuperscript{11}. The partial currents associated with these two processes are given by:

\[
i_c = nF k_c c_o^S
\]

\[
i_a = nF k_a c_R^S
\]

where \(c_o^S\) and \(c_R^S\) are the electrode surface concentrations of the oxidised and reduced species and \(k_c\) and \(k_a\) are the potential dependent rate constants. The net current flowing through the system is given by:

\[
i = i_c - i_a
\]

\[
i = nF (k_c c_o^S - k_a c_R^S)
\]
It was found that the variation of $k_c$ and $k_a$ with the electrode potential was exponential and the rate constants have the form:

$$k_c = k_c^0 \exp \left( -\frac{\alpha nFE}{RT} \right) \quad (2.14)$$

$$k_a = k_a^0 \exp \left( \frac{(1-\alpha)nFE}{RT} \right) \quad (2.15)$$

where $E$ is the potential of the electrode measured against any convenient reference electrode and $k_c^0$ and $k_a^0$ are the values of $k_c$ and $k_a$ at this reference potential. Therefore, we obtain:

$$i = nF \left( k_c^0 C_o^S \exp \left( -\frac{\alpha nFE}{RT} \right) - k_a^0 C_R^S \exp \left( \frac{(1-\alpha)nFE}{RT} \right) \right) \quad (2.16)$$

At the reversible potential $E_r$, $i = 0$ and hence:

$$i_c = i_a = i_o$$

$$i_o = nF k_c^0 C_o^S \exp \left( -\frac{\alpha nFE_r}{RT} \right)$$

$$i_o = nF k_a^0 C_R^S \exp \left( \frac{(1-\alpha)nFE_r}{RT} \right) \quad (2.17)$$

where $i_o$ is the exchange current and the overpotential, $\eta$, is defined as:

$$\eta = E - E_r \quad (2.18)$$

Introducing (2.17) and (2.18) into equation (2.16) gives:

$$i = i_o \left( \exp \left( -\frac{\alpha nF \eta}{RT} \right) - \exp \left( \frac{(1-\alpha)nF \eta}{RT} \right) \right) \quad (2.19)$$

This expression (2.19) has been verified using a quantum mechanical treatment by Horiuti and Polanyi$^{12}$. 
For low overpotentials \(|\eta| \ll \frac{RT}{F}\) the overpotential/current curve is linear and the proportionality between the overpotential and the current corresponds to an electrical resistance, the charge transfer resistance, \(R_D\):

\[
R_D = -\left(\frac{\partial \eta}{\partial i}\right)_{i \to 0} \quad (2.20)
\]

Differentiating (2.19) and putting \(n = 0\) the expression is:

\[
\left(\frac{\partial i}{\partial \eta}\right)_{\eta = 0} = -\frac{nF_i_0}{RT} \quad (2.21)
\]

Therefore

\[
R_D = \frac{RT}{nF} \times \frac{1}{i_0} \quad (2.22)
\]

Thus the exchange current density may be obtained from the charge transfer resistance at equilibrium \(\eta = 0\).

For high cathodic overpotentials the Erdey-Gruz and Volmer equation (2.19) gives the Tafel relationship:\(^{13}\)

\[
n = \frac{RT}{anF} \log i_0 - \frac{RT}{anF} \log i \quad (2.23)
\]

and for high anodic overpotential

\[
n = \frac{RT}{(1-a)nF} \log i_0 - \frac{RT}{(1-a)nF} \log i \quad (2.24)
\]

Hence the magnitude of the exchange current density may also be obtained from high overpotential measurements by extrapolation of the current/potential curves back to the equilibrium potential \(E_r\).

The dependence of the exchange current on the reactant concentration has also been established\(^{14}\) and for reaction (2.2) it can be shown that:
\[ i_0 = nFk^0 a_R^\alpha a_0^{1-\alpha} \quad (2.25) \]

\(a_R\) and \(a_0\) are usually replaced by the corresponding concentrations, since activities are usually unknown. \(k^0\) is the apparent standard rate constant.

2.4 The Rotating Disc Electrode

Consider the reaction

\[ 0 + ne^- \xrightarrow{k_c} R \]

\(k_a\)

The net current, \(i\), flowing through the system is given by

\[ i = nFA (k_a C_R^S - k_c C_O^S) \quad (2.26) \]

For convenience an anodic current is considered positive in this derivation\(^{15}\). Introduction of Fick's first law into (2.26) gives

\[ i = \frac{nFA \delta_R}{\delta_R} (C_R^b - C_R^s) = \frac{nFA \delta_O}{\delta_O} (C_O^S - C_O^b) \quad (2.27) \]

A limiting current occurs when \(C_R^S = 0\), thus

\[ i_{L,R} = \frac{nFA \delta_R}{\delta_R} C_R^b \quad (2.28) \]

Combination of (2.27) and (2.28) gives

\[ i = i_{L,R} - \frac{nFA \delta_R \delta^S_R}{\delta_R} = nFA \frac{\delta_R}{\delta_O} C_O^S - nFA \frac{\delta_R}{\delta_O} i_{L,0} \quad (2.29) \]

Solution of (2.29) for \(C_R^S\) and \(C_O^S\) gives

\[ C_R^S = (i_{L,R} - i) \frac{\delta_R}{nFAD_R} \quad (2.30) \]

\[ C_O^S = (i + i_{L,0}) \frac{\delta_O}{nFAD_O} \]
Substitution of this expression for \( C_R^C \) and \( C_O^C \) in equation (2.26) gives

\[
i = k_a \frac{\delta_R}{D_R} (i_{L,R} - i) - k_c \frac{\delta_o}{D_o} (i + i_{L,o}) \quad (2.31)
\]

which can be re-arranged to give

\[
i (1 + k_a \frac{\delta_R}{D_R} - k_c \frac{\delta_o}{D_o}) = k_a \frac{\delta_R}{D_R} i_{L,R} - k_c \frac{\delta_o}{D_o} i_{L,o} \quad (2.32)
\]

\[
= nFA \left( k_a c_R^b - k_c c_o^b \right) \quad (2.33)
\]

(obtained by substituting for \( i_{L,R} \) and \( i_{L,o} \) from (2.28))

\[
= i_\infty
\]

\( i_\infty \) is used since surface concentrations have been replaced by bulk concentrations.

From (2.32) and (2.33)

\[
i_\infty = i (1 + k_a \frac{\delta_R}{D_R} - k_c \frac{\delta_o}{D_o}) \quad (2.34)
\]

thus

\[
\frac{1}{i_\infty} + \frac{1}{i_\infty} (k_a \frac{\delta_R}{D_R} - k_c \frac{\delta_o}{D_o}) = \frac{1}{i} \quad (2.35)
\]

By use of the Levich\(^{16}\) equation which predicts the dependence of \( \delta \) on \( \omega \)

\[
\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (2.36)
\]

we obtain

\[
\frac{1}{i_\infty} + \frac{K}{\omega^{1/2}} = \frac{1}{i} \quad (2.37)
\]
Thus a plot of $i^{-1}$ versus $\omega^{-1/2}$ should be linear with an intercept of $i_\infty^{-1}$ and slope $K$.

$$\text{Slope } K = \frac{k_a (\delta_R/\omega^{-1/2})}{D_R} + \frac{k_c (\delta_o/\omega^{-1/2})}{D_o} \quad (2.38)$$

Substituting (2.33) into (2.38) and dividing through by $k_a$ we obtain

$$K = \frac{(\delta_R/\omega^{1/2})}{D_R} + \frac{k_c}{k_a} \frac{(\delta_o/\omega^{1/2})}{D_o} \quad (2.39)$$

by expressing $k_c/k_a$ in terms of $\frac{k_c}{k_a} \exp\frac{nFE}{RT}$ from equations (2.14) and (2.15) and putting $\frac{k_c}{k_a} = k'$ we obtain

$$K = \frac{(\delta_R/\omega^{1/2})}{D_R} + k' e^{\frac{nF}{RT}} \exp\frac{nFE}{RT} \frac{(\delta_o/\omega^{1/2})}{D_o} \quad (2.40)$$

when $R$ is a solid ($\delta_R/\omega^{1/2} = 0$, and if $C^b_R \gg k^e e^{\frac{nF}{RT}} C^b_o$, because $C^b_o$ is small, i.e. no $C^b_o$ in solution or in the Tafel region so that one side of the reaction can be neglected.

$$K = k^e e^{\frac{nF}{RT}} \exp\frac{nFE}{RT} \frac{(\delta_o/\omega^{1/2})}{D_o} \quad (2.41)$$

i.e. $\log K = \frac{nF}{RT} n$.
2.5 Impedance

For a reaction controlled only by charge transfer and diffusion in solution, Randles\textsuperscript{17} showed that the electrode system may be represented by the analogue shown in Figure (2-2a). Where $R_{\text{sol}}$ is the electrolyte ohmic resistance, $C_{\text{dl}}$ is the double layer capacitance which varies with the d.c. voltage in a manner depending on the concentration and nature of the electrolyte\textsuperscript{18}. $\theta$ is the charge transfer resistance and is related to the exchange current density by the expression

$$i_0 = \frac{1}{\theta} \cdot \frac{RT}{nF}$$ (2.41)

The Warburg impedance $W$ is the impedance to a.c. current due to the charged species diffusing to and from the electrode. Randles\textsuperscript{17} derived the following expressions for $\theta$ and $W$,

$$W = \sigma \omega^{-1/2} - j\sigma \omega^{-1/2}$$ (2.42)

and at $E_r$

$$\sigma = \frac{RT}{n^2F^2\gamma^2} \left( \frac{1}{C_o^{1/2}} + \frac{1}{C_R^{1/2}} \right)$$ (2.43)

The activation polarisation resistance, $\theta$, is related to the concentrations $C_o^b$ and $C_R^b$ and the reaction rate constant $k_{\text{sh}}$ by

$$\theta = \frac{RT}{n^2F^2k_{\text{sh}}} \frac{C_o^\alpha}{C_R^{1-\alpha}}$$ (2.44)

Various methods were proposed for the determination of $\theta$ and $\sigma$ from impedance measurements. Vector methods were used by Randles\textsuperscript{17} and Delahay\textsuperscript{19}. Gerischer\textsuperscript{20} determined $\theta$ and $\sigma$ but neglected the imaginary part of the Warburg impedance. The cell impedance was corrected for the double layer capacitance and ohmic resistance by Vetter\textsuperscript{21}. 
**FIG. 2-2a** Electrical analogue of the electrode interphase

\[ R_d + C_d = W \]

**FIG. 2-2b** Complex plane display - diffusion control
Sluyters \(^{22}\) interpreted the total impedance of the cell in terms of \(R_{\text{sol}}, C_{\text{dl}}, \theta\) and \(\sigma\). It was shown that these quantities could be obtained directly from cell impedance measurements when treated as a vector in the complex plane. From Figure (2-2a) it follows that the cell impedance is:

\[
Z + R_{\text{sol}} + \frac{1}{j\omega C_{\text{dl}}} + \frac{1}{\theta + \sigma \omega^{-1/2} - j\sigma \omega^{-1/2}} \tag{2.45}
\]

Sluyters \(^{22}\) expanded equation (2.45) and separated the real and imaginary parts of \(Z\). The relationship obtained had two interesting limiting cases:

(i) At low frequencies the impedance reduced to

\[
Z = R_{\text{sol}} + \theta + \sigma \omega^{-1/2} - j(\sigma \omega^{-1/2} + 2\sigma^2 C_{\text{dl}}) \tag{2.46}
\]

When \(Z''\) (the imaginary part of \(Z\)) was plotted against \(Z'\) (the real part of \(Z\)) a straight line of unity slope was obtained (Figure 2-2b).

(ii) If concentration polarisation can be neglected (i.e. at high frequencies and an irreversible electrode reaction) the impedance can be represented by

\[
Z = R_{\text{sol}} + \frac{\theta}{1 + \omega^2 C_{\text{dl}}^2 \theta^2} - j \frac{\omega C_{\text{dl}} \theta^2}{1 + \omega^2 C_{\text{dl}}^2 \theta^2} \tag{2.47}
\]

When the imaginary and real parts \((Z''\) and \(Z'\)) were plotted against each other a semi-circle was obtained (Figure 2-3a).

The charge transfer resistance \(\theta\) was obtained directly from the radius of the semi-circle (Figure 2-3a). From the top of the semi-circle \(\omega = \frac{1}{\theta C_{\text{dl}}}\), the value of the double layer capacitance in the presence of the redox-system was computed.
FIG. 2-3a Complex plane display - charge transfer control

\[ \omega = \frac{1}{\theta C_{dl}} \]

\[ \omega = \infty \]

\[ \omega = 0 \]

FIG. 2-3b Complex plane display - mixed control
For a reaction with a degree of reversibility, the diffusion polarisation gives rise to a distortion of the semi-circle at low frequencies, (i.e. at the right hand side of the semi-circle) as shown by Figure 2-3b. At lower frequencies a line of 45° slope is obtained.

At potentials different from \( E_r \)

\[
Z = R_{\text{sol}} + \frac{1}{j\omega C_{dl} + \frac{1}{\theta' + \sigma'_0 \omega^{-1/2} - j\sigma'_0 \omega^{-1/2}}}\]  

where

\[
\theta' = \frac{RT}{nF} \cdot \frac{1}{i_0'} \]  

and

\[
\sigma' = \frac{RT}{nF \sqrt{v_2}} \left( \frac{1}{C_0^s D_0^{1/2}} + \frac{1}{C_R^s D_R^{1/2}} \right) \]  

\( i_0' \) is the interfacial current alone. At each potential \( i_0' \) can be determined from the radius of the semi-circle and a plot of \( \log i_0' \) against \( E \) gives a Tafel slope. The concentration dependence and the value of the Tafel slope give information about the kinetics of the interfacial reactions.

A discussion of the transformation of the measured series resistance and capacitance to the parallel components is given in a later chapter.

2.6 Some Aspects of Spectroscopy

2.6 (i) Infra-Red

Infra-red radiation promotes transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy states.
In a simple diatomic molecule A-B the only vibration which can occur is a periodic stretching along the A-B bond. Stretching vibrations resemble the oscillations of two bodies connected by a spring and the same mathematical treatment, namely Hooke's law, is applicable to a first approximation. For stretching of the A-B bond the vibrational frequency \( v(\text{cm}^{-1}) \) is given by

\[
v = \frac{1}{2\pi c} \left( \frac{f}{\mu} \right)^{-1/2}
\]

(2.51)

where \( c \) is the velocity of light, \( f \) the force constant of the bond, and \( \mu \) the reduced mass of the system as defined by

\[
\mu = \frac{m_A \cdot m_B}{m_A + m_B}
\]

(2.52)

Stretching vibrations of individual bonds within more complex molecules may be considered similarly, though other vibrations become possible and absorption band frequencies are influenced by steric effects, nature, size and electronegativity of neighbouring atoms, phase changes and hydrogen bonding.

An infra-red spectrometer operates according to simple principles and the mechanical and electrical complexities involved are technical devices to transform minute energy absorption variations into an accurate spectrum recording.

2.6 (ii) Raman Spectra

The Raman effect is a phenomenon which bears some relation to fluorescence, whereby radiation is emitted from the sample with a change in wavelength from the exciting incident radiation. However, the incident radiation in order to produce the Raman effect must not be
appreciably absorbed. The shift in wavelength in the Raman effect is caused by the extraction of energy from the quanta of incident radiation to raise molecules to higher vibrational states. Since the vibrational levels are subject to quantum rules, the energy change in the Raman effect is also quantized, and discrete wavelength shifts are observed.

Vibrational transitions can be observed both in infra-red absorption and in the Raman effect but not all possible transitions are observable in both. Infra-red absorption results from vibrations which are accompanied by a change in the dipole moment of the molecule. However, only vibrational modes which result in a change in polarizability will be visible in Raman spectroscopy. Polarizability may be defined as the ability of a molecule to be deformed by an electric field, separating temporarily the centres of positive and negative charge.

The information required of a Raman spectrometer is the shift in frequency (or wave number) between the primary and scattered radiation. The Raman shifts are associated with specific bond types, just as are infra-red absorptions. The spectra are generally simpler, as fewer combinations of frequencies and overtones appear. Correlation tables and charts are available covering the range from zero to about 4000cm⁻¹. Atlases of Raman spectra have also been compiled.

The samples are usually liquids, either pure or as solutions. Water is often an appropriate solvent, as its interference bands in the infra-red are inactive in the Raman mode.

2.6 (iii) **Nuclear Magnetic Resonance**

A radically different type of interaction between matter and electromagnetic forces can be observed by subjecting a sample
simultaneously to two magnetic fields, one stationary \( H \), and the other varying at some radio frequency \( f \), 5MHz or higher. At particular combinations of \( H \) and \( f \), energy is absorbed by the sample, and the absorption can be observed as a change in the signal developed by a radio-frequency detector and amplifier.

This energy absorption can be related to the magnetic dipolar nature of spinning nuclei. Quantum theory indicates that nuclei are characterized by a spin quantum number \( I \) which can have positive values of \( n/2 \) (in units of \( \hbar/2\pi \); \( \hbar \) is Planck's constant), where \( n \) can be 0, 1, 2, 3, ... If \( I = 0 \), the nucleus does not spin, and cannot be observed by this method. Maximum sharpness of absorption peaks occurs with nuclei for which \( I = \frac{1}{2} \), including amongst others \( ^1H \).

The spinning nuclei simulate tiny magnets, and so interact with the externally impressed field \( H \). It might be supposed that they would all line up with the field like so many compass needles but instead their rotary motion causes them to precess like a gyroscope in a gravitational field. According to quantum mechanics, there are \( 2I + 1 \) possible orientations, and hence energy levels, which means that the proton has two such levels. The difference between them is given by

\[
\delta \text{Energy} = hf = \frac{\mu H}{I} \tag{2.53}
\]

where \( \mu \) is the magnetic moment of the spinning nucleus. The characteristic frequency \( f \) is called the Larmor frequency. If an alternating flux is applied at right angles to the field, at frequency \( f \), the nuclei in the lower energy state will absorb the resonant energy, and the absorption can be noted at the detector. Another effect of the imposed alternating field at the Larmor frequency is to cause all the spinning nuclei to precess in phase. Thus there are a multitude of
nuclea~oscillators which according to electromagnetic theory must radiate energy; since they are in phase with each other, they will act as a coherent source. Their radiation can be picked up by another coil in the neighbourhood of the sample, positioned with its axis mutually perpendicular to those of the oscillator coil and the fixed field. Hence two types of n.m.r. spectrometer are possible, the single-coil instrument, in which absorption is measured, and the two coil variety, which measures resonant radiation. In these experiments a single coil instrument was used.

Every nucleus is surrounded by a cloud of electrons in constant motion. Under the influence of the magnetic field these electrons are caused to circulate in such a sense as to oppose the applied field. This has the effect of partially shielding the nucleus from the external field. It follows that either the frequency or the field will have to be changed slightly to bring the shielded nuclei into resonance. The value of the shift depends on the chemical environment of the proton, since this is the source of variations in shielding by electrons; it is thus called the chemical shift. Although the chemical shift is measured as a field or frequency, it is in reality a ratio of the necessary change in field to the applied field, or of the necessary change in frequency to the standard frequency, and hence it is a dimensionless constant designated by \( \delta \) and specified in parts per million.

There is no absolute standard with which to compare shifts, therefore, an arbitrary comparison standard was adopted. Tetramethylsilane (TMS), \((\text{CH}_3)_4\text{Si}\), was the internal standard chosen because not only are all its hydrogen atoms in an identical environment, they are more strongly shielded than the protons in any purely organic compound. The position of (TMS) on the chemical shift scale is arbitrarily assigned the value \( \delta = 0 \).
3.1 Electrolytic Systems

3.1.(i) Electrolytes

Electrolyte solutions were prepared from AnalAr grade chemicals using water bidistilled from deionised stock. Potassium silicate (Fisons S.G.1.33) was the extender material generally used. (Analyses of electrolyte are described in APPENDIX 1.)

Electrolytes were purified by constant pumping over specially prepared activated charcoal. Nitrogen, de-oxygenated by passing over copper at 400°C and pre-humidified, was used to circulate electrolytes in the cells. (The preparation of the charcoal is described in APPENDIX 1.) In general about two weeks electrolyte circulation was necessary to achieve a satisfactory level of cleanliness.

3.1.(ii) Electrolytic Cells

Various designs of glass and Perspex cells have been used in this study and they are shown in Figures 3-1 to 3-4. The cells and all the other glassware used were cleaned by steeping in a 50/50 mixture of concentrated nitric and sulphuric acids for a minimum period of 48h. The acid was removed by numerous washings with de-ionised water, after which they were allowed to stand for 24h in bi-distilled water, and finally washed with bi-distilled water.

3.1.(iii) Electrodes

Polycrystalline micro-test electrodes were prepared from metal wire of 99.999% purity supplied by Koch Light Laboratories, Ltd. The wires were soldered to contact wires and inserted into glass tubes. The wires were then sealed into the glass tubes by encapsulating the
FIG. 3-1  Differential capacitance cell

N₂ lift pump

H₂O trap

charcoal
FIG. 3-2a Rotating disc electrode cell

FIG. 3-2b H-type cell
**FIG. 3-3b THE SLURRY CELL**

- Slurry
- Anode mesh
- Air cathode
- Cathode current collector

**FIG. 3-3a THE PLATE CELL**

- Cathode current collector
- Air manifold
- KOH outlet
- KOH inlet
- Zinc anode
- Air cathode
FIG. 3-4a Linear potential sweep cell

FIG. 3-4b Impedance cell
wire and glass tube in polythene. The reacting area was exposed by cutting the polythene at right angles to the long axis (Figure 3-5a). This type of test electrode was used for all the analytical experiments except those involving a rotating disc electrode.

The rotating disc electrode was of the type used by Blurton and Riddiford\textsuperscript{24}, where the zinc was embedded in Teflon rod (1.25 cm diameter) which had been drilled and tapered to give a tight push fit (Figure 3-5b). The electrical contact between the rotating disc electrode and the external circuit was made by means of a mercury pool.

The counter electrode used for all analytical experiments was a large area platinum gauze except for impedance measurements when the platinum gauze was concentric with the working electrode.

A wick type saturated calomel (Pye Cat. No. 11161) was used in the differential capacitance studies. In all the other analytical techniques a wick type Hg/HgO was used as the reference electrode.

In the zinc/air cell the working electrode was a plane zinc sheet (99.95%) and the superficial area of the electrode in contact with the solution was 50cm\textsuperscript{2}. In the zinc/air slurry cell the anode was a silver-plated expanded nickel sheet (250 holes cm\textsuperscript{-2} and 0.02 cm thick, supplied by Expanded Metals, Ltd.).

In both types of zinc/air cell the cathode was an air electrode, constructed from a microporous hydrophobic, polyvinyl chloride sheet (Porvic) with a pore size of 1-10 microns. One side of the sheet was electroplated with silver and then sprayed with a mixture of palladium and carbon. The silver layer was used to conduct the current from the air cathode to a current collector which consists of a rhodium-plated silver sheet in contact with the silver of the air cathode. In operation
FIG. 3-5a Test electrode construction

FIG. 3-5b Rotating test electrode

- CONTACT WIRE
- GLASS WALLED TUBE
- POLYTHENE SHEATH
- ZINC

- STEEL SHAFT
- BRASS COLLAR
- TEFLOM SHEATH
- CONTACT SPRING
- ZINC
the air electrode was fed with compressed air at a pressure of 2 lb.in.\(^{-2}\) (13.8 kN \(\text{m}^{-2}\)) and a rate of 0.8 m \(\text{s}^{-1}\).

3.2 Anodic Behaviour in Flowing Systems

3.2.(i) General Apparatus

A schematic diagram of the experimental system is shown in Figure 3-6. The cell, Figure 3-3a, is constructed of Perspex and contains an electrode compartment (dimensions, 0.5 x 5 x 10 cm) which contained a nylon mesh separator. The electrolyte solution was circulated by a vibrational pump (Cole Parmer Technical Equipment). The solution was pumped upwards in the cell to ensure even flow and to eliminate trapped air pockets, and returned to a reservoir which was purged with N\(_2\) to eliminate CO\(_2\). The flow rate was adjusted with a Variac and monitored by a MeTeRate flowmeter tube. A volume of 0.10 dm\(^3\) of electrolyte was used in these experiments.

The apparatus for the zinc/air slurry cell (Figure 3-3b) was very similar, but provisions were made for the addition of Zn powder (AnalaR, B.D.H.) to the reservoir and the electrolyte solution was circulated by a centrifugal pump (Charles Austen Pumps, Ltd., Model C25).

3.2.(ii) Electrical Circuit

The electrical circuit for these experiments was as shown in Figure 3-6. The load system consisted of a conventional lead/acid battery (6V) connected through an ammeter (Cambridge Instruments Unipivot) and a variable resistance. The potential across the cell was measured using a digital voltmeter (Advance D.P.M. 300 series) and recorded on a chart recorder (Leeds Northrup Speedomax H). Passivation (transition) times were measured with a stop clock.
FIG. 3-6 Flowing system circuit

- Oxygen free nitrogen
- KOH
- D.V.M.
- Recorder
- Load system
- Zinc-air cell
- Pump
- Rotameter
- Compressed air
- To atmos.
3.3. **Double Layer and Faradaic Impedance**

3.3.(i) **Electrical Circuit**

A Schering\(^{25}\) bridge (Figure 3-7) was used to match the interphase as a series combination of resistance and capacitance\(^{26}\).

A wave analyser (Hewlett Packard, Type 302A) was used as an a.c. generator and tuned voltmeter for null detection (B.F.O. mode). The generator had a frequency range of 10Hz - 50kHz in divisions of 10Hz. A single control tuned both the oscillator and the voltmeter. The voltmeter had a narrow pass band with meter ranges from 30 μV - 300V F.S.D. The output from the generator was applied to the bridge through an isolated 65:1 step down transformer. The amplitude of the perturbing a.c. was adjusted to 6.5mV peak to peak. The bridge components used were all Muirhead 0.1% grade. The bridge was polarised symmetrically and during all the experiments the test electrode was connected to earth in order to avoid screening difficulties. The a.c. and d.c. circuits were separated by a 40H choke. The potential was measured using either an electrometer (E.I.L. Vibron, Type 33B) or a digital multimeter (Hewlett Packard, Type 3490A). Both instruments had high input impedance (greater than 10\(^{10}\) Ω) and consequently potentials could be constantly monitored. The impedance of a cell analogue (high stability resistance and standard capacitance in series) was measured over a range of frequencies and it was found that the bridge could be satisfactorily operated in the frequency range 100Hz - 10kHz.

3.4 **Potentiostatically Controlled Studies**

3.4.(i) **Linear Sweep Voltammetry (L.S.V.)**

Current-bias potential curves were obtained using a scanning potentiostat (Kemitron 0.5A, built and designed by J.S. Drury) and recorded on an X-Y recorder (Bryans 26000A4). Potentials were measured accurately using a digital multimeter (Hewlett Packard, Type 3490A).
FIG. 3-7  Schering bridge circuit
A block diagram of the overall circuit is shown in Figure 3-8a.

3.4(ii) Rotating Disc Electrode Studies

The currents were measured at fixed potentials as a function of rotation speed with a galvanometer (Pye, Cat.No. 7892/s). The potential was controlled using a potentiostat (Chemical Electronics, Type I.C. 20-0.5A) and measured on a digital multimeter (Hewlett Packard, Type 3490A). The rotation speed was controlled (60-3400 r.p.m.) by a control unit (designed by O.R. Brown, Newcastle-upon-Tyne) and calibrated using a stroboscope (Dawe, Type 1200E). Figure 3-8b. show a block diagram of the circuit.

3.5 Galvanostatic Single Impulse Studies

The circuit diagram is shown in Figure 3-9. A square current pulse was obtained from a pulse generator (Solartron, Type G01377 or Hewlett Packard, Type 214A). The current amplitude was established by measuring the potential developed across a standard resistance. Measurements of the potential of the test electrode were made against an unpolarised reference electrode (99.999% pure Zn identical to the working electrode) using a storage oscilloscope (Advance OS2200). The oscilloscope was triggered by a pre-pulse obtained from the pulse generator.

3.6 Concentrated Potassium Zincate Studies

3.6(i) Potentiometric Measurements

These measurements were made in H-type cells (Figure 3-2b) of the type

Zn(Hg) | Zincate Solution | Liquid Junction | Reference \textsuperscript{(3.1)}

The reference was either a wick type calomel or Hg/HgO electrode. Potentials were measured with a digital multimeter (Hewlett Packard, Type 3490A) having an input impedance greater than $10^{10}$ \( \Omega \) and the
FIG. 3-8a Linear potential sweep circuit

SCANNING POTENTIOSTAT

X-Y RECORDER

MULTIMETER

FIG. 3-8b Rotating disc electrode circuit

AMMETER

POTENTIOSTAT

MULTIMETER

POTENTIOMETER
FIG. 3-9  Galvanostatic pulse circuit

PULSE GENERATOR

C.R.O.

STORAGE C.R.O.

R_{L}
temperature \((298^{\pm} 0.01K)\) was controlled using a large volume water bath with contact thermometer (Jackson Thermoregulator, Type T.D.) and relay.

3.6.(ii) **Viscosity Measurements**

These determinations were made using an Ostwald viscometer (Type BS188-1937, No. 0720) at a temperature of \(298^{\pm} 0.01K\).

3.6.(iii) **Analysis of Solutions**

Alkali solutions were prepared from solid KOH and standardised with sulphamic acid\(^{27}\). Additions of potassium silicate were made to the electrolyte solution when required; a 2% addition corresponding to a concentration of 0.15 mol dm\(^{-3}\) in the bulk solution. Solutions were analysed for zinc content using EDTA with eriochrome black in triethanolamine as indicator\(^{28}\) (For details of analysis methods see APPENDIX 1.)

3.6.(iv) **Determination of Infra-Red Spectra**

Spectra \((4000-250 \text{ cm}^{-1})\) were recorded on a Perkin Elmer spectrometer (Type 457). Solutions were sealed in polythene envelopes \((20 \times 20 \text{ mm})\) with all air expelled, the films being about 0.25 mm thick.

3.6.(v) **Determination of Nuclear Magnetic Resonance Spectra**

Spectra were recorded on a Perkin Elmer R32 90 MHz n.m.r. spectrometer. Samples were placed in a 5 mm i.d. precision n.m.r. tube (type 505 ES, Wilmad Glass Co., U.S.A.) and the reference in a precision coaxial tube 5 mm o.d. (Type 520-2, Wilmad Glass Co.). The reference was an aqueous solution of the sodium salt of 3-(Trimethylsilyl) propionic acid.

3.6.(vi) **Raman Spectra**

Samples were filtered (No. 4 sinter) and transferred to a 10 mm Spectrosil grade quartz cuvette. Spectra were obtained with a Cary 83 double mono-chromator laser Raman spectrometer, using an Ar\(^+\) laser
(488.0 nm) and d.c. detection. The laser beam was focused, and produced a power level at the sample of about 35 mW, measured on a silicon solar power meter (Cary). A neon lamp was used to calibrate the $\Delta \text{cm}^{-1}$ scale. Spectral bandwidths in the range $9 - 15 \text{ cm}^{-1}$ at 471 $\Delta \text{cm}^{-1}$ were used. Additional spectra were run by Varian Associates, using a Cary 82 triple mono-chromator instrument with 514.5 nm Ar$^+$ excitation, a s.b.w. of 5 cm$^{-1}$, a power of 500 mW and photon counting detection.

3.7 Vapour Pressure Studies

When determining the vapour pressure by the Ramsay and Young method$^{29}$ a constant pressure is maintained and the temperature at which the liquid boils under that pressure is measured. The apparatus (Figure 3-10) is similar to that described previously$^{30}$, but in the present case a manostat was used to control the pressure.
FIG. 3-10 Apparatus for determining vapour pressure

- Sample
- Thermometer
- To atmosphere
- Liquid trap
- Dewar flask
- Manostat
- Manometer
- To pump
CHAPTER 4

A REVIEW OF THE RELEVANT LITERATURE

Studies of reactions occurring at zinc electrodes in alkaline solution have been made by numerous workers. Much of this work has been reviewed by Bobker\(^31\) and Hampson\(^32\) and reference to these articles should be made for a complete review. The following briefly reviews the reported work of interest in connection with the present study.

4.1 Galvanostatic Polarisation

4.1(i) Stationary Electrodes

The electrode potential as a function of time at constant current density was investigated by Hampson and various co-workers\(^33\)-\(^39\) and by Eisenberg et al\(^40\) for various electrode orientations and conditions of electrolyte flow, concentration and temperature. It was shown\(^33\)-\(^40\) that zinc passivation occurs when the concentration of dissolution products at the surface reaches some critical value.

Attempts were made\(^41\) to rationalise the build-up of concentration at the electrode surface in terms of diffusion using the equation for semi-infinite linear diffusion under galvanostatic conditions developed by Sand\(^42\),

\[
i = nF \Delta C(4t_p \pi)^{1/2}
\]

where \(t_p\) is the time to passivation, \(\Delta C\) is the difference between the concentration at the electrode/electrolyte interphase and the bulk of the solution, and \(D\) is the diffusion co-efficient of the zincate ion: \(n\) and \(F\) have their usual meanings. This equation applies when all non-diffusional forms of mass transfer are eliminated from the electrolyte system. Assuming passivation occurs when the interfacial concentration of Zn (II) reaches a critical value \(C_c\) equation (4.1) can be written as
It follows from equation (4.2) that for a given values of $C$, KOH concentration and temperature the current is inversely proportional to $t_p^{1/2}$,

$$i = k t_p^{-1/2} + \text{const.}$$  \hspace{1cm} (4.3)

Experiments on zinc passivation\textsuperscript{33,35,40} in which non-diffusional mass transport processes were minimised by using a horizontal face up anode showed that the empirical relationship (4.3) applied. Hampson et al\textsuperscript{36} regarded the constant term as being a critical current density, $i_c$, below which passivation was not expected to occur. Thus a modified empirical relationship was derived\textsuperscript{36}

$$i - i_c = k t_p^{-1/2}$$  \hspace{1cm} (4.4)

A finite value for $i_c$ was observed because convection currents cannot be entirely eliminated. However, when ZnO-free KOH solutions were used\textsuperscript{33}, very low values of $i_c$ were recorded and the results approximated closely to those predicted theoretically.

According to Elder\textsuperscript{43} the parameter $k$ in equation (4.4) is not a constant. He found that $k$ went through a maximum value at a current density of 130 mA cm$^{-2}$ in 6.29 mol dm$^{-3}$ KOH solution saturated with ZnO. However, Dirkse et al\textsuperscript{37} disputed Elder's\textsuperscript{43} reasoning that activation processes modify the value of $k$.

4.1.(ii) Rotating Electrodes

Hydrodynamic difficulties associated with static electrodes were considerably simplified by Russian workers\textsuperscript{44} using rotating disc techniques. In agreement with other investigations\textsuperscript{34,45} mass transport in the electrolyte was shown to control the passivation process.
4.1.(iii) Flowing Electrolyte Systems

Brook and Hampson\textsuperscript{36} investigated the relationship between $i$ and $t_p$ at a vertically orientated zinc electrode in a flowing electrolyte. The data obtained were well represented by the relationship (4.4) for all electrolyte velocities and all zincate concentrations. The hydrodynamic implications of the results were qualitatively discussed and it is argued that because $t_p$ never exceeded 25s diffusion was the active mode of mass transport of Zn(II) species away from the electrode surface.

Farmer and Webb\textsuperscript{46} developed a mathematical model for the passivation process. This model involves the hydrodynamics of the electrolyte and zinc ion diffusion through a growing oxide film on the zinc surface. Using this model a function relating passivation time to linear electrolyte velocity was derived, and a plot of experimentally determined $t_p$ data versus electrolyte velocity fitted closely to the line corresponding to the theoretically derived function. Expressions were also derived\textsuperscript{46} relating temperature and current density to $t_p$.

4.2 Double-Layer Capacitance

Electrometric and impedance measurements\textsuperscript{47} at both single crystal (0001) plane and polycrystalline electrodes in a number of aqueous electrolytes showed that the zinc electrode was not ideally polarisable. The experimentally polarisable region being larger for the single crystal than for polycrystalline electrodes because the close packed (0001) plane is less effective for the h.e.r., visible hydrogen evolution occurring at less negative potentials from the polycrystalline surface.

Several workers have used the differential capacitance of zinc to detect the adsorption of ionic and neutral compound\textsuperscript{48-52}, others have investigated the potential of zero charge\textsuperscript{53-56}. The differential
capacitance of the zinc electrode is critically dependent on the solution pH\(^47\). Baugh and Lee\(^57\) have shown that the differential capacitance profile is effected by the specific adsorption of OH\(^-\) in solutions of NaCl\(_4\) and NH\(_4\)Cl\(_4\) (at neutral or near neutral pH) and obscures the true double layer over the ideally polarisable region. The suppression of OH\(^-\) was affected by lowering the pH\(^57\). This effect was also demonstrated by Hampson et al\(^58\) and by Batrakov and Sidnim\(^50\).

4.3 The Exchange Reaction

4.3.(i) The Zn(II)/Zn(Hg) Exchange Reaction

In alkaline solution the exchange reaction involves the formation of a complex. The overall reaction may be written conveniently as:

\[
\text{Zn(Hg)} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_2^2^- + 2e^- \quad (4.5)
\]

Studies of the effect of concentration of electro-active species on the exchange current\(^59\) indicated that the overall reaction occurred in two stages, involving charge transfer

\[
\text{Zn(Hg)} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)}_2^- + 2e^- \quad (4.6)
\]

followed by complex formation

\[
\text{Zn(OH)}_2^- + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} \quad (4.7)
\]

These findings were later confirmed by radiochemical techniques\(^60\) and the faradaic impedance method\(^61\).

4.3.(ii) The Zn(II)/Zn Exchange Reaction

Dirkse et al\(^62\) attempted to measure \(i_0\) for the zinc/alkaline system using Zn\(^65\) to monitor the reaction. The slow corrosion of zinc in strong alkaline solution inhibited the measurement of the exchange process so that no conclusive results were obtained.
Several investigations\textsuperscript{63-69} have been carried out using electrochemical techniques to determine \( i_0 \) for the zinc/alkaline system. The results of these investigations are presented in Table 4.1.

The electrochemical technique employed influenced the results, and the highest values of \( i_0 \) were determined using the galvanostatic double pulse technique\textsuperscript{63,67} with reaction times less than 10\( \mu \)s.

Electrode preparation prior to the electrochemical measurement had a considerable influence on the values of \( i_0 \) obtained. Bockris et al\textsuperscript{64} cathodically polarised zinc electrodes for several minutes in dilute KOH solution before measurements were made, whilst Hampson and co-workers\textsuperscript{63,65-69} allowed the electrode to equilibrate in the test solution.

Experiments carried out by Bockris et al\textsuperscript{64}, in 0.1 - 3.0 mol dm\(^{-3}\) KOH solutions, showed \( i_0 \) to be virtually independent of pH. A linear regression analysis of Zn(II) concentration versus log \( i_0 \) data resulted in a slope of 0.67. Hampson et al\textsuperscript{66-69} carried out measurements in KOH solutions ranging from 0.1 - 13.8 mol dm\(^{-3}\) and found that \( i_0 \) varied with KOH concentration reaching a maximum value at concentrations of 7-8 mol dm\(^{-3}\) KOH solution. The \( i_0 \) value was found\textsuperscript{63,65-69} to be independent of zincate concentration. Dirkse and Hampson\textsuperscript{69} followed up work on the influence of KOH using mixtures of KOH with KF, and NaOH with NaF and found the hydroxyl ion concentration to be controlling the process, not the total ionic strength.

A reaction sequence was developed\textsuperscript{69} for the zinc dissolution process in which water was regarded as a reactant:
<table>
<thead>
<tr>
<th>Reference number</th>
<th>Method used and reaction time</th>
<th>$OH^-$ conc. range mol dm$^{-3}$</th>
<th>Potential range mV</th>
<th>Anodic exchange current density mA cm$^{-2}$</th>
<th>Cathodic exchange current density mA cm$^{-2}$</th>
<th>Influence of Zn(II) conc. $\frac{\partial \log i_0}{\partial \log [Zn(II)]}$</th>
<th>Influence of $OH^-$ conc. $\frac{\partial \log i_0}{\partial \log [OH^-]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>Galv. pulse 5-10 $\mu$s</td>
<td>7.0</td>
<td>0-10</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>64</td>
<td>Galv. &amp; Pot. pulse 10-200 $\mu$s</td>
<td>0-3.0</td>
<td>0-10</td>
<td>30-40</td>
<td>30-100</td>
<td>0.67</td>
<td>0.14</td>
</tr>
<tr>
<td>65</td>
<td>Galv. pulse 650 $\mu$s</td>
<td>7.0</td>
<td>50-100</td>
<td>70-220</td>
<td>200</td>
<td>$\sim$0</td>
<td>0.11</td>
</tr>
<tr>
<td>66</td>
<td>Galv. pulse 15 $\mu$s</td>
<td>0.6-12.5</td>
<td>0-10</td>
<td>20-310</td>
<td>20-150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>67</td>
<td>Galv. pulse 5-10 $\mu$s</td>
<td>0.1-13.8</td>
<td>0-10</td>
<td>20-300</td>
<td>20-310</td>
<td>$\sim$0</td>
<td>-</td>
</tr>
<tr>
<td>68</td>
<td>Pot. pulse 50 $\mu$s</td>
<td>7.0</td>
<td>0-100</td>
<td>140</td>
<td>40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>69</td>
<td>Galv. pulse 5-10 $\mu$s</td>
<td>2-13</td>
<td>0-10</td>
<td>20-310</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Zn\textsubscript{kink} + OH$^-$ $\leftrightarrow$ Zn\textsubscript{ad} OH$^-$ (4.8)

Zn\textsubscript{ad}OH$^-$ + OH$^-$ $\rightarrow$ Zn(OH)\textsubscript{ad} + e$^-$ (4.9)

Zn(OH)\textsubscript{ad} + OH$^-$ $\leftrightarrow$ Zn(OH)$_2$ + e$^-$ (4.10)

Zn(OH)$_2$ + 2OH$^-$ + 2H$_2$O $\leftrightarrow$ Zn(OH)$_4$·2H$_2$O$^{2-}$ (4.11)

Reaction (4.9) was thought to be rate determining if the reaction time was less than 10 $\mu$s otherwise surface diffusion effects or the rate of kink site generation associated with reaction (4.8) can become rate governing$^{68}$.

Bockris et al$^{64}$ proposed a different scheme for the anodic reaction sequence:

Zn + OH$^-$ $\leftrightarrow$ ZnOH + e$^-$ (4.12)

ZnOH + OH$^-$ $\leftrightarrow$ Zn(OH)$_2$ (4.13)

Zn(OH)$_2$ + OH$^-$ $\rightarrow$ Zn(OH)$_3$ + e$^-$ (4.14)

Zn(OH)$_3$ + OH$^-$ $\leftrightarrow$ Zn(OH)$_4$ (4.15)

In this reaction scheme (4.14) is rate determining and the cathodic reaction is the exact reverse of the given anodic sequence.

4.4. Current Density-Bias Potential Characteristics and Oxide Formation on Anodic Polarisation

A number of workers$^{70-81}$ have investigated this aspect of the electrochemistry of zinc. For a more detailed review reference should be made to Jolas$^{77}$ and Powers and Brieter$^{75}$.

4.4.(i) Stationary Electrodes

Vozdvizhenskii and Kochman$^{70}$ carried out the first detailed cyclic voltametric study of the anodic behaviour of zinc in alkaline solution
and observed two current peaks which they attributed to the formation of two types of oxide. Powers\textsuperscript{71-74}, Powers and Brieter\textsuperscript{75} and Brieter\textsuperscript{76} found evidence for the existence of two types of oxide coatings referred to as "Type I" and "Type II" films. The Type I film is white, thick and flocculent and forms when electrolyte convection is minimal. The Type II film is dark, coherent and tightly bound to the electrode surface. Photomicrographs showing various stages of zinc passivation have been reported by Powers\textsuperscript{74} and Powers and Breiter\textsuperscript{75}.

Dirkse and Hampson\textsuperscript{78} carried out passivation experiments using linear sweep voltammetry and observed double current peaks and rapid oscillations in current density over a narrow range of potential. Dirkse and Hampson\textsuperscript{78} found that voltammetrygrams were similar for both horizontal face upwards and horizontal face downwards electrodes, which differs from the observations of Powers\textsuperscript{74} and Powers and Breiter\textsuperscript{75}.

4.4.(ii) Rotating Electrodes

Hull et al\textsuperscript{79} and Toni\textsuperscript{80} used voltammetry in conjunction with rotating disc and rotating ring-disc electrodes to investigate the influence of hydrodynamics on the anodic dissolution of zinc in alkali. It was reported\textsuperscript{79,80} that the first peak was due to a potential dependent reaction with the eventual formation of Zn(OH)\textsubscript{2}. Further increases in potential changes the constitution of the film and leads to complete passivation of the electrode. These observations\textsuperscript{79,80} are in direct conflict with results obtained at stationary electrodes.

Armstrong et al\textsuperscript{81} studied the anodic dissolution of zinc in alkali using rotating disc electrodes. The dissolution of the zinc in both the active and passive branches was found to occur with simultaneous zinc deposition. For active dissolution the Tafel slope was 42mV/decade and
passivity was caused by the formation of an anodic phase monolayer on
the electrode surface, which had a reversible potential 100 mV anodic
of the Zn/ZnO electrode.

4.5 Characteristics of Alkaline Zincate Solutions

Zincate solutions are produced when zinc oxide or zinc hydroxide
are dissolved in alkali, or when zinc electrodes are discharged in
alkaline electrolyte solution. Schumacher\textsuperscript{82} has reviewed much of the
relevant literature. The equilibrium concentration of Zn(II) in alkali
of a given concentration and temperature is rather difficult to define\textsuperscript{83-88}
because it depends on the details of preparation of the solution. The
solubility of ZnO appears\textsuperscript{89} to increase monotonically with KOH concentration
up to a value of 14.5 mol dm\textsuperscript{-3}. Solutions in which the zincate concentra-
tion is greater than that produced by dissolving ZnO in KOH are readily
prepared\textsuperscript{40,89} by cooling saturated solutions of ZnO, or by discharging
zinc electrodes into KOH solutions\textsuperscript{40,90}. Thus Eisenburg et al\textsuperscript{40} found
for zinc electrodes discharged in 6.9 mol dm\textsuperscript{-3} KOH solution saturated with
ZnO (0.69 mol dm\textsuperscript{-3}) that zinc concentrations up to 2.42 mol dm\textsuperscript{-3} could be
measured and interfacial zinc concentrations as high as 3.20 mol dm\textsuperscript{-3}
could be calculated. Dirkse\textsuperscript{90} reported that by anodically dissolving
zinc in 6.29 mol dm\textsuperscript{-3} KOH solution zinc concentrations of 1.5 mol dm\textsuperscript{-3}
were obtained and that the resulting solutions which were initially clear
subsequently became turbid, with a reduction in the concentration of zinc.
It was estimated\textsuperscript{35} that at the point of anodic passivation of the zinc
electrode there exists a Zn(II) concentration at the electrode interphase
equivalent to the initial hydroxide concentration of the electrolyte
solution.

Factors effecting the rate at which ZnO precipitates from super-
saturated zincate solutions were investigated by Flerov\textsuperscript{91,92} and at the
Lucas Group Research Centre found that increasing the temperature was the easiest way of reducing the zincate concentration. An investigation into the effect of additives on the rate of \( \ce{ZnO} \) precipitation found that only \( \ce{Si0_2^-} \) and \( \ce{Li^+} \) had any appreciable influence, and both acted as retardents to the ageing process.

The species present in dilute potassium zincate solutions have been identified as belonging to a series of stepwise reactions:

\[
\begin{align*}
\ce{Zn(II)_s} & \rightleftharpoons \ce{Zn(OH)_2} & (4.16) \\
\ce{Zn(OH)_2} + \ce{OH^-} & \rightleftharpoons \ce{Zn(OH)_3^-} & (4.17) \\
\ce{Zn(OH)_3^-} + \ce{OH^-} & \rightleftharpoons \ce{Zn(OH)_4^{2-}} & (4.18)
\end{align*}
\]

where \( \ce{Zn(II)_s} \) represents one form of \( \beta-\ce{Zn(OH)_2} \), \( \gamma-\ce{Zn(OH)_2} \), \( \varepsilon-\ce{Zn(OH)_2} \), amorphous \( \ce{Zn(OH)_2} \), \( \ce{ZnO(stable)} \) or \( \ce{ZnO(active)} \) and is present when the solution is saturated.

Attempts to elucidate the constitution of the zincate solutions within the limit of \( \ce{Zn(II)} \) concentrations obtained by shaking \( \ce{ZnO} \) with \( \ce{KOH} \) have been made. The effect of hydroxyl ion concentration on the e.m.f. of a zinc electrode in \( \ce{KOH} \) solution saturated with \( \ce{ZnO} \) was investigated by Mendzheretskii and Bagotskii. They found that the e.m.f. of the cell

\[
\ce{Zn, ZnO | KOH,aq,sat.ZnO | HgO,Hg}
\]

was independent of the alkali concentration for solutions of 4.0 mol dm\(^{-3}\) or more in \( \ce{KOH} \). Dirkse reported potentiometric measurements confirming that the complex \( \ce{Zn(OH)_4^{2-}} \) was the main solution species. The same conclusion was also reached by Fordyce and Baum who examined solution using infra-red and Raman spectral techniques and Newman and Blomgren using n.m.r. spectroscopy to examine the zincate solutions.
At higher Zn(II) concentrations the situation is not clear. Dirkse\textsuperscript{96} reported a slight fall-off from rectilinearity in the potential-bias Zn(II) concentration curve and this was later confirmed by Hampson et al\textsuperscript{99}. It was not possible to account for this deviation from linearity by assuming a formula Zn(OH)\textsubscript{4}.2H\textsubscript{2}O\textsuperscript{2-} for the solution species. Boden, Wylie and Spera\textsuperscript{100} investigated the effect of varying KOH and Zn(II) concentration upon the e.m.f. of the cell:

\[ \text{Hg(Zn)} \mid \text{KOH, Zn(II),aq} \mid \text{Hg,HgO} \quad (4.20) \]

Very similar results to those of Dirkse\textsuperscript{96} and Hampson et al\textsuperscript{99} were obtained\textsuperscript{100}, however, the change of activity co-efficient of the zincate ion with molar concentration was used to explain the data.

Laser Raman work by Jackovitz and Langer\textsuperscript{101} indicated that as the Zn(II) concentration rose above 1.37 mol dm\textsuperscript{-3} the Raman spectral intensity increased much less than expected. They showed that the addition of large quantities of Zn(II) either electrolytically or in the form of a halide does not appreciably increase the concentration of the zinc hydroxy complex, as indicated by the intensity of the characteristic peak, already present. Further, these workers\textsuperscript{101} were unable to detect any spectral bands corresponding to new zinc-hydroxy compounds. These observations are in agreement with those of Dirkse\textsuperscript{96} and Hampson et al\textsuperscript{99} in that the quantity of Zn(II) in solution estimated potentiometrically or spectroscopically appear to be less than the amount indicated by chemical analysis.
THE ANODIC BEHAVIOUR OF ZINC IN FLOWING ELECTROLYTES

5.1 Introduction

The commercial exploitation of the zinc/air cell depends upon sustained high rates of zinc dissolution without undue polarisation of the zinc anode. Anodic behaviour of zinc in alkali has been studied by a variety of techniques under a wide range of conditions. It has been shown\(^\text{33}\) that the upper limit for the 5 hour rate of discharge of a zinc electrode in static 7 mol dm\(^{-3}\) KOH electrolyte would be 10 mA cm\(^{-2}\). This value is increased significantly when mass transport is not solely confined to diffusion. If mass transport includes natural convection, for example by using vertically orientated electrodes with a system\(^\text{34}\) containing an infinite amount of 7 mol dm\(^{-3}\) KOH, then the upper limit of current density is increased to 150 mA cm\(^{-2}\). However, this value is unrealistic since in all practical systems the quantity of electrolyte is limited and operates at continually diminishing concentrations of OH\(^-\) and increasing concentration of Zn(II). The optimisation problem can be rendered relatively simple by using flowing electrolytes. Here, however, there is a distinct lack of published information. Brook and Hampson\(^\text{36}\) have shown that in an infinite volume of flowing electrolyte (7 mol dm\(^{-3}\)) a limiting current density exists below which the electrode can never passivate. This limit depends upon the velocity and concentration of the Zn(II). Decreasing the flow rate and increasing concentration of Zn(II) both reduce the limiting current density.

Farmer and Webb\(^\text{46}\) have studied the behaviour of electrodes (9.5 x 5 cm) in a large volume (7 dm\(^3\)) of flowing KOH. A satisfactory model was formulated in terms of the diffusion of soluble species through a growing porous solid layer on the electrode and through the electrolyte diffusion layer. The situations considered by Farmer and Webb\(^\text{46}\) are
commercially poor in that the maximum capacity of the electrolyte to
dissolve zinc from the anode as Zn(II) is not fully realised.

The present experiments were designed to isolate conditions under
which zinc anodes could be discharged with maximum discharge capacity
for a given volume of electrolyte. This capacity might be expected to
be related to the saturation limit of the electrode product in the
electrolyte. However, for the Zn(II) species considerable doubt exists
as to the exact position of the solubility limit in solutions produced
electrolytically: indeed, to some extent the composition of concentrated
Zn(II) solutions is not firmly established although in the normal solubi-
licity region the composition\textsuperscript{97,98} of these solutions is Zn(OH)\textsubscript{2}\textsuperscript{-}.

5.2 Experimental
5.2.(i) General Apparatus

A schematic diagram of the experimental system is shown in
Figure 3-6. The cell, Figure 3-3a, was constructed from Perspex and
contains an electrode compartment of dimensions 0.5 x 5 x 10 cm. The
ancillary equipment has been described in section 3.2. The working
electrode was a plane zinc sheet (99.95% pure) pre-treated by polishing
with glass paper and etching for 10s in 10%v HCl. The superficial area
of the working electrode in contact with the solution was 50 cm\textsuperscript{2}. The
cathode was an air electrode and has been described in section 3.1.(iii).

5.2.(ii) Electrolyte Systems

Alkali solutions were prepared from KOH (AnalaR) and standardised
with sulphamic acid\textsuperscript{27}. Fresh solutions in the range 1-14 mol dm\textsuperscript{-3} were
used for each experiment to minimise carbonation. Additions of potassium
silicate solution (Fisons, S.G. 1.33) were made to the electrolyte, when
required, before the commencement of the experiment.
5.2.(iii) Procedure

The air electrode was vacuum impregnated with dilute KOH solution in order that the three-phase interphase between the air/catalyst/electrolyte occurred within the catalyst layer.

The cell (Figure 3-3a) with the air electrode pressurised with air 2 lb in\(^{-2}\) (13.8 kN m\(^{-2}\)) was primed with electrolyte. The open-circuit cell potential was allowed to reach a stable value before the experiment was commenced by closing the electrical circuit with the current at a pre-set value. The passivation time was determined from the beginning of the experiment to the time the potential between the zinc anode and the air cathode dropped abruptly. As this drop in potential was of the order of 0.7 V and the potential fell immediately to zero, the point of passivation was unequivocal.

The solution from the cell after passivation was immediately removed and analysed\(^{28}\) for Zn(II).

New or completely depassivated electrodes were used in these experiments.

5.2.(iv) Galvanostatic Pulse Experiments

The electrical circuit has been described in section 3.5 and is shown diagramatically in Figure 3-9. The electrolytic cell used in these experiments is shown in Figure 3-4a. The working electrode, described in section 3.1.(iii) and shown in Figure 3-5a, was mechanically polished on a roughed glass surface, etched in HClO\(_4\) (10%v) washed with double-distilled water and inserted wet into the electrolytic cell. Experiments were commenced after an open-circuit period of five minutes.
5.3 Results

5.3.1 Flowing Electrolyte Experiments

Figure 5-1a shows the results of discharging the cell at a series of current densities using a fixed volume of KOH (0.10 dm$^3$) at three different concentrations. The curves show, for each concentration of KOH, that a constant passivating charge is observed until the limiting current density is reached. Above this current density the passivating charge begins to fall rapidly. In Figure 5-1b the data are presented in the conventional it$^{1/2}$ form. At high current densities, the curves extrapolate through the positive i axis at low current densities the curves intersect the t$^{-1/2}$ axis.

Figure 5-2 shows the results of galvanostatic polarisation of the electrolytic system at a constant current density of 0.040 A cm$^{-2}$ for a series of KOH concentrations in the range up to 14 mol dm$^{-3}$. The points connecting passivating charge and KOH concentration lie close to a straight line passing through the origin.

Analyses of the final electrolyte immediately after the termination of the experiments represented in Figure 5-2 show that the electrolytes were considerably supersaturated with Zn(II) species beyond that expected from the thermodynamic solubility data. This was confirmed by allowing the solutions to stand overnight when a dense white precipitate was formed. Figure 5-3 shows the effect of an addition of 0.002 dm$^3$ potassium silicate per 0.10 dm$^3$ KOH on the discharge characteristics of the cell.

An apparently anomalous dissolution region exists at a concentration of about 3 mol dm$^{-3}$ KOH, termed the slurry region in this thesis. The potential/time curve corresponding to experiments within this range (2.56 to 3.03 mol dm$^{-3}$) is shown in Figure 5-4 and compared with a potential/time curve for a typical silicate free system.
FIG. 5-1 Passivating charge versus current density; 25°C; flow velocity 0.4 cm s⁻¹
FIG. 5-2 Effect of [KOH] on passivating charge; 25°C; 0.4 cm s⁻¹; current density 0.04 A cm⁻²
FIG. 5-3 Effect of [KOH] on passivating charge and [Zn(II)] of the final solution; conditions as fig 5-2 + 0.15 mol dm$^{-3}$ pot. silicate
FIG. 5-4 Cell voltage versus time curves; conditions as fig 5-2

Cell voltage /V

Time /h

3.0 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate

pure KOH

1.5

0.5

0
In Figure 5-3 are also shown the final analyses of the electrolyte after the termination of the experiments (the solutions were centrifuged before analysis to remove suspended matter). The concentrations of Zn(II) in solution of high KOH concentration with added potassium silicate are generally much higher than those in corresponding solutions without the addition of potassium silicate. In concentrations of KOH corresponding to the slurry region the concentration of Zn(II) in the centrifuged solutions are almost identical to the concentrations of Zn(II) in solutions without potassium silicate. It can be seen that the calculated concentration of Zn(II) species is much greater than the experimental values in the slurry region. At higher KOH concentrations the two values tend to converge.

Figure 5-5 shows the results of discharging the cell at a series of current densities for a fixed volume of 3 mol dm$^{-3}$ KOH electrolyte (0.10 cm$^3$) containing 0.002 dm$^3$ of potassium silicate solution. It can be seen that continuous precipitation was maintained until a critical value of current density was reached, after which the passivating charge falls rapidly with increasing current density. By increasing the solution velocity this limit is displaced towards higher current densities.

Figure 5-6 shows the results of discharging the cell under the same conditions as previously used (e.g. Figure 5-5) but with the addition of 0.004, 0.006 and 0.01 dm$^3$ of potassium silicate solution respectively. It can be seen that the addition of further silicate solution not only broadens the slurry region but also displaces it towards regions of higher KOH concentration, making the system more attractive for commercial applications because of improved conductivity. However, with the addition 0.01 dm$^3$ of potassium silicate solution the trend is broken and no slurry region is observed, and the passivating charge is generally lower than with a 0.006 dm$^3$ addition of potassium silicate solution.
FIG. 5-5  Passivating charge versus current density;  
3·0 mol dm$^3$ KOH + 0·15 mol dm$^3$ potassium silicate; 23°C
FIG. 5-6  Effect of [KOH] on passivating charge with the addition of potassium silicate; conditions as fig 5-2
5.3.(ii) **Galvanostatic Pulse Experiments**

In Figure 5-7 are shown exchange current density data calculated\(^6^3\) from faradaic current overpotential data corresponding to a concentration range of 2-10 mol \(\text{dm}^{-3}\) KOH at 23°C.

In Figure 5-8 are presented typical ohmic overpotential/faradaic current curves for the zinc electrode in alkaline solution with and without the addition of 0.002 dm\(^3\) of potassium silicate solution. Both series of points lie on a straight line passing through the origin.

5.4 **Discussion**

Although there have been a number of reports in the literature which interpret isolated aspects of the observations reported here, none of them provide a complete explanation. In particular the anomalous behaviour at concentrations around 3 mol \(\text{dm}^{-3}\) with added silicate (Figure 5-3) has not been reported previously.

5.4.(i) **Silicate Free Solutions**

It is well established that for diffusion-controlled experiments the active/passive transition for the dissolution of zinc anodes in KOH solution is limited by conditions in the electrolyte layer immediately surrounding the anode\(^3^3,3^4\). Thus an electrode passivated in a static electrolyte can give further active dissolution after the current has been switched off for a sufficient time for the products to diffuse away from the anode. This has been observed in current-interruption experiments by Hampson et al\(^3^4\) and treated mathematically\(^1^0^2\), and experimentally by Bushrod and Hampson\(^1^0^3\). In the present experiments with flowing electrolyte further active dissolution, following passivation, is only possible when the electrode has been polarised at a sufficiently high rate for the electrochemical generation of Zn(II) species to exceed their rate of removal by convective-diffusion. Thus
FIG. 5-7 Exchange current density versus 
[KOH]; 25°C; 0.15 mol dm⁻³ Zn(II);
total ionic strength 10 mol dm⁻³

exchange current / mA cm⁻²

pure KOH

+ 0.15 mol dm⁻³ pot. silicate

[KOH] / mol dm⁻³
FIG. 5-8 Ohmic overpotential versus current density; 3.0 mol dm⁻³ KOH; other conditions as fig. 5-7.

- 0.15 mol dm⁻³ pot. silicate
- Pure KOH
further dissolution could only be achieved in experiments at high current densities, where the passivating charge has fallen from its plateau value as shown in Figure 5-1. These results, at high current densities, agree both with those of Farmer and Webb\textsuperscript{46} and earlier results in flowing electrolyte\textsuperscript{36}. However, this region of high current densities is not the main area of interest. Electrodes that have been passivated at low current densities, where the plateau value of the passivating charge had been reached (Figure 5-1), could not be induced to further dissolution even by resting on open-circuit overnight. It can be concluded, therefore, that in the plateau region the concentration of Zn(II) has reached the solubility limit throughout the solution.

If the current density is plotted against the passivation time $t_p^{-1/2}$ (Figure 5-1b), the intercept on the $t_p^{-1/2}$ axis, does not agree with any theory based on a model in which the current flow is limited by diffusion across a stagnant layer in the sense that Sand\textsuperscript{104} used in discussing the case for semi-infinite linear diffusion. It should be noted, however, that Farmer and Webb\textsuperscript{46} found quantitatively similar results to those reported here. In these authors' representations a model was developed in which the divergence from the rectilinear curve was caused by the increasing effect of a growing porous layer (of Zn(II) species) on the electrode surface which provided an increasingly effective carrier to the removal of the products of the zinc dissolution and consequently a more rapid accumulation of Zn(II) species at the electrode surface. It was found that at higher current densities, the straight lines show that the $t_p^{-1/2}$ relationship exists which is in agreement with the theoretical discussion of Farmer and Webb and the experiments of Brook and Hampson.

Although, the behaviour of silicate-free solutions at high current densities can be interpreted in terms of existing theories\textsuperscript{46,102}, the
horizontal plateau in the passivating charge observed at low current densities (Figure 5-1a) can only be interpreted as a limitation on discharge caused by the accumulation of Zn(II) species to a critical level of concentration in the electrolyte as a whole. Once this limit is reached the active dissolution ceases, by one of two possible mechanisms:

(a) the Zn(II) species can "back precipitate" onto the electrode surface;
(b) the zinc anode can be directly oxidized to zinc oxide.

Either mechanism produces a coherent insulating film on the electrode surface that effectively stops the active dissolution of the zinc electrode.

For experiments conducted in the plateau region (i.e. low current densities) the passivating charge and the equivalent Zn(I) yield steadily increase as the KOH concentration is increased. This plateau region behaviour can be contrasted with high-current density experiments in stagnant conditions\textsuperscript{33,34} where a maximum discharge performance is achieved at about 8 mol dm\textsuperscript{-3} KOH. Comparison of terminal Zn(II) concentrations with published solubility data, indicates that at all KOH concentrations a considerable degree of supersaturation exists, amounting to about double the equilibrium solubility of the zinc oxide in KOH solution. This is in agreement with the observed instability of the final electrolyte solutions.

5.4.(ii) Electrolytes Containing Silicate

Figure 5-3 shows that an addition of potassium silicate to the electrolyte increases the charge required to bring about passivation of the zinc anode at all concentrations of the KOH electrolyte and comparison with Figure 5-3 shows that the passivating charge is increased
about 30% by the addition of 0.002 dm$^3$ potassium silicate solution.

At concentrations in the region of 3 mol dm$^{-3}$ KOH a new feature is evident. Here the passivating charge increases markedly, and for this rate of discharge is apparently boundless (the slurry region). Systems under constant rates of discharge within this region become stable with time, a constant electrode potential is observed and zinc oxide is deposited in the solution continually (Figure 5-4). Whereas in silicate-free systems the potential decreases slowly but smoothly and almost linearly, the silicate-containing systems show a temporary decrease in the potential of about 30mV. In these experiments the electrode becomes passive because of the inability of the pump to remove the contents of the cell cavity, which is ultimately a stiff paste. As shown in Figure 5-3 in the region 2-7 mol dm$^{-3}$ KOH, the curve for the faradaic yield lies everywhere above the electrolyte Zn(II) concentration curve. This indicates that the products of the electrode region are not remaining in solution. This is most evident in the region around 3 mol dm$^{-3}$ KOH where precipitation was apparent after about four hours discharge. Centrifuging was necessary in order to analyse these solutions and it is interesting to note that the analyses of the centrifuged (or decanted) solutions corresponding to the whole series of experiments formed a continuous curve and this curve was identical to the maximum zincate concentration obtainable by discharging Zn into KOH solution in the region below 7 mol dm$^{-3}$ KOH but lay above these values at higher KOH concentrations. It would appear that at higher KOH concentrations the potassium silicate is acting as a classical discharge capacity extender$^{92,93,105}$.

At concentrations below 7 mol dm$^{-3}$ KOH it seems likely that with the addition of potassium silicate a fraction of the products of the reaction is precipitated as zinc oxide during the course of the electrode
discharge. Precipitation apparently does not take place at the electrode in such a way as to block the dissolution process, but occurs in the bulk electrolyte. In the 3 mol dm$^{-3}$ concentration region this form of precipitation continues at the same rate as the faradaic production so that the precipitation reaction

$$\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (5.1)$$

furnishes hydroxyl ions at the same rate as they are removed electrolytically

$$\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad (5.2)$$

$$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (5.3)$$

This is confirmed by the steady potential (Figure 5-4) which implies a constant hydroxyl ion concentration. The open-circuit cell voltage follows from the Nernst equation. The cell potentials under galvanostatic polarisation both with and without potassium silicate show similar initial characteristics which rise with increasing KOH concentration because of the increasing conductivity of the electrolyte solution. At very high KOH concentrations the cell potentials tend to decrease because of a decrease in conductivity owing to the increasing viscosity and change in the hydration of ions. Figure 5-5 shows the effect of increasing current density on silicate-containing solutions in the 3 mol dm$^{-3}$ KOH region. The effect of an increase in current density can be offset by increasing the solution flow velocity.

Galvanostatic experiments (Figure 5-8) have shown the possibility of a film adsorbed on the electrode surface and this is reflected in the high ohmic overpotential. On inspection the anodes from the flowing system in the slurry region had an electropolished finish.

The exchange current density in silicate-free systems as measured by galvanostatic pulse experiments agree generally with previously reported
results using this technique$^{63,69}$. When compared with data from silicate-containing systems it is clear that the effect of the silicate species is to reduce the magnitude of the exchange current density. Such a reduction may arise either from the adsorption of silicate ions at active sites on the electrode or by the creation of a thick layer analogous to the type produced during electropolishing$^{106}$ through which Zn(II) species must pass before entering the bulk electrolyte. Support for this is provided by the ohmic overpotential data (Figure 5-8), where the addition of silicate ions increases the electrode resistance markedly.

Flerov has reported on the behaviour of silicate ions as a capacity extender$^{92,93}$. However, his work has been limited to static solutions and to bulk electrolyte in the classical region at high KOH concentrations (i.e. 7 mol dm$^{-3}$). In this Russian work it is considered that the silicate ion acts by stabilising Zn(II) species in a micellar structure and so increasing the capacity of the electrolyte for Zn(II) species. The exact role of the silicate ion in the micelle cannot be taken as settled however, Flerov considers that the silicate ion may be chemisorbed in the inner layer of the postulated micelle engendering higher stability possibly through a more extensive hydration sheath.

The existence of the slurry region at relatively low KOH concentrations, however, cannot be explained simply in terms of stabilisation of the colloidal particles in the bulk solution. The remarkable fact that the precipitation of the electrode products does not occur at the electrode and does not block further reaction appears to be a contradiction to the general rule that precipitation should occur down a concentration gradient.

5.4.(iii) A Possible Interpretation
A tentative explanation of the results may be advanced based on
(a) the formation of a relatively thick silicate-rich layer around the anode;
(b) the stabilisation of Zn(II) species in solution by silicate ions.

The first phenomenon is well known in the electropolishing literature\textsuperscript{107-109} and is supported by the galvanostatic pulse experiments, and the second factor has been demonstrated by Flerov\textsuperscript{92,93} for bulk solutions.

It can be postulated on the basis of these observations that Zn(II) species have a higher solubility in the silicate-rich layer adjacent to the electrode, than in the rest of the solution. Now considering the electrode, operating in the slurry region where zinc oxide is being continuously precipitated, it can be seen that, provided the higher solubility limit of Zn(II) in the silicate-rich layer is not exceeded, the Zn(II) will diffuse through the silicate-rich layer as solution species. When the Zn(II) reach the outer part of the diffusion layer, where their solubility is lowered, they are precipitated as zinc oxide at a point remote from the electrode surface itself.

At higher current densities the surface concentration of Zn(II) species increases and eventually the solubility limit of even the silicate-rich layer is exceeded and precipitation occurs actually at the electrode surface, so causing passivation in the normal way.

The formation of an adsorbed layer of silicate must be seen as a competitive process essentially between the silicate species and the hydroxyl ions. Thus at high KOH concentrations so many hydroxyl ions are adsorbed that an effective silicate-rich layer is unable to form and the anomalous slurry region is absent. However, the addition of further silicate ions would shift the point where hydroxyl ions compete successfully with the silicate ions towards higher hydroxyl concentrations, as is observed in Figure 5-6, since the slurry region extends to higher KOH concentrations with increasing silicate addition.
Diffusion in the viscous silicate-rich layer will be slower than in the rest of the solution, resulting in an increased concentration gradient in the silicate-rich layer relative to the rest of the diffusion layer. The addition of further silicate will thicken the silicate-rich layer relative to the total diffusion layer thickness, as well as thickening the diffusion layer itself by increasing the bulk viscosity. Thus, the consequence of adding too much silicate can be explained, since the increased thickness of the silicate-rich layer combined with the steep concentration gradient across it could readily lead to the solubility limit being exceeded even at modest current densities and so to the passivation of the electrode without observing a slurry region (e.g. Figure 5-6c).

The absence of a slurry region at low concentrations of KOH may be explained in terms of the low solubility of Zn(II) species in dilute KOH solution alone, so the effect of added silicate is insufficient to raise the solubility in the silicate-rich layer above the value required to prevent passivation.

The argument is based on some simplifications of the physical chemistry of the electrode interphase region. The main simplification being the assumption that the concept of solubility as applied to a bulk solution can be applied on the microscopic scale to a silicate-rich layer which may only be a few molecules thick. However, the key hypothesis in the explanation of the existence of a slurry region is that the species formed at the electrode with added silicate are more stable in solution very close to the surface than they are elsewhere.
5.5 Conclusions

1. The passivating charge for the dissolution of zinc in alkaline media below a certain current density is controlled by the solubility of the zinc species in the media.

2. The apparent solubility of the zinc species exceeds the equilibrium value, especially when potassium silicate is added.

3. A region of composition exists for the ternary system $\text{KOH}/K_2\text{SiO}_3/\text{ZnO}$ in which zinc undergoes continuous anodic dissolution, $\text{Zn(II)}$ being continuously removed from solution as zinc oxide. The region is influenced by the current density, the flow velocity of the electrolyte flow and the amount of added potassium silicate. In the region of continuous dissolution/precipitation the electrode systems have dissolution potentials which are constant with time.

4. The novel slurry region, produced by the addition of potassium silicate has commercial applications and these are discussed in Chapter 11.

5. The $\text{Zn/Zn(II)}$, $\text{OH}^-$ electrode reaction in the presence of potassium silicate takes place through a film. The nature of this system can be explained on the assumption that $\text{Zn(II)}$ species are more soluble within the film than outside it.
CHAPTER 6

THE DIFFERENTIAL CAPACITANCE OF ZINC IN AQUEOUS SOLUTION

6.1 Experimental

The electrode interphase was matched as a series combination of resistance $R_{xs}$ and capacitance $C_{xs}$ using a Schering bridge\(^{25}\) as described in Section 3.3.

6.1.(i) Electrolyte System

The electrolytic cell in which the electrolyte was subjected to continuous purification by adsorption of impurities on charcoal is shown in Figure 3-1. The electrolyte solutions, electrodes and the preparation of the electrolytic cell have been described in Section 3.1.

6.1.(ii) Electrode Pretreatment

All measurements were made using the same test electrode, a diagram of which is shown in Figure 3-5a. The surface of the electrode was prepared by mechanically polishing on fine carborundum paper, followed by a light polish on roughened glass using bidistilled water as a lubricant in order to remove any embedded material. The electrode was then etched (30s; HCl, 10%v), rinsed with dilute alkali ($0.1 \text{ mol dm}^{-3}$) and washed with bidistilled water and placed in the cell wet. This pretreatment yielded a bright surface which appeared flat and scratch free under the optical microscope.

6.2 Results

Figure 6-1 shows typical differential capacitance versus potential curves for a polycrystalline zinc electrode in aqueous potassium chloride solution at different concentrations. The potential of minimum capacitance for the $0.003 \text{ mol dm}^{-3}$ concentration occurs at $-1.120\text{V}$.
FIG. 6-1 Differential capacitance curves for polycrystalline zinc in KCl solutions

- 1.0 mol dm$^{-3}$
- 0.10 mol dm$^{-3}$
- 0.05 mol dm$^{-3}$
- 0.003 mol dm$^{-3}$

pH 3.4; 23°C
Figure 6-2 shows typical differential capacitance versus potential curves in different concentrations of aqueous potassium nitrate solution.

Typical faradaic current bias potential curves for a polycrystalline zinc electrode in aqueous potassium chloride, and potassium chloride with an addition of potassium silicate are shown in Figure 6-3. The curves illustrate the extent of experimental polarisability, the range extending from -1.0 to -1.2 V for KCl electrolytes at pH 3.0. Hydrogen evolution was observed at -1.35 V. Figure 6-4 shows the typical faradaic current versus potential curves for a polycrystalline zinc electrode in a series of different concentrations of aqueous potassium nitrate solution at pH 3.0. Also included on this diagram are the faradaic current data for the polycrystalline zinc electrode in aqueous potassium nitrate with added potassium silicate. The extent of the experimentally available polarisable region in the nitrate system is less than in the equivalent chloride system, the difference being due to pronounced cathodic current flow at less negative potentials in aqueous nitrate solutions. The differential capacitance of the electrode over the corresponding range is shown in Figure 6-5 at three frequencies. A maximum A is observed at potentials between -1.1 and -1.3 V. Also shown inserted on Figure 6-5 is a plot of $\frac{1}{\omega C_{XS}}$ versus $R_{XS}$ at -1.025 V where the frequency dispersion is minimal.

Figure 6-6 shows the differential capacitance versus potential curves for the zinc electrode in 1.0 mol dm$^{-3}$ KCl and 1.0 mol dm$^{-3}$ KCl and 1.0 mol dm$^{-3}$ KNO$_3$ with an addition of 0.15 mol dm$^{-3}$ potassium silicate. The pseudocapacitance rise due to lattice dissolution is shifted to more positive potentials with the addition of silicate ions and the differential capacitance are generally lower especially at potentials around -0.9 to -1.2 V.
FIG. 6-2  Differential capacitance for polycrystalline zinc in KNO₃ solutions

-1.4  -1.2  -1.0
Potential (S.C.E.) / V

0.01 mol dm⁻³
0.11 mol dm⁻³
0.5 mol dm⁻³
1.0 mol dm⁻³

pH 3.4, 23°C
FIG. 6-3 Faradaic current-potential curves for zinc in KCl solutions

- 1.0 mol dm$^{-3}$ KCl
- 0.1 mol dm$^{-3}$ KCl
- 1.0 mol dm$^{-3}$ KCl + 0.15 mol dm$^{-3}$ potassium silicate

pH~3.4; 23°C
FIG. 6-4 Faradaic current-potential curves for zinc in KNO₃ solutions

- 1.0 mol dm⁻³ KNO₃
- 0.5 mol dm⁻³ KNO₃
- 0.11 mol dm⁻³ KNO₃
- 1.0 mol dm⁻³ KNO₃ + 0.15 mol dm⁻³ potassium silicate
  pH 3.4; 23 °C
Fig. 6-5. Differential capacitance curves for zinc in 1.0 mol dm⁻³ KNO₃ solution.
FIG. 6.6 Differential capacitance curves for zinc in aqueous solutions

- 1.0 mol dm$^{-3}$ KCl
- 1.0 mol dm$^{-3}$ KCl + 0.15 mol dm$^{-3}$ potassium silicate
- 1.0 mol dm$^{-3}$ KNO$_3$ + 0.15 mol dm$^{-3}$ potassium silicate

1KHz; pH~3.4; 23°C

Potential (S.C.E.) / V

Differential capacitance / $\mu$Fcm$^{-2}$
Figure 6-7 shows the variation of the electrode resistance $R_{xs}$, with potential for both 1.0 mol dm$^{-3}$ KCl and KOH with and without an addition of potassium silicate. One striking feature is the increase in $R_{xs}$ with the addition of potassium silicate.

Figure 6-8 shows differential capacitance versus potential curves for the zinc electrode in 1.0 mol dm$^{-3}$ KOH and 0.1 mol dm$^{-3}$ KOH over a wide range of potential, and shown on Figure 6-9 are typical differential capacitance bias potential curves for aqueous KOH solutions of different concentrations containing additions of potassium silicate. (It should be noted that the possibility of removal of silicate ions from the Pyrex glass vessel is recognised and about 10 days circulation of electrolyte through activated charcoal is required before satisfactory curves for Hg in 0.5 mol dm$^{-3}$ KOH are obtained).

Figure 6-10 shows typical faradaic current versus potential for aqueous KOH solutions both with and without additions of potassium silicate.

A certain amount of hysteresis was observed in the differential capacitance versus potential curves for aqueous KOH solutions containing potassium silicate. This is shown in Figure 6-11.

6.3 Discussion

The position of the differential capacitance minimum indicating the potential of zero charge seems to be in some doubt, and doubt has been cast upon the possibility of its identification due to the intrusion of the lattice dissolution potential$^{48}$. From an examination of the published work on zinc the reported values of the p.z.c. range from -1.74 V to -0.84 V (SCE). Many authors do not quote the pH of their electrolyte solutions although the importance of the pH on the measured
FIG. 6-7 Electrode resistance curves for zinc in aqueous solutions

- 1.0 mol dm$^{-3}$ KCl + 0.15 mol dm$^{-3}$ potassium silicate
- 1.0 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ potassium silicate
- 1.0 mol dm$^{-3}$ KCl
- 1.0 mol dm$^{-3}$ KOH

1K Hz; 23°C

Potential (S.C.E.) / V

Electrode resistance / $\Omega$ cm$^2$
FIG. 6-8 Differential capacitance for zinc in alkaline solutions

- 1.0 mol dm$^3$ KOH
- 0.1 mol dm$^3$ KOH

1K Hz; 23°C

Potential (S.C.E.) / V

Differential capacitance / µFcm$^{-2}$
Differential capacitance curves for zinc in silicate containing alkaline solutions
FIG 6-10 Faradaic current-potential curves for zinc in alkaline solutions.

- △ 1.0 mol dm$^{-3}$ KOH
- ○ 1.0 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ potassium silicate
- ○ 0.01 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ potassium silicate

Potential (S.C.E.) / V

Faradaic current / $\mu$Acm$^{-2}$
0.1 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ potassium silicate; pH 12.8; 23$^\circ$C

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

Potential (S.C.E.) / V

FIG. 6.11

Hysteresis of differential capacitance with reversal of scanning direction for zinc in alkaline solution.
double layer capacitance has been emphasised\textsuperscript{57}. Baugh and Lee\textsuperscript{57} confirmed the work of Hampson et al\textsuperscript{47}, showing that the differential capacitance measurements made on the polycrystalline zinc electrode in high pH aqueous solutions are not the true zinc metal/aqueous solution interface, but are characteristic of a surface complicated by the formation/removal of a hydroxide or oxide film or the adsorption of OH\textsuperscript{-} ions. In aqueous solutions of low pH the differential capacitance measured may be the true metal/solution interphase. The family of curves shown in Figure 6-1 on successive dilutions of aqueous KCl solution begin to show a distinct minimum at -1.120 V. The curve obtained for 0.1 mol dm\textsuperscript{-3} KCl is very similar to that obtained by Baugh and Lee for 0.1 mol dm\textsuperscript{-3} NaClO\textsubscript{4} at pH 3.4, but the capacitance values of the latter are lower than those observed in chloride electrolyte. Baugh and Lee found, however, that the magnitude of capacitance measured was dependent on the electrode used.

The curves of Figure 6-1 show that the interaction of OH\textsuperscript{-} with the electrode surface has been effectively suppressed by decreasing the pH and the minimum in 0.003 mol dm\textsuperscript{-3} solution does suggest a diffuse layer minimum however complicated at the positive branch by the lattice dissolution process. The electrometric measurements (Figure 6-3) evince that the Zn/KCl aqueous system is nowhere ideally polarisable. This is indicative of the relatively high exchange current for the h.e.r. on zinc and the rather electropositive nature of zinc.

Data concerning the double layer structure of solid metals in aqueous nitrate electrolytes have been recorded\textsuperscript{110,111}. Hampson and Piercy\textsuperscript{112}, however, have observed the reduction of the nitrate ion in aqueous KNO\textsubscript{3} at the indium electrode at potentials of -1.2 V to -1.5 V and Kabanov et al\textsuperscript{113} have shown that nitrate reduction can occur at the lead electrode
under certain conditions. In the present work the differential capacitance measurements of the zinc electrode in aqueous potassium nitrate solution do not conform to those of the true zinc metal/inert aqueous electrolyte solution interface. A maximum (A) occurs in the differential capacitance profile which appears to be dependent on the concentration of KNO$_3$ at constant pH. The maximum diminishes and moves to more negative potentials with progressive dilution of the KNO$_3$. At potentials corresponding to A considerable faradaic current flows. The frequency dispersion at A (Figure 6-5) was too large to be due to surface roughness. It is likely that the peak is due to faradaic processes occurring at the electrode surface. Since this effect was not observed with other aqueous potassium salts it can be postulated that the nitrate ion is involved in the faradaic process.

In order to test this supposition, experiments were conducted with a large area zinc electrode potentiostatically polarised in KNO$_3$ solution (1 mol dm$^{-3}$) at various potentials. After a few hours the solution was acidified and tested for nitrite$^{112}$. At potentials more negative than -1.05 V the presence of nitrite was observed, but not at potentials more positive than -1.025 V. It was also noticed with the reduction of nitrate a precipitate of Zn(OH)$_2$ was also formed. Two schemes which account for the observations may be formulated:

$$\text{Zn} + 2\text{OH}^- \longrightarrow \text{Zn(OH)}_2 + 2\text{e} \quad (6.1)$$

$$2\text{H}^+ + \text{NO}_3^- + 2\text{e} \longrightarrow \text{NO}_2^- + \text{H}_2\text{O} \quad (6.2)$$

and

$$\text{Zn} + \text{H}_2\text{O} + \text{NO}_3^- \longrightarrow \text{Zn(OH)}_2 + \text{NO}_2^- \quad (6.3)$$

No nitrite was detected at potentials more positive than -1.0 V and this suggests that the chemical reaction (6.3) does not occur to any significant extent.
The impedance behaviour in the region of A has been analysed on the basis of the Randles series circuit. The measured bridge components $R_{xs}$ and $C_{xs}$ were converted to the series resistance $R_s$ and capacitance $C_s$ contributions of the electrode impedance per unit area after subtracting the solution resistance $R_{sol}$ ($R_{sol}$ being obtained from a plot of $1/\omega C_{xs}$ vs $R_{xs}$ extrapolated to infinite frequency\textsuperscript{114}, Figure 6-5). $R_s$ and $C_s$ were converted to the equivalent parallel circuit values $R_p$ and $C_p$ and analysed assuming negligible charge transfer resistance ($R_{ct} = 0$) for the case $C_R \gg C_O$ and negligible surface roughness.

The plots of $C_p$ versus $\omega^{-1/2}$ (Figure 6-12) show that at -1.15 V, when it has been shown that the reduction of nitrate occurs, there is a significant faradaic component of $C_p$. At -1.025 V when no nitrate reduction occurs the slope of the $C_p$ versus $\omega^{-1/2}$ curve must be due to surface roughness. The concentration of electroactive species at -1.15 V ($C_0$) is $9.4 \times 10^{-6}$ mol dm$^{-3}$ for $n = 2$ and $D_0 = 10^{-5}$ cm$^2$ s$^{-1}$. The extrapolation of the $C_p$ data to infinite frequency at -1.15 V indicates low values for $C_d1 \sim 7 \mu F \ cm^{-2}$, at -1.025 V the value of $C_d1 \sim 10 \mu F \ cm^{-2}$ is still rather low. Graphs of $C_p$ versus $1/\omega R_p$\textsuperscript{114} (Figure 6-12) are linear at potentials of -1.15 V and -1.20 V. At -1.15 V the slope is close to 45°, which would be expected for a diffusion controlled process or one in which $R_{ct} \neq 0$. From this one can conclude that the reduction of nitrate at the zinc electrode is a fast faradaic process with diffusion control.

The precise nature of the silicate ion in aqueous solution is in some doubt and a variety of crystalline compounds have been isolated and studied\textsuperscript{115}. Soluble silicates characterized by silica-to-alkali ratios of up to 2 dissolve to give true solutions, but the nature of the anion is not necessarily the tetrahedral $SiO_4^{2-}$ ion and may be a larger...
FIG. 6-12 $C_p$ versus $\omega^{-1/2}$ for zinc in 1.0 mol dm$^{-3}$ KNO$_3$ at 23°C
Polynuclear ion\textsuperscript{116}. Thus hydroxylated species have been detected by Raman spectra\textsuperscript{117,118}. Figure 6-6 shows the effect on the electrode capacitance of the zinc electrode by adding potassium silicate to the solution.

The reduction of nitrate can be effectively suppressed by the addition of potassium silicate to the potassium nitrate solution. A negative result was obtained for the azo dye test\textsuperscript{112} when the electrode was potentiostatted at potentials more negative than -1.025 V. As can be seen from the differential capacitance curves in nitrate solutions the addition of potassium silicate completely removes the maximum A (Figures 6-2 and 6-6) observed in 1.0 mol dm\textsuperscript{-3} \( \text{KNO}_3 \). Also the pseudocapacitance rise due to metal dissolution occurs at a much more positive potential, and this is also shown by the faradaic current curves (Figures 6-3 and 6-4). The h.e.r. in both chloride and nitrate solutions at this pH is suppressed by the addition of potassium silicate. Due to the h.e.r. it was impossible to balance the bridge in silicate free 1.00 mol dm\textsuperscript{-3} \( \text{KCl} \) at potentials more negative than -1.35 V. With the addition of potassium silicate it was possible to obtain differential capacitance measurements in 1.0 mol dm\textsuperscript{-3} \( \text{KCl} \) at potentials of -2.0 V, although there was some evidence of hydrogen forming at -1.8 V.

The characteristic differential capacitance curves observed for zinc in alkaline solution are shown in Figure 6-8. A pseudocapacitance peak is exhibited in pure potassium hydroxide solution due to the interaction of the OH\textsuperscript{-} ion with the electrode surface in which region the electrode undergoes active dissolution. The capacitance rises sharply at potentials more positive than -1.5 V and the current (Figure 6-10) also becomes large, and negative (anodic) at this potential. The magnitude of the pseudocapacitance at -1.5 V is similar for both 1.0 mol dm\textsuperscript{-3} \( \text{KOH} \) and 0.1 mol dm\textsuperscript{-3} \( \text{KOH} \) solutions.
In alkali, the addition of potassium silicate markedly suppresses the pseudocapacitance and shifts it to more negative values. An increase in capacitance values at more negative potentials is due to the increase in the h.e.r. with the addition of potassium silicate confirmed by the faradaic current (Figure 6-10). This effect is similar to that of mercury^19 where the specific adsorption of anions lowers the hydrogen overvoltage. At lower concentrations of KOH the pseudocapacitance peak is further decreased. The addition of potassium silicate, therefore inhibits the dissolution of zinc by limiting the interaction of OH\(^-\) with the zinc surface. It appears that the silicate ion is more strongly adsorbed than the OH\(^-\) ion. This is also indicated by the reduced anodic current flow (Figure 6-10) with an addition of potassium silicate, adsorption apparently hindering lattice dissolution in agreement with previous results where it was found that the exchange current density was greatly reduced by the addition of potassium silicate. In dilute alkali the lattice dissolution pseudocapacitance peak is quite small and the dissolution of zinc is almost totally suppressed by the silicate as can be seen from the negligible anodic current flow (Figure 6-10). (It should be noted that when additions of potassium silicate are made to alkaline solutions there is a small shift in pH, but this shift does not account for the effects observed). With the addition of potassium silicate the resistive component measured is increased. This is similar to the effects observed previously using the galvanostatic pulse technique. The ohmic overpotential was found to increase significantly with the addition of potassium silicate. In the present measurements the effect is not so pronounced, but in these measurements the solution resistance is a large proportion of the total measured resistance.

A certain amount of hysteresis was observed in the differential capacitance curves in dilute alkaline solution with added potassium
silicate when the direction of scanning was reversed. When scanning from negative to more negative potentials the position of the pseudo-capacitance peak was shifted by 0.075 V to a more negative potential and the differential capacitance due to the h.e.r. was reduced. This could be due to changes in surface topography due to polarising the electrode at more positive potentials or adsorption sluggishness which has been observed for some other metals with adsorbed anions. An alternative explanation in terms of the difficulty of desorbing a large isopolysilicate ion can also be made, however, the lack of definite data concerning the nature of the silicate ion in the adsorbed state hampers further discussion.

6.4 Conclusions

1. In confirmation of previous work the double layer capacitance of zinc can be measured without the interaction of OH⁻ with the surface in low pH aqueous solutions.

2. The reduction of the nitrate ion occurs at the zinc electrode at potentials of around -1.1 V vs. S.C.E. This reduction is suppressed by the adsorption of the silicate ion.

3. The addition of potassium silicate to the solution increases the measured electrode resistance.

4. The silicate ion is adsorbed at the electrode at a potential close to the dissolution potential. This adsorption limits the OH⁻ interaction with the surface and inhibits the dissolution process of zinc.

5. A potential of minimum capacitance occurs in dilute solution of KCl in low pH (-1.12 V (vs. S.C.E.)). This cannot be definitely ascribed as a diffuse layer minimum, however, there is doubt about its rejection as the p.z.c. on the grounds of lattice dissolution potential.
CHAPTER 7

THE EFFECT OF POTASSIUM SILICATE ON THE EXCHANGE IN ALKALI

7.1 Introduction

Several workers\textsuperscript{31,32} have examined the fundamental electrochemistry of the Zn/Zn(II), OH\textsuperscript{-} system. Conflicting data and tentative conclusions reflect the relative complexity of the system. Some of the difficulties possibly arise from surface changes occurring in processes of lattice dissolution and oxide formation\textsuperscript{57}. There is also the possibility that the reaction involves the diffusion of adsorbed intermediates on the surface of the electrode, the presence of these was recently confirmed in an elegant manner by Armstrong et al\textsuperscript{122}. These workers showed as a result of measurement at very low frequency that the charge-transfer reaction occurred in stages, the adsorbed intermediate corresponding to Zn(I). Extension of the frequency range has further shown that the adsorption follows a Langmuir isotherm rather than a Henry's Law isotherm. At higher overpotential the surface concentration of the adsorbed species is increased. No effect was observed by Armstrong et al\textsuperscript{122} which could be ascribed to metallurgical control.

Evidence has accumulated that kinetic parameters observed for the Zn/Zn(II), OH\textsuperscript{-} system are to some extent dependent on the method of determination. Thus values of $i_0$ have ranged\textsuperscript{63} from 300 mA cm$^{-2}$ down to 114 mA cm$^{-2}$ for the exchange reaction in 7 mol dm$^{-3}$ KOH containing Zn(II) and values of the anodic Tafel slope have ranged from 30 mV/decade\textsuperscript{123} to 65 mV/decade\textsuperscript{63}.

The galvanostatic pulse technique seems to have some inherent difficulties when used on this system. In particular the extrapolation of n/t data\textsuperscript{66} and the influence of ohmic resistance\textsuperscript{63,124} effects treated in earlier work have recently been criticised\textsuperscript{64}. Such factors may
account for the reported insensitivity of the exchange current density to changes of zincate concentration\textsuperscript{63}.

The discovery (Chapter 5) of an electrolyte in which a zinc electrode can be galvanostatically polarised (below the critical current density) without passivation is of interest in the zinc/air system. This electrolyte was used in a flowing system containing additions of potassium silicate. It has been shown by double layer capacitance measurements (Chapter 6) that in this electrolyte there exists an adsorbed layer of silicate at the electrode/electrolyte interphase which hinders the dissolution of zinc.

In order to obtain a better understanding of the Zn/Zn(II), \( \text{OH}^- \) system both with and without additions of potassium silicate experiments were carried out using a rotating disc electrode. The data and conclusions drawn from such an investigation are reported in this chapter.

7.2 Experimental

7.2.(i) Electrolytic System

The electrolytic cell (Figure 3-2a) was cylindrical and 5.5 cm diameter so that the walls did not interfere with the electrolyte solution flow about the electrode\textsuperscript{24}. The test electrode (0.136 cm\(^2\)) was prepared from 99.999\% pure zinc supplied by Koch-Light Laboratories, Limited, and has been described in Section 3.1.(iii). The counter electrode was a large area platinum gauze. The reference electrode was a wick type \( \text{Hg/HgO} \) in \( 1 \text{ mol dm}^{-3} \) KOH solution to which all potentials are referred. A closed liquid seal tap in conjunction with a Luggin capillary system separated the working and reference compartments of the cell. Electrolyte solutions were prepared from Ana\textlA\textregistered R grade chemicals and bidistilled water from deionised stock. Additions of potassium silicate (Fisons SG.1.33) were made when required. All electrolytic
solutions investigated were made up to constant ionic strength 3 mol dm\(^{-3}\) with KCl and deoxygenated with nitrogen prior to the electrochemical measurements.

7.2.(ii) **Instrumental**

The electrical circuit used in these experiments has been described in Section 3.4.(ii) and Figure 3-8b shows a block diagram of the electrical circuit.

7.2.(iii) **Electrode Pretreatment**

All measurements were made using the same test electrode\(^{125}\) which was mechanically polished on fine carborundum paper, followed by a light polish on roughened glass using bidistilled water as a lubricant in order to remove any embedded material. The electrode was then etched (30s; HCl, 10%v) rinsed with dilute alkali (0.1 mol dm\(^{-3}\)), washed with distilled water and placed in the cell wet.

7.3. **Results and Discussion**

7.3.(i) **Tafel Slopes and Orders of Reaction**

The rotation speed dependence of the dissolution currents of polycrystalline zinc in alkaline solution has been described previously by Armstrong and Bulman\(^{81}\).

For \(i>i_d\), limiting current density due to OH\(^-\) diffusion and a deposition reaction that is first order in zincate.

\[
i = i(\infty) - nFk_cC_0
\]  
(7.1)

and

\[
\frac{1}{i} = \frac{1}{i(\infty)} + \frac{k_c1.61D_0^{-2/3}\nu^{-1/6}w^{-1/2}}{i(\infty)}
\]  
(7.2)

At a given potential \(E\), \(C_o^E\) is the concentration of anodic products in equilibrium with the zinc electrode and
Therefore plots of $i^{-1}$ versus $\omega^{-1/2}$ should have an intercept of $i(\omega^{-1})^{-1}$ and a slope showing a 30 mV/decade dependence on potential. This behaviour was observed in the present experiments (Figures 7-1 and 7-2).

A series of Tafel slopes for polycrystalline zinc in various concentrations of alkaline solution are shown in Figure 7-3. The currents were corrected for mass transport in solution by extrapolation of $i^{-1}$ versus $\omega^{-1/2}$ curves. The Tafel slopes obtained were curved especially at the more negative potentials, however, it was possible to obtain data for an order of reaction determination. Figure 7-4 shows the plot of $\log i(\omega)$ versus $\log \text{OH}^-$ concentration. A value of 4.0 was obtained for $\frac{\partial \log i(\omega)}{\partial \log \text{OH}^-}E'$ which is similar to the value of 3.5 obtained by Armstrong and Bulman. More rectilinear Tafel curves were obtained (Figure 7-5) from experiments carried out in Zn(II)-containing alkaline solutions (40 - 90 mV overpotential). Shown on Figure 7-6 is the plot of $\log i(\omega)$ versus $\log \text{OH}^-$ concentrations at constant potential. A value of 1.9 was obtained for $\frac{\partial \log i(\omega)}{\partial \log \text{OH}^-}E'$.

A satisfactory explanation of the reason for the difference between the two orders of reaction can be made as follows. There exists a strong hydrogen evolution current when polycrystalline zinc is polarised in alkaline solutions even at those potentials at which the overall current in the active region is anodic. The h.e.r. has a more pronounced effect at more negative potentials becoming less prominent at more positive potentials. Thus, the Tafel slopes obtained are curved and the currents show a greater dependence on potential than for zinc dissolution alone. The order of reaction obtained from these Tafel slopes is likely to be erroneous. The contribution of the h.e.r. to the total current in the
FIG. 7-1  

$i^{-1}$ versus $\omega^{-\frac{1}{2}}$ for the potentials shown in 3.0 mol dm$^{-3}$ KOH solution
FIG.7-2 Slope as a function of potential for zinc in alkaline solutions
Current-potential curves, corrected for mass transport effects, for zinc in alkaline solutions
FIG. 7-4  Anodic reaction order in hydroxyl (for Tafel curves in Fig. 7-3) for zinc in alkaline solutions

- KOH
- KOH + 0.15 mol dm$^{-3}$ pot. silicate
- KOH + 0.15 mol dm$^{-3}$ pot. silicate

$23^\circ$C, $-1.280$ V, 3.0 mol dm$^{-3}$ ionic strength (KCl)
In zincate containing alkaline solutions for mass transport effect, for zinc current-potential curves corrected.

FIG. 7-5
FIG. 7-6 Anodic reaction order in hydroxyl (for Tafel curves in Fig. 7-5) for zinc in alkaline solutions. Inserted cathodic reaction order in hydroxyl.

Anodic reaction order in hydroxyl for zinc in alkaline solutions. Inserted cathodic reaction order in hydroxyl. KOH + 0.15 mol dm$^{-3}$ potassium silicate 23°C, −1300 V, 30 mol dm$^{-3}$ ionic strength (KCl).
zinc dissolution region in the zincate containing electrolytes should be negligible because the potential region is remote from that of significant hydrogen evolution. The anodic order of reaction for OH\(^-\) obtained in this way is similar to that obtained for the amalgam\(^{59}\) and closer to the value 2.6 obtained by Bockris et al.\(^{64}\).

After the elimination of diffusion effects a Tafel slope of 110 mV/decade was obtained for the cathodic reaction. The deposition reaction was found to be approximately first order in zincate and a value of -2.2 was obtained for the dependence of the cathodic current on the OH\(^-\) concentration (Figure 7-6a).

7.3.(ii) Exchange Currents

The rotation speed dependence of the anodic currents was investigated close to the equilibrium in alkaline solutions containing Zn(II). As before the currents were corrected for mass transport effects in solution (Figure 7-7a). Figure 7-7 shows a plot of \(i(\infty)\) versus potential. The reaction resistance \(R_D\) was calculated

\[
R_D = -(\frac{\sigma n}{a + 1}) n \rightarrow 0 \quad (7.4)
\]

the exchange current density following from

\[
i_o = \frac{RT}{(a_c + a_a)} e^{\frac{RT}{m}} \cdot \frac{1}{R_D} = \frac{RT}{m} \cdot \frac{1}{R_D} \quad (7.5)
\]

Figure 7-8 shows a plot of log \(i_o\) versus log Zn(II) concentration, a value of 0.75 being obtained for the slope dependence of the exchange current on Zn(II) concentration. The magnitude of \(i_o\) changes very little with OH\(^-\) concentration, a value of 0.22 being obtained for the slope \(\frac{\partial \log i_o}{\partial \log C_{OH^-}} C_{Zn(II)}\) as shown in Figure 7-9.
FIG. 7-7  Typical current-potential plots for zinc in alkaline solutions (corrected for mass transport effects)
Dependence of exchange current on $[\text{Zn(II)}]$ for zinc in alkaline solutions

**FIG. 7-8**

- $1.0 \text{ mol dm}^{-3} + 0.075 \text{ mol dm}^{-3} \text{ pot. silicate}$
- $1.0 \text{ mol dm}^{-3} + 0.0375 \text{ mol dm}^{-3} \text{ pot. silicate}$
- $1.0 \text{ mol dm}^{-3} \text{ KOH}$

$23^\circ \text{C}; 3.0 \text{ mol dm}^{-3}$ ionic strength ($\text{KCl}$)

- Logarithm of exchange current $i_0$ vs. logarithm of $[\text{Zn(II)}]$.
FIG. 7-9 Dependence of exchange current on [OH\(^{-}\)] for zinc in alkaline solutions; 23°C, ionic strength 3.0 mol dm\(^{-3}\) (KCl), 0.003 mol dm\(^{-3}\) Zn(II)
7.3.(iii) Choice of Mechanism

In the thermodynamic solubility range the solution species have been confirmed as the tetrahedral $\text{Zn(OH)}_4^{2-}$ ion, and the overall electrode reaction has been shown to be

$$\text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad (7.6)$$

Therefore, the simplest possible reaction mechanism must consist of several steps, the number of viable reaction pathways being limited by the experimentally determined kinetic parameters (Table 7.1). There exists

\[\text{TABLE 7.1}\]

<table>
<thead>
<tr>
<th>Measured Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic Tafel slope</td>
<td>45 mV/decade</td>
</tr>
<tr>
<td>Cathodic Tafel slope</td>
<td>110 mV/decade</td>
</tr>
<tr>
<td>Anodic reaction order $[\text{OH}^-]$</td>
<td>1.9</td>
</tr>
<tr>
<td>Cathodic reaction order $[\text{OH}^-]$</td>
<td>-2.2</td>
</tr>
<tr>
<td>Anodic reaction order $[\text{Zn(II)}]$</td>
<td>~ 0</td>
</tr>
<tr>
<td>Cathodic reaction order $[\text{Zn(II)}]$</td>
<td>0.9</td>
</tr>
<tr>
<td>$(\frac{\partial \ln i_o}{\partial \ln [\text{OH}^-]})) [\text{Zn(II)}]$</td>
<td>0.22</td>
</tr>
<tr>
<td>$(\frac{\partial \ln i_o}{\partial \ln [\text{Zn(II)}]})) [\text{OH}^-]$</td>
<td>0.75</td>
</tr>
</tbody>
</table>

the possibility that the reaction may proceed via a simultaneous two electron change or a consecutive two step mechanism, however, the latter is the more plausible reaction route in view of the finding of Armstrong et al.\(^{122}\).

For a reaction of the type

$$\text{Zn(0)} \rightleftharpoons \text{Zn(I)} + \text{e}^- \quad (7.7)$$

$$\text{Zn(I)} \rightarrow \text{Zn(II)} + \text{e}^- \quad (7.8)$$

the polarisation curve has the form\(^{126}\)

$$i = i_a - i_c = i_o \left( \exp \left( \frac{\alpha F \eta}{RT} \right) - \exp \left( -\frac{\alpha F \eta}{RT} \right) \right) \quad (7.9)$$
where
\[ \alpha_a = m - 1 + \beta_a \quad \text{and} \quad \alpha_c = n - m + \beta_c \quad (7.10) \]

and
\[ \alpha_a + \alpha_c = n = 2 \quad (7.11) \]

For the case of a stepwise mechanism the transfer coefficients \( \alpha_a \) and \( \alpha_c \) can be obtained experimentally from the Tafel slope of the polarisation curve and the dependence of \( i_0 \) on [OH\(^-\)] and [Zn(II)] is given by
\[
\left( \frac{\partial \ln i_0}{\partial \ln [\text{OH}^-]} \right)_{[\text{Zn(II)}]} = \frac{\alpha_c}{n} \quad \text{and} \quad \left( \frac{\partial \ln i_0}{\partial \ln \text{[Zn(II)]}} \right)_{[\text{OH}^-]} = \frac{\alpha_a}{n} \quad (7.12)
\]

The symmetry coefficients \( \beta_c \) and \( \beta_a \) characterising the shape of the energy barrier for the limiting step can only be determined by considering the limiting step in isolation. For the case of a simple one-step process the ratio \( \alpha_a / \alpha_c \) is usually close to unity. A deviation of this ratio from unity is an indication of a stepwise mechanism and the value of the ratio can indicate which is the limiting step.

In the present case \( \alpha_a / \alpha_c \sim 3 \) from both Tafel slopes and exchange current measurements and hence \( m = 2 \), i.e. the rate limiting step is the transfer of the second electron.

7.3.(iv) Suggested mechanism

\[
\begin{align*}
\text{Zn} + \text{OH}^- \quad &\longrightarrow \quad \text{ZnOH}_{\text{ad}} + \text{e}^- \\
\text{ZnOH}_{\text{ad}} + \text{OH}^- \quad &\rightarrow \quad \text{Zn(OH)}_2^- + \text{e}^- \\
\text{Zn(OH)}_2^- + \text{OH}^- \quad &\longrightarrow \quad \text{Zn(OH)}_3^- \\
\text{Zn(OH)}_3^- + \text{OH}^- \quad &\longleftrightarrow \quad \text{Zn(OH)}_4^{2-}
\end{align*}
\]

These equations are consistent with the experimental data (Table 7.1). The mechanism is written in the anodic direction and the cathodic reaction proceeds by the exact reverse since \( \alpha_a + \alpha_c = 2 \).

The selected mechanism agrees with a later proposal (Chapter 9), that polycrystalline zinc dissolves to give a final solution species
of Zn(OH)$_4^{2-}$ up to the thermodynamic solubility limit of Zn(II). In saturated zincate solutions the final solution species was found to be Zn(OH)$_3^-$ and in the final stages of dissolution the anodic product was an isopolion built up of Zn(OH)$_2^-$ units. In the given reaction sequence the two chemical reactions (7-15, 7-16) cease to take place, as the OH$^-$ concentration of the solution is depleted, giving the solution species detected. It is difficult to see how these species could be produced by a previously proposed mechanism$^{64}$.

7.3.(v) Effect of Potassium Silicate on the Rotation Speed Dependence

Figure 7-10 shows a plot of $i^{-1}$ versus $\omega^{-\frac{1}{2}}$ for the dissolution of polycrystalline zinc in alkaline solution containing potassium silicate. The slope of the $i^{-1}$ versus $\omega^{-\frac{1}{2}}$ plots show a 30 mV/decade dependence on potential (Figure 7-11) confirming that Zn(OH)$_4^{2-}$ is the species in equilibrium with the electrode.

7.3.(vi) Effect of Potassium Silicate on the Tafel Slopes and Orders of Reaction

Figure 7-12 shows a series of Tafel slopes for the anodic dissolution of polycrystalline zinc in various solution concentrations with an addition of 0.15 mol dm$^{-3}$ potassium silicate. The order of reaction for OH$^-$ concentration is $\sim 2$ for Tafel slopes measured with an exchangeable ion in solution (Figure 7-6).

Figure 7-13 shows a series of Tafel slopes for the anodic dissolution of polycrystalline zinc in 3 mol dm$^{-3}$ KOH with various additions of potassium silicate. The Tafel slopes become less potential dependent as the potassium silicate content is increased varying from 36 mV/decade with no additions to 52 mV/decade with 0.75 mol dm$^{-3}$ potassium silicate added. The effect on the current (Figure 7-14) at constant potential is almost a first order decrease with the addition of potassium silicate.
The graph shows the relationship between $\omega^{-1/2}$ and $i^{-1}$ for different potentials. The potentials are shown in the legend and include $-1.361 \text{ V}$, $-1.356 \text{ V}$, $-1.351 \text{ V}$, $-1.346 \text{ V}$, and $-1.336 \text{ V}$. The graph is labeled as Figure 7-10 in the document.
FIG. 7-11 Slope as a function of potential for zinc in silicate containing alkaline solutions

- 1.0 mol dm$^{-3}$ KOH
- 2.0 mol dm$^{-3}$ KOH
- 23°C, 0.15 mol dm$^{-3}$ pot. silicate

$\log \text{slope} / \text{cm}^2 \text{mA}^{-1} \text{s}^{-1/2}$

potential vs Hg/HgO / V
FIG 7-12 Current-potential curves, corrected for mass transport effects, in silicate containing alkaline solutions
FIG. 7-13 Current-potential curves, corrected for mass transport effects, for zinc in solutions based on 3.0 mol dm$^{-3}$ KOH with additions of potassium silicate.

- No addition
- 0.0375 mol dm$^{-3}$
- 0.075 mol dm$^{-3}$
- 0.15 mol dm$^{-3}$
- 0.30 mol dm$^{-3}$
- 0.75 mol dm$^{-3}$

23°C.
FIG. 7-14 Dependence of anodic current on the potassium silicate concentration.
Conditions as fig. 7-13
7.3.(vii) **Effect of Potassium Silicate on the Exchange Current Densities**

Figure 7-8 shows the effect of potassium silicate on the exchange current for polycrystalline zinc in 3 mol dm$^{-3}$ KOH. The value of the slope ($\frac{\partial \ln i_0}{\partial \ln [\text{Zn(II)}]} [\text{OH}^-]$) is decreased progressively with the addition of potassium silicate. A value of 0.75 was obtained with no addition compared to 0.68 for an addition of 0.0375 mol dm$^{-3}$ and 0.61 with 0.075 mol dm$^{-3}$ added potassium silicate.

7.3.(viii) **Effects of Potassium Silicate on the Dissolution Reaction**

From the dependence of the $i^{-1}$ versus $\omega^{-1/2}$ on potential plots and the anodic order of reaction with respect to OH$^-$ concentration it can be seen that the reaction is proceeding via the same mechanism and the reaction product is Zn(OH)$_4^{2-}$ when additions of potassium silicate are made, as has been shown previously.

Polycrystalline zinc becomes progressively more difficult to dissolve in alkaline solution as the concentration of potassium silicate is increased (Figure 7-14). Calculation of the symmetry coefficients from exchange current measurement (Figure 7-8) using equation (7.10) indicates that the energy barrier to anodic dissolution is becoming more asymmetric as the potassium silicate concentration is increased. This suggests that the dissolution reaction is becoming less energetically favourable.

It has been shown (Chapter 6) that the silicate ion is adsorbed at potentials where the dissolution reaction takes place which agreed with the postulation that the dissolution reaction takes place through a viscous electropolishing type layer.
7.4 Conclusions

The present measurements show that the exchange reaction in the double layer region and the diffusion of products away from the electrode surface are effected by the adsorption of a layer of silicate at the electrode.
CHAPTER 8
THE EFFECT OF POTASSIUM SILICATE ON THE DISSOLUTION OF ZINC IN ALKALI

8.1 Introduction

A number of workers\textsuperscript{32} studying the anodic behaviour of poly-crystalline zinc in KOH solutions have established that after a period of active dissolution the electrode becomes passive, caused by a layer of oxy-products based on Zn(II) covering the electrode surface.

Investigations\textsuperscript{40,33,34} of the anodic behaviour using galvanostatic polarisation have been unable to yield information about the actual mechanism by which the passive layer is formed.

Powers and Breiter\textsuperscript{75} and Powers\textsuperscript{74} have made L.S.V. measurements coupled with simultaneous microscopic examination of the working electrode. Two processes were identified, both of which engendered the formation of an electrode film. The formation of Zn(OH)\textsubscript{2} on the electrode via back precipitation from a supersaturated solution and the formation of ZnO directly from the lattice were observed\textsuperscript{75}. Hampson et al\textsuperscript{67} also used L.S.V. in KOH solutions ranging in concentration from 1 to 13 mol dm\textsuperscript{-3} to obtain information on the mode of passivation.

In Chapter 7 of the present study it was shown that an adsorbed layer of silicate species at the zinc electrode inhibits the dissolution reaction. The overall reaction has been shown to be
\[
\text{Zn} + 4\text{OH}^- \longrightarrow \text{Zn(OH)}_2^- + 2e^- \quad (8.1)
\]
by various workers\textsuperscript{90,97,98}, using many techniques. From the rotation speed dependence (Chapter 7) it was concluded that potassium silicate did not effect this overall reaction.

In this Chapter are presented some further data on the dissolution of zinc and the processes of passivation.
8.2 Experimental

8.2.(i) Electrical Circuits

The electrode interphase was matched as a series combination of resistance $R_{xs}$ and capacitance $C_{xs}$ using a Schering bridge as described in Section 3.3. Current-bias potential curves were obtained using a scanning potentiostat (Kemitron 0.5A) and recorded on an X-Y recorder (Bryans 26000A4) or photographed from the screen of an oscilloscope (Hewlett-Packard 130C) as described in Section 3.4.(i).

8.2.(ii) Electrolytic System

Electrolyte solutions were prepared from AnalR grade reagents and bidistilled deionised water. Additions of potassium silicate (Fisons, S.G.1.33) were made when required. The reference in all studies was the Hg/HgO electrode, which was separated from the main cell by a closed liquid seal tap in conjunction with a Luggin capillary system. The zinc working electrode and electrode pretreatment have been described previously in Sections 3.1.(iii) and 6.1.(ii).

For L.S.V. measurements the counter electrode was a large area platinum gauze; for impedance measurements a cylindrical platinum gauze concentric with the working electrode was used.

8.3. Results

Typical current-bias potential curves are shown in Figure 8-1 for the L.S.V. response of polycrystalline zinc in alkaline solution both with and without the addition of potassium silicate. Figure 8-2 shows plots of peak height versus Zn(II) concentration for the linear potential sweep of polycrystalline zinc in two alkaline solutions. Extrapolation of the curves to the Zn(II) concentration axis yields a value of approximately half the hydroxyl concentration for the electrode/electrolyte system having zero active region. Similar extrapolations
FIG. 8-1  Cyclic voltammograms for a stationary zinc electrode in alkaline solutions

-4.0
-2.0
0.0
2.0
4.0

potential vs. Hg/HgO/V

-1500
-1300
-1100

1.0 mol dm⁻³ KOH
1.0 mol dm⁻³ KOH + 0.15 mol dm⁻³ pot. silicate, 0.03 V⁻¹, 23°C.
FIG. 8-2  Peak height versus [Zn(II)] for zinc in alkaline solutions; 23°C; 0.030 V s⁻¹
can be made for the passivating charge versus Zn(II) concentration plots (Figure 8-3). A semi-logarithmic plot of current against potential for the rising portion of the wave (Figure 8-1) is shown in Figure 8-4.

With the addition of potassium silicate to the electrolyte the characteristics of the polarisation curves changed markedly. Most interesting was the amount of charge passed in passivation, as Figures 8-5 and 8-6 illustrate. At low sweep rates the charge passed with silicate present was much lower than without. At higher sweep speeds a limiting value was approached in the two cases. The curves in 1 mol dm$^{-3}$ could not be obtained because of the high ohmic overpotential as a consequence of the large currents flowing.

The impedances of polycrystalline zinc electrodes in alkaline solutions, some containing potassium silicate, were analysed by the Argand diagram method of Sluyters$^{22}$ (Figures 8-7 to 8-9). Figure 8-10 shows semilogarithmic plots of $\theta$, the charge transfer resistance, versus anodic overpotential.

Figure 8-11 shows plots of $C_p$ versus $\omega^{-1/2}$ for polycrystalline zinc. In alkaline solution the addition of silicate left the form of the curves unchanged; the slopes and intercepts at $\omega \to \infty$ were, however, greater in the absence of the additive.

8.4 Discussion

8.4.(i) Linear Sweep Voltammetry

The results obtained in KOH solution are in agreement with the findings of Breiter and Powers$^{75}$, who concluded that the oxidation of zinc in KOH solution could take place via two parallel paths; a dissolution-precipitation process, and a solid-state reaction involving direct attack by the OH$^-$ ion upon the zinc surface. It was found$^{75}$ that
FIG. 8-3 Passivating charge versus [Zn(II)] for zinc in alkaline solutions; 23°C; 0.030Vs⁻¹
FIG. 8-4  Semi-logarithmic plots for the rising portion of an L.S.V. curve (as shown in fig 8-1); 23°C; 0.030Vs⁻¹

- ○ 1.0 mol dm⁻³ KOH + 0.45 mol dm⁻³ pot. silicate
- △ 1.0 mol dm⁻³ KOH + 0.15 mol dm⁻³ pot. silicate
- ▲ 1.0 mol dm⁻³ KOH + 0.075 mol dm⁻³ pot. silicate
- • 1.0 mol dm⁻³ KOH

potential vs Hg/HgO / V

log₁₀ i / mAcm⁻²
FIG. 8-5 Passivating charge versus sweep rate for zinc in alkaline solutions.

- 0.5 mol dm$^3$ KOH
- 0.1 mol dm$^3$ KOH

passivating charge / mC cm$^{-2}$ vs. sweep rate / Vs$^{-1}$
FIG. 8-6 Passivating charge versus sweep rate for zinc in alkaline solutions

![Graph showing passivating charge versus sweep rate for zinc in alkaline solutions.](image-url)
FIG. 8-7  Complex plane display of electrode impedance as a function of frequency

3.0 mol dm$^3$ KOH + 0.05 mol dm$^3$ Zn(II)

$Z''/\Omega \text{cm}^2$ vs. $Z'/\Omega \text{cm}^2$

$0.4$ $0.8$ $1.2$ $1.6$ $2.0$ $2.4$ $2.8$ $3.2$

$0.4$ $0.6$ $0.8$ $1.0$ $1.2$ $1.4$ $1.6$ $1.8$ $2.0$ $2.2$ $2.4$ $2.6$ $2.8$ $3.0$ $3.2$ $3.4$ $3.6$ $3.8$ $4.0$ $4.2$ $4.4$ $4.6$ $4.8$ $5.0$ $5.2$ $5.4$ $5.6$ $5.8$ $6.0$ $6.2$ $6.4$ $6.6$ $6.8$ $7.0$ $7.2$ $7.4$ $7.6$ $7.8$ $8.0$ $8.2$ $8.4$ $8.6$ $8.8$ $9.0$ $9.2$ $9.4$ $9.6$ $9.8$ $10.0$ $10.2$ $10.4$ $10.6$ $10.8$ $11.0$ $11.2$ $11.4$ $11.6$ $11.8$ $12.0$

$1K$ $1.3K$ $1.8K$ $3K$ $5K$ $140$ $200$ $300$ $400$ $600$ $800$
3.0 mol dm$^{-3}$ KOH + 0.005 mol dm$^{-3}$ Zn(II)
frequencies (Hz) given by superscripts to upper semicircle

$Z'' / \Omega \text{cm}^2$

$Z' / \Omega \text{cm}^2$

FIG. 8-8
Complex plane display of electrode impedance as a function of frequency and potential.
FIG. 8-9  Complex plane display of electrode impedance

3.0 mol dm$^{-3}$ KOH
0.005 mol dm$^{-3}$ Zn(II)
-1.360V (Hg/HgO)

0.00375 mol dm$^{-3}$ pot. silicate

$Z''/\Omega \text{cm}^2$

$Z'/\Omega \text{cm}^2$

no additions
FIG. 8-10 Semi-logarithmic plots of \( \Theta \) versus overpotential for zinc in alkaline solutions

3.0 mol dm\(^{-3}\) KOH
0.005 mol dm\(^{-3}\) Zn(II)

\[ \log_{10} \Theta / \Omega \text{cm}^2 \]

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

- 0.00375 mol dm\(^{-3}\) pot. silicate
- no addition
FIG. 8-11  \( C_p \) versus \( \omega^{-1/2} \) for zinc at 23°C in.
3.0 mol dm\(^{-3}\) KOH + 0.15 mol dm\(^{-3}\) potassium silicate
at potentials below the critical value for the initiation of the solid state reaction the oxidation of zinc takes place by a Zn(II) solution mechanism. Assuming a high degree of reversibility in the electron transfer step, the concentration implied by the Nernst equation will results in an exceeded solubility product as the potential is made more positive. A progressive precipitation of Zn(II) will then occur in the electrode layer. Harrison\textsuperscript{127} has described the mechanism by which this solution-formed solid material may find its way back to the electrode surface. The initial film was found to be white, loose and flocculant, being predominantly Zn(OH)\textsubscript{2}. A more compact greyish-black film of ZnO was observed at more positive potentials formed by the solid-state oxidation of the zinc surface.

It was tentatively\textsuperscript{35} suggested that the Zn(II) concentration at the electrode surface at the point of passivation was equivalent to the hydroxyl ion concentration in the bulk solution. This suggestion is substantiated by the L.S.V. measurements reported here (Figure 8-2 and 8-3). Certainly it seems that when extenders such as silicate ions are present in alkaline solutions in which zinc is dissolving the electrolyte Zn(II) concentration approaches the equivalent OH\textsuperscript{-} concentration. Thus a value of 4.29 mol dm\textsuperscript{-3} Zn(II) has already been obtained in solutions of 10 mol dm\textsuperscript{-3} KOH using a flowing system (Chapter 5). It would appear, therefore, that the maximum solubility of Zn(II) species in alkaline solution occurs when all the available OH\textsuperscript{-} ions are involved in the formation of a macromolecule of the type (Zn(OH)\textsubscript{2})\textsubscript{n}. This situation is not reached in practice, however, because of the difficulties involved in solvating such a large molecule. The precipitation of this macromolecule onto the electrode surface, as observed by Breiter and Powers\textsuperscript{75}, is involved in the initial stages of passivation.
The addition of potassium silicate to the electrolyte generally results in a decrease in the charge necessary to cause passivation at low sweep speeds. An adsorbed layer of silicate reduces the diffusion rate of anodic products away from the electrode and the solubility limit is exceeded more readily. The effect becomes less pronounced at higher sweep rates and the passivating charge tends to a limiting value of \( \approx 3 \text{ mC cm}^{-2} \). The passivating charge in potassium hydroxide alone tends to the same value, which is in general agreement with Kabanov et al.\(^{128}\) for the charge required in the formation of a monolayer coverage of ZnO. The semi-logarithmic plots (Figure 8-4) shows a 30 mV/decade slope for the rising part of the current-bias potential for dissolution in KOH solution, as expected for a reversible reaction controlled by diffusion. However, with the addition of potassium silicate the slope becomes progressively less as the diffusion of anodic products away from the electrode becomes hindered.

8.4.(ii) Complex Plane Displayed Impedance Measurements

Figure 8-7 shows that in KOH solutions of Zn(II) concentrations greater than 0.05 mol dm\(^{-3}\) the exchange reaction is controlled by diffusion. This can be seen from the complex plane display of \( Z' \) and \( Z'' \) which gives a straight line which approximates to unity slope.

Well defined semicircles were obtained (Figure 8-8) for the impedance of the zinc electrode in low zincate-containing KOH solutions. The potential dependence of the charge-transfer resistance \( \Theta' \) is connected with the transfer coefficient \( \alpha \) and the standard heterogeneous rate constant \( k_{sh} \) by the equation\(^{129}\)

\[
\ln \Theta = \ln \frac{RT}{nFk_{sh}^2} - \frac{(1-\alpha)nF}{RT} (E-E^0) \quad (8.2)
\]
Figure 8-10 shows a semilogarithmic plot of $\theta$ versus anodic over-potential. A value for the transfer coefficient of 0.16 was obtained from the slope. This is in good agreement with the previously obtained value of 0.22 obtained by a rotating disc electrode method. A value of $k_{sh} = 1.54 \times 10^{-4}$ cm s$^{-1}$ was obtained from the extrapolation of log $\theta$ versus potential to the experimentally determined $E^0$.

The addition of potassium silicate to the electrolyte produced a change in the complex plane display (Figure 8-9). The high frequency semicircle was larger for an equivalent anodic overpotential and the line of approximately unity slope representing diffusion in solution appeared within the experimental frequency range. This is an indication that diffusion of solution-soluble species is controlling the reaction at higher frequencies in the presence of silicate.

Analysis of the potential dependence of log $\theta$ gives the following values for the kinetic parameters $\alpha$ and $k_{sh}$ shown in Table 8.1.

<table>
<thead>
<tr>
<th>Additive conc/mol dm$^{-3}$</th>
<th>$\alpha$</th>
<th>$k_{sh}$/cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.16</td>
<td>$1.54 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.0375</td>
<td>0.22</td>
<td>$8.87 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0750</td>
<td>0.30</td>
<td>$6.64 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The complex plane display of impedance indicates that potassium silicate effects the dissolution reaction, introducing further irreversibility into the charge transfer step as evinced by the change in $k_{sh}$ and $\alpha$, effecting the diffusion of soluble Zn(II) species from the electrode.
8.4.(iii) Parallel Circuit Impedance Measurements

The impedance behaviour in zincate-free alkaline solutions both with and without the additions of potassium silicate has been analysed on the basis of the Randles series circuit. The measured bridge components $R_{xs}$ and $C_{xs}$ were converted to the series resistance $R_s$ and capacitance $C_s$ contributions of the electrode impedance per unit area, after subtracting the solution resistance $R_{sol}$. $R_{sol}$ was obtained from a plot of $1/wC_{xs}$ versus $R_{xs}$ extrapolated to infinite frequency\textsuperscript{114}. $R_s$ and $C_s$ were converted to the equivalent parallel circuit values $R_p$ and $C_p$ and analysed assuming negligible charge transfer resistance ($R_{ct}=0$) for the case $C_R \gg C_o$. Under these conditions $R_p$ and $C_p$ can be found using

$$R_p = \frac{2\sigma}{(\omega^{-1/2}C_o)} \quad \text{and} \quad C_p = C_{dl} + C_o/(2\sigma \omega^{-1/2}) \quad (8.3)$$

where: $\sigma = 1000RT/n^2F^2(2D_o)^{1/2}$ and $C_o$ is in mol dm$^{-3}$. These equations are only strictly applicable when the reaction has zero charge transfer resistance. When $i_0$ becomes smaller the method becomes less exact as at low frequencies the limiting values extrapolates to a lower value than $C_{dl}$. At higher frequencies a curve is observed which has the correct value of $C_{dl}$ on the capacity axis and approximately the correct slope. Some justification for using the parallel circuit analysis in this study can be established from the form of the Argand diagrams for polycrystalline zinc in these solutions and the potentials applied (Figure 8-11a) and from the fact that the plots of $C_p$ versus $\omega^{-1/2}$ obtained are straight lines and not curves. The transfer from a series $R_{xs} - C_{xs}$ connection to the parallel $R_p - C_p$ arrangement was affected using the equations

$$R_p = (1 + \beta^2) (R_{xs} - R_{sol}) \quad \text{and} \quad C_p = \left(\frac{\beta^2}{1 + \beta^2}\right)C_{xs} \quad (8.4)$$
where \( \beta = (\omega C_{xs} (R_{xs} - R_{sol}))^{-1} \)

The effect of surface roughness can be introduced in the parallel equivalent circuit (8.3) by assuming the double layer capacity to be potential independent in the region around the dissolution potential. Here, according to de Levie\(^{130}\) the apparent parallel capacity due to surface roughness is proportional to \( \omega^{-1/2} \) and can therefore be assessed.

Thus the total measured parallel capacity may be written

\[
C_p = C_{dl} + \frac{C_0}{2\sigma \omega^{1/2}} + \frac{q}{\omega^{1/2}} \quad (8.5)
\]

For a plot of \( C_p \) versus \( \omega^{-1/2} \) at a potential where no faradaic reaction occurs a linear plot is obtained having an intercept of \( C_{dl} \) and slope \( g \), where \( g \) is a measure of the surface roughness. Plots of \( C_p \) versus \( \omega^{-1/2} \) confirm that as the potential becomes progressively more anodic the faradaic component of \( C_p \) becomes more prominent (Figure 8-11). The slope \( \frac{\Delta C_p}{\Delta \omega^{-1/2}} \) is minimal at \(-1.500 \text{ V}\), increasing at more negative potentials due to h.e.r. and increasing at less negative potentials due to the anodic dissolution of zinc. Assuming the slope at \(-1.500 \text{ V}\) to be due to surface roughness \( g \), the faradaic slope \( C_0/2\sigma \) can be found by subtracting the roughness slope, \( g \), from the total slope \( \frac{\Delta C_p}{\Delta \omega^{-1/2}} \).

By assuming a value of \( 0.7 \times 10^{-5} \) for the \( D_o \) value\(^{131}\) the interfacial concentration \( C_0 \) can be calculated. The potential dependence of \( C_0 \) in 3 mol dm\(^{-3}\) KOH solution both with and without additions of potassium silicate is shown in Figure 8-12. The slope obtained from \( C_0 \) versus potential corresponds closely to the expected "Nernstian" slope of 30 mV/decade for a 2e\(^-\) reversible electron transfer. Thus the measurements are consistent with the overall dissolution reaction being

\[
\text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2\text{e}^- \\
\text{even in the presence of potassium silicate. This is in agreement with the rotation speed dependence obtained previously (Chapter 7).}
FIG. 8-12 $C_0$-dependence on potential for zinc in alkaline solutions; 3.0 mol dm$^{-3}$ KOH
It is apparent from Figure 8-12 that the $C_0$ calculated for silicate containing solutions is considerably lower. However, from solubility measurements it would appear that the two values should be approximately the same. A likely explanation of the difference between the two values is that the adsorbed layer of silicate effects the diffusion rate of species in the vicinity of the electrode surface. In order to obtain the same $C_0$ value in silicate-containing solutions a $D_0$ value of $1 \times 10^{-8}$ cm$^2$ s$^{-1}$ has to be used in the calculation.

The graphical extrapolation of $C_p$ data to infinite frequency was used to evaluate the $C_{d1}$ data for polycrystalline zinc in alkaline solution both with and without potassium silicate additions. A plot of $C_{d1}$ versus potential is shown in Figure 8-13. The value of $C_{d1}$ is fairly constant up to potentials of significant dissolution. $C_{d1}$ then starts to rise sharply due to the adsorption of the anion for the dissolution reaction. However, with the addition of potassium silicate this rise is not apparent until more positive potentials. This shows the silicate ion is more strongly adsorbed than the OH$^-$ ion at these potentials and the dissolution reaction is being inhibited by the silicate layer obstructing the OH$^-$ ion interaction with the zinc surface.

8.5. Conclusions

Potassium silicate has two effects on the dissolution of polycrystalline zinc in potassium hydroxide:

1. The diffusion rate of species in the vicinity of the electrode surface are modified.

2. An adsorbed layer of silicate species inhibits the dissolution reaction by reducing the interaction of the OH$^-$ ion with the zinc surface.
FIG. 8-13  \( C_{dl} \) dependence on potential for zinc in alkaline solutions; 3.0 mol dm\(^{-3}\) KOH
CHAPTER 9

A STUDY OF POTASSIUM ZINcate SOLUTIONS

9.1 Introduction

The nature of concentrated potassium zincate solutions has been in doubt for many years in spite of a number of investigations. Principal reasons for this are the relatively limited concentration ranges investigated and the unstable nature of concentrated solutions. In view of the importance of the zinc/alkali electrode system in the energy conversion field the constitution of concentrated solutions of Zn(II) in potassium hydroxide solution is of considerable interest.

The major factor limiting the experimental approach to this problem has been the lack of stability of solutions of high Zn(II) concentration. It is known that a considerable degree of stability can be obtained by the addition of small quantities of potassium silicate and this has enabled examination of zincate solutions to be extended to hitherto inaccessible regions. Extended studies, based on potentiometry, viscometry and laser Raman, infra-red and nuclear magnetic resonance spectroscopy, are presented in this Chapter.

9.2. Experimental

All chemicals were AnalaR, and zinc samples were either 99.95% (for preparation of solutions) or Specpure (for potentiometry). Zinc oxide (Fisons) had been produced by direct combination of the elements, followed by calcination at 1170 K. Water was bidistilled from deionised stock.

9.2.(i) Preparation of Potassium Zincate Solutions

Solutions containing Zn(II) at concentrations up to the normal solubility of ZnO in KOH were obtained at room temperature by mechanical agitation of ZnO with KOH solutions for several months until equilibrium
was reached, as shown by analysis. Precautions were taken to prevent carbonation.

Supersaturated solutions were obtained by dissolving zinc anodically in flowing KOH solution. This procedure was adopted since in stationary solutions the electrode passivated before solutions of high Zn(II) concentration were achieved. In flowing systems passivation is avoided by elimination of high local Zn(II) concentrations at the electrode. Concentration gradients are minimised throughout the solution, thereby facilitating the bulk production of concentrated Zn(II) solutions before the onset of passivation. The presence of a counter electrode at which the cathodic process is the hydrogen evolution reaction can produce undesirable effects arising from the entrapment of hydrogen gas in the cell. These effects were eliminated by use of an air cathode at which the presence of palladium at the three phase interphase catalysed the reaction.

\[ \frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^- \]  

(9.1)
The construction of the electrolytic cell, (Figure 3-3a), electrodes and ancillary apparatus, (Figure 3-6) used in the present experiments are described in Chapter 3.

9.2.(ii) Potentiometric Measurements

These were made in H-type cells (Figure 3-2b) of the type

Zn(Hg) | Zincate solution | Liquid junction | Reference  

(9.2)
The reference was either calomel or mercury oxide. The apparatus used for the determination of potentials is described in Section 3.6.(i).

9.2.(iii) Viscosity Measurements

These were made using an Ostwald viscometer (Type BS188-1937, No. 0720) at a temperature of 298 ± 0.01 K.
9.2.(iv) **Analysis of Solutions**

Alkali solutions were prepared from solid KOH and standardised with sulphamic acid. Additions of potassium silicate (Fisons SG 1.33) were made to the electrolyte solution when required; a 2\% addition corresponding to a concentration of 0.15 mol dm\(^{-3}\) in the bulk solution. Solutions were analysed for zinc content using EDTA with eriochrome black in triethanolamine as indicator.

9.2.(v) **Determination of Spectral Data**

The details of apparatus and techniques used for the determination of spectral data are given in Section 3.6.

9.3. **Results**

9.3.(i) **Solubility Data**

Figure 9-1 shows the maximum Zn(II) concentration which could be obtained using the electrolytic technique (the reported equilibrium solubility data for ZnO in KOH solution\(^{35,83-88}\) are included for comparison). The solutions were not very stable, and within twelve hours of preparation and storage in clean, unscratched Pyrex vessels a cloudiness would appear, developing in the course of a few days into a precipitate of Zn(II)\(_s\), mainly ZnO. The time stability of these solutions was vastly improved in the presence of 0.15 mol dm\(^{-3}\) potassium silicate.

9.3.(ii) **Potentiometric Data**

Figure 9-2 shows the emf of cells (9.2) for unstabilised solutions based on 10 mol dm\(^{-3}\) KOH, the potentials being plotted against logarithmic functions of \([\text{OH}^-]^3\) and \([\text{OH}^-]^4\). The time dependence was examined, but useful data were limited due to the onset of precipitation. Figure 9-3 shows corresponding values for a series of solutions stabilised with potassium silicate. The variation with time of the emf of fresh
FIG. 9-1 Solubility data for Zn(II) species in KOH solutions.

- ZnO at 25°C
- ZnO from ref. 35
- ZnO from ref. 83
- ZnO from ref. 84
- ZnO from ref. 85
- ZnO from ref. 86
- ZnO from ref. 87
- Solutions from the flowing system as above +0.45 mol dm$^{-3}$ silicate
FIG. 9-2 e.m.f. against log[Zn(II)]/[OH]$^{-}$

- Freshly prepared
- After 5h
- After 15h

10 mol dm$^{-3}$ KOH; 23$^\circ$C
FIG. 9-3 e.m.f. against log [Zn(II)]/ [OH]⁺

- Region A-B
- Region B-C

- o freshly prepared
- + after 2 days
- △ after 4 days
- ♦ after 13 days

10 mol dm⁻³ KOH + pot. silicate; 25 °C
supersaturated solutions was studied until there was no further significant change, and was found to be first order as illustrated by Figure 9-4.

9.3.(iii) Viscosity Data

Figure 9-5a shows the viscosity versus Zn(II) concentration plots for a series of silicate stabilised solutions, both when freshly produced and after 45 days ageing. There was a significant viscosity decrease on ageing, particularly for more concentrated solutions. Figure 9-5b shows the variation in viscosity during ageing for 4.29 mol dm$^{-3}$ Zn(II) solution. Again, the change was first order.

9.3.(iv) Nuclear Magnetic Resonance Data

A typical n.m.r. spectra for both the protons in a potassium zincate solution and bidistilled water is shown in Figure 9-6. Figure 9-7 shows the change in chemical shift ($\Delta \delta$) plotted against Zn(II) concentration for a series of stabilised solutions, both immediately after production and after 45 days ageing. Also shown are results from samples made by dissolving ZnO in 10 mol dm$^{-3}$ KOH, both with and without the addition of silicate. The widths of the peaks at half height plotted against Zn(II) concentration (Figure 9-8) correlate, as would be expected, with the viscosity results (Figure 9-5).

9.3.(v) Raman and Infra-Red Spectra

The Raman spectrum of 3.17 mol dm$^{-3}$ Zn(II) in 10 mol dm$^{-3}$ KOH solution is shown in Figures 9-9 and 9-10, no silicate interference being detectable. Details and some comparisons are given in Table 9.1 of Raman data obtained. An intense band lay at 471.2 $\pm$ 0.9 $\Delta$ cm$^{-1}$ (99% confidence limits), very different from the literature values of 484$^{97}$ and 480$^{101}$ $\Delta$ cm$^{-1}$. The frequency was unaffected by KOH concentration (7-14 mol dm$^{-3}$), s.b.w. (5-15 cm$^{-1}$) and Zn(II) concentration (0.25-4.3 mol dm$^{-3}$).
FIG. 9-4 $\log \left( \frac{E_\infty - E_o}{(E_\infty - E_t)} \right)$ versus time for the ageing of a solution of $10 \text{ mol dm}^{-3}$ KOH + $0.15 \text{ mol dm}^{-3}$ pot. silicate + $4.29 \text{ mol dm}^{-3}$ Zn(II)
FIG. 9-5  Viscosity versus [Zn(II)]

○ freshly prepared
△ after ageing

10 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate

Viscosity / cSt

ageing from A to B

[Zn(II)] / mol dm$^{-3}$

0 2.0 4.0 6.0

time / days

0 0.2 0.4 0.6

viscosity / cSt

0 2.0 4.0
FIG. 9-6  A typical n.m.r. spectrum

A typical n.m.r. spectrum is shown in the figure. The spectrum is plotted on a logarithmic scale with intensity in arbitrary units on the vertical axis and P.P.M. on the horizontal axis. The spectrum shows a sharp peak labeled as the sample peak at 4 P.P.M. and a broader peak labeled as the $H_2O$ peak at 5 P.P.M. The separation between the two peaks is denoted by $\Delta \delta$. The area under the curve is shaded to represent the intensity of the peaks.
FIG. 9-7 Change in chemical shift versus [Zn(II)]

- ZnO in 10 mol dm$^{-3}$ KOH
- ZnO in 10 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate
- Zn(II) produced by discharge of Zn in 10 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate
- as above after ageing
FIG. 9-8 n.m.r. peak width versus [Zn(II)]

10 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate; 34°C

n.m.r. peak width (half height) / Hz

[Zn(II)] / mol dm$^{-3}$

freshly prepared

after ageing
FIG. 9-9  Raman spectra in the region 140-700 Å cm⁻¹

10 mol dm⁻³ KOH + 0.15 mol dm⁻³ potsilicate + 3.17 mol dm⁻³ Zn(II)

Raman intensity/ arbitrary units

Frequency / Å cm⁻¹
FIG. 9-10 Raman spectra in the region 2200 - 3800 cm⁻¹

- 10 mol dm⁻³ KOH + 0.15 mol dm⁻³ pot. silicate
- + 3.17 mol dm⁻³ Zn(II)
- H₂O
TABLE 9.1

Raman spectral data for 3.17 M Zn(II) in 10 M KOH solution, and comparison data for CCl₄ and VO₄³⁻.

<table>
<thead>
<tr>
<th>Band frequency / Δ cm⁻¹</th>
<th>Assignment</th>
<th>ρ₁</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td></td>
<td></td>
<td>Present in absence of Zn(II)</td>
</tr>
<tr>
<td>310</td>
<td>KOH/H₂O</td>
<td>~0⁺</td>
<td>Ref.10 quotes 283 and 313 Δ cm⁻¹.</td>
</tr>
<tr>
<td>430</td>
<td>Zn(OH)₄²⁻; V₃</td>
<td>~0.25⁺</td>
<td>Cary 82: ρ₁ = 0.17. Refs. 3 and 10 quote 430 Δ cm⁻¹.</td>
</tr>
<tr>
<td>471.2*</td>
<td>Zn(OH)₄²⁻; V₁</td>
<td>0.05</td>
<td>Cary 82: ρ₁ = 0.012.</td>
</tr>
<tr>
<td>ca 1655</td>
<td>H₂O; V₂</td>
<td></td>
<td>Broad, weak</td>
</tr>
<tr>
<td>ca 2400-3800</td>
<td>O-H stretch (H-bonded)</td>
<td></td>
<td>ca 2900-3700 Δ cm⁻¹ in pure H₂O.</td>
</tr>
<tr>
<td>3620</td>
<td>OH⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>CCl₄; V₁</td>
<td>0.009</td>
<td>0.00</td>
</tr>
<tr>
<td>459</td>
<td>CCl₄; V₄</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>335</td>
<td>VO₄³⁻; V₂; V₄</td>
<td>0.76</td>
<td>0.75</td>
</tr>
<tr>
<td>785</td>
<td>VO₄³⁻; V₃</td>
<td>~0.3</td>
<td>0.75</td>
</tr>
<tr>
<td>825</td>
<td>VO₄³⁻; V₁</td>
<td>0.08</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* Fordyce⁹⁷ and Jackovitz¹⁰¹ concluded tentatively that these bands were depolarised.

† Refs. 97 and 101 quote 484 and 480 Δ cm⁻¹, respectively.
Asymmetry of the peak shows it overlaps another and resolution of the band into its components revealed a minor band at 430 \( \Delta \text{cm}^{-1} \) (Ref. 101 quotes 450 \( \Delta \text{cm}^{-1} \)) with less than 9% of the main band intensity. Widths at half height (42 cm\(^{-1}\)) and band intensity ratios were unaffected by KOH or Zn(II) concentrations, establishing that the bands belong to the same species. For fresh solutions and constant instrument settings, the relative intensity of the 471\( \Delta \text{cm}^{-1} \) band, in terms of its peak height above the baseline, varied linearly\(^97,101\) with Zn(II) concentration up to 3 mol dm\(^{-3}\). Above this value the intensity was approximately constant (Figure 9-11a). However, dilution of a sample having Zn(II) concentrations between 3 and 4.29 mol dm\(^{-3}\) with 10 mol dm\(^{-3}\) KOH, yielded points on the linear region (Figure 9-11a). This figure also shows, in aged solution (several weeks old), a linear intensity variation over the whole range of Zn(II) concentrations. Results for solutions made by dissolving ZnO in 10 mol dm\(^{-3}\) KOH (0.25-1.0 mol dm\(^{-3}\) Zn(II)) correlated excellently with those from cell solutions. Relative band intensities were unchanged when integrated areas of the 471 and 430 \( \Delta \text{cm}^{-1} \) bands were substituted for peak heights of the 471 \( \Delta \text{cm}^{-1} \) band. In contrast, weak bands near 283 and 310 \( \Delta \text{cm}^{-1} \), hitherto assigned\(^97,101,132\) to Zn(OH)\(_4\)^{2-}, were unaffected by Zn(II) concentration. They were, however, still present in the spectra of pure KOH solutions, with an intensity proportional to the KOH concentration. These bands, and analogous ones present in NaOH solutions (299 and 344 \( \Delta \text{cm}^{-1} \)), but not in KNO\(_2\) solution or in water, must therefore be associated with OH\(^-\) and not Zn(II).

A feature of Zn(II) solutions was the high background level below 400 \( \Delta \text{cm}^{-1} \). This has been attributed\(^{101}\) to stray light but use of a triple monochromator (Cary 82; s.b.w. \( =5 \text{ cm}^{-1} \)) with virtually complete stray light rejection confirms that the background is not an artefact. Almost identical high backgrounds are shown by pure KOH solutions and fresh Zn(II) solutions up to 3 mol dm\(^{-3}\). Above this value there is
FIG. 9-11a & b  

(a) Intensity of Raman 471 Å cm⁻² band versus [Zn(II)] at 600 Å cm⁻¹ versus [Zn(II)]

10 mol dm⁻³ KOH + 0.15 mol dm⁻³ pot. silicate
- freshly prepared
- after ageing

• freshly prepared 4.29 mol dm⁻³ Zn(II) diluted to 2.14 and 1.43 mol dm⁻³ respectively

○ freshly prepared 3.76 mol dm⁻³ Zn(II) diluted to 1.25 mol dm⁻³

(b) Background intensity level at 600 Å cm⁻¹/arb. units

- freshly prepared
- after ageing

solution as (a)
a rapid rise in the level which for the most concentrated solutions fluctuated markedly over periods of minutes. In solutions several weeks old (i.e. aged) there was an almost constant low background for all values of Zn(II) concentration (Figure 9-11b).

The infra-red spectra\textsuperscript{97-101} revealed a medium strength band at 435 cm\textsuperscript{-1} (Figure 9-12), and broad, intense absorption in the region 2450-3700 cm\textsuperscript{-1}.

9.4 Discussion

9.4.(i) Solubility Data

Although the solubility of ZnO in KOH solutions has been measured by many investigators\textsuperscript{83-88} the results show much variation, and it has further been noted that the solubility undergoes changes on standing\textsuperscript{133-135}. This may be related to the form of oxide in equilibrium with the saturated solution, but details of the solid phase have not always been given. In spite of this, there is fair agreement for a large proportion of the reported values (Figure 9-1). Most of the solubility data lie on smooth curves, divergent values showing higher solubilities which probably relate to metastable solid phases.

It has long been known\textsuperscript{40,90} that solutions from Zn/KOH cells after discharge have zinc contents substantially higher than those for solutions in equilibrium with solid ZnO. However, earlier results\textsuperscript{40,90,136,137} have been strictly limited by the method of production of the solutions. Only when zinc is anodically polarised at low current densities in flowing alkaline solutions is it possible to achieve the greatest solubility. The passivation charge of such zinc electrodes depends only on the volume of the electrolyte solution (Chapter 5). Since the solutions produced in this way are very unstable and ZnO precipitates slowly on standing, the nature of zinc species in the supersaturated region is of importance. A
FIG. 9-12  Typical infra-red spectra

10 mol dm$^{-3}$ KOH

10 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate + 3.17 mol dm$^{-3}$ Zn(II)
spectral study would be expected to reveal any differences in nature between dilute and concentrated zinicate solutions, and so the whole concentration range must be considered.

9.4.(ii) Raman and Infra-Red Spectra

In dilute solutions of ZnO in aqueous KOH the principal zinc species has been shown potentiometrically to be \( \text{Zn(OH)}_2^- \). However, its structure, as opposed to its composition, is less firmly substantiated by Raman and infra-red studies than would appear to have been the case. If each OH group be regarded as a single unit then a tetrahedral configuration may be postulated, based on the general stereochemistry of zinc. Octahedral zinc cations are known but are not common.

In this work it has been shown that only the Raman bands at 471 and 430 cm\(^{-1}\) belong to \( \text{Zn(OH)}_2^- \). The 471 cm\(^{-1}\) band is completely polarised and so correlates unambiguously with the zinc-oxygen symmetric stretch \( (\nu_1) \). This result also establishes that the point group is \( T_d \) and not \( D_{4h} \) since only for cubic point groups \( (T_d, O_h) \) is \( \rho_\nu = 0 \) for a totally symmetric stretch; for non-cubic point groups \( 0 < \rho_\nu < 0.75 \). The weak band at 430 cm\(^{-1}\) must then belong to the antisymmetric stretch \( (\nu_3) \). It often arises that \( \nu_1 < \nu_3 \) but not always. For example, \( \text{AsO}_4^{3-}, \text{VO}_4^{3-}, \text{MoO}_4^{2-}, \) etc. all have \( \nu_1 > \nu_3 \).

Although it is not conclusive that \( \text{Zn(OH)}_2^- \) is tetrahedral, the new data are not inconsistent with this proposal, as discussed so far. Octahedral structures (incorporating \( 2\text{H}_2\text{O} \)) may be eliminated since there would be either no infra-red bands in common with the Raman ones, or all of them in common. Supporting evidence is the absence of \( \nu_1 \) in the infra-red (Figure 9-12) which, however, does show a peak at 435 cm\(^{-1}\), coincident with \( \nu_3 \) (Raman). The only datum not in accord with a
tetrahedral structure is the $\rho_\perp$ value of 0.2 for the $v_3$ band, (theory value $= 0.75^{145}$). However, the accuracy of $\rho_\perp$ is limited for two reasons. Firstly, the weak 430 $\Delta$cm$^{-1}$ band is partly overlapped by the 471 $\Delta$cm$^{-1}$ band, and secondly, the background below 400 $\Delta$cm$^{-1}$ permits only an approximate determination of the intensity of the minor peak. The comparison data for VO$_4^{3-}$ (Table 9.1) reveal a similar situation for $v_1$ and $v_3$ (intensity ratio $\sim 10$) as exists for Zn(OH)$_4^{2-}$; in the case of $v_2$ and $v_4$ (intensity ratio $v_1/(v_2 + v_4) = 4$), which for VO$_4^{3-}$ are coincident at 335 $\Delta$cm$^{-1}$ and not overlapped, $\rho_\perp$ is within one percent of 0.75.

The $v_2$ and $v_4$ bands of Zn(OH)$_4^{2-}$ should be near 200 and 230 $\Delta$cm$^{-1}$, respectively, by comparison with other tetra-oxo anions$^{143}$. The presence of weak, Raman bands in this region was rendered undetectable by the high background. Furthermore, the region was overlapped by bands of the KOH solution (200-350 $\Delta$cm$^{-1}$ approx.) and of water (100-250 $\Delta$cm$^{-1}$ approx.). The infra-red active $v_4$ would be expected to lie below the cut-off frequency of the spectrophotometer.

Irrespective of the shape and symmetry of Zn(OH)$_4^{2-}$, the relative intensity of the 471 $\Delta$cm$^{-1}$ peak would be expected to vary linearly with [Zn(II)] as was observed up to $\approx 3$ mol dm$^{-3}$. For [Zn(II)] greater than 3 mol dm$^{-3}$ and up to the maximum attainable value (4.29 mol dm$^{-3}$), the approximately constant peak intensity showed that the additional zinc was not present as discrete Zn(OH)$_4^{2-}$ anions. However, no new bands appeared even in the most concentrated solution. This effect has been observed previously$^{101}$ but at a much lower relative level of zinc supersaturation. The high, fluctuating background level of fresh, concentrated solutions, and the constancy of the 471 $\Delta$cm$^{-1}$ peak intensity above 3 mol dm$^{-3}$ reveals that a significant change occurs in the solution towards the attainment of maximum zincate solubility. However, samples
which had stood at room temperature for a month or longer did then show a linear response between band intensity (471 Å cm⁻¹) and [Zn(II)] even up to 4.29 mol dm⁻³ (Figure 9-11a). Furthermore, since the slope of the band intensity vs. [Zn(II)] plot was the same as the slopes for synthetic solutions (ZnO/10 mol dm⁻³ KOH) and for electrochemically formed solutions with [Zn(II)] < 3 mol dm⁻³, it would appear that at equilibrium zinc is always present in the same form, except in fresh solutions with [Zn(II)] > 3 mol dm⁻³. The form in which zinc is present in such solutions must be such that it is readily convertible to Zn(OH)₄²⁻, since dilution of a fresh ~ 4 mol dm⁻³ zinicate solution, for example, with 10 mol dm⁻³ KOH solution to bring the [Zn(II)] below 3 mol dm⁻³ yielded a 471 Å cm⁻¹ band intensity on the linear part of the plot (Figure 9-11a). The above evidence indicates that under conditions of high concentration, Zn(OH)₄²⁻ anions, together with OH⁻ and water molecules produce, at first, polymeric species which break down to Zn(OH)₄²⁻ slowly on standing (ageing effect), or rapidly on dilution. There is analogous behaviour, with respect to polymerisation and ageing, in alkaline solutions of the aluminate ion[139,146].

9.4.(iii) Nuclear Magnetic Resonance and Viscosity Data

The n.m.r. investigation reveals that there is only a single proton peak at all values of [Zn(II)] and that its displacement (Δδ) from its position in the spectrum of pure 10 mol dm⁻³ KOH solution[98] is a function of [Zn(II)] (Figure 9-7). There must, therefore, be rapid proton exchange among all the species, the observed increase in peak bandwidth with [Zn(II)] (Figure 9-8) being attributable to the concomitant increase in solution viscosity[147] (Figure 9-5). However, Figure 9-7 shows two breaks in the plot of Δδ versus [Zn(II)], near 1.25 and 2.95 mol dm⁻³, showing that there are small, additional constant changes in the average proton environment introduced at these concentrations. That no
corresponding breaks are found in the plot of Raman band intensity against \([\text{Zn(II)}]\) (Figure 9-11a) is understandable if the zinc atom is always surrounded by four oxygens as in \((4\text{OH}^-)\); \((3\text{OH}^-, \text{H}_2\text{O})\); \((2\text{OH}^-, 2\text{H}_2\text{O})\), with proton exchange making the oxygens equivalent. The great increase in width of the O-H band (Figure 9-10) near \(3300\Delta \text{cm}^{-1}\) in KOH and KOH-zincate solutions, compared with that in pure water shows greatly enhanced hydrogen bonding in which \(\text{Zn(OH)}_4^{2-}\) will participate.

9.4.(iv) Potentiometric Data

Confirmation of the hypothesis that tetrahedrally coordinated zinc species other than \(\text{Zn(OH)}_4^{2-}\) are formed as \([\text{Zn(II)}]\) increases is provided by "electrochemical" evidence as may be seen from the potentiometric measurements plotted in Figure 9-2a. At low \([\text{Zn(II)}]\) the data conform to the reaction.

\[
\text{Zn(OH)}_4^{2-} + 2\text{e}^- \rightarrow \text{Zn} + 4\text{OH}^- \quad (9.3)
\]

occurring at the negative electrode. Thus the plot of emf vs \(\log_{10}[\text{Zn(II)}]/[\text{OH}^-]^4\) has the slope expected for a two-electron transfer reaction. As \([\text{Zn(II)}]\) increases above 1.25 mol dm\(^{-3}\), in initially 10 mol dm\(^{-3}\) KOH solution, a break occurs in the emf vs \(\log_{10}[\text{Zn(II)}]/[\text{OH}^-]^4\) plot. Below 1.25 mol dm\(^{-3}\) Zn(II) concentration the slope

\[
\frac{\Delta E}{\Delta \log_{10}\left[\frac{[\text{Zn(OH)}_4^{2-}]}{[\text{OH}^-]^4}\right]}
\]

is \(\log_e \frac{10 \cdot \text{RT}}{2F}\), i.e. 29 mV; at higher \([\text{Zn(II)}]\) this slope is decreased. To maintain a prelogarithmic factor in the Nernst equation corresponding to a two-electron charge transfer reaction it is necessary to consider the slope

\[
\frac{\Delta E}{\Delta \log_{10}\left[\frac{[\text{Zn(OH)}_3^-]}{[\text{OH}^-]^3}\right]}
\]
as shown in the inset (Figure 9-2b). This region of [Zn(II)] extends to ~2.0 mol dm\(^{-3}\) and thereafter the solutions become unstable on standing, typified by the data of Figure 9-2a, where after 15h solutions with [Zn(II)] greater than ~2.0 mol dm\(^{-3}\) had precipitated.

Figures 9-3a and b show the effect of the 0.15 mol dm\(^{-3}\) potassium silicate which makes possible the preparation of solutions with [Zn(II)] as high as 4.29 mol dm\(^{-3}\). The general features of Figure 9-3 parallel those of Figure 9-2 but above 3.0 mol dm\(^{-3}\) a region of unique electroactivity was observed. Initially, on preparing solutions with Zn(II) concentrations 3.0 - 4.29 mol dm\(^{-3}\), the emf of the cell (9.2) was independent of [Zn(II)], but on standing the potential underwent a first order change (Figure 9-4), attaining an approximately constant value after 14 days. A two-electron charge transfer can be related with the zinc electrode reaction in this concentration region after ageing, by considering the function

\[
\frac{\Delta E}{\Delta \log_{10} \frac{[\text{Zn(OH)}_2]}{[\text{OH}^{-}]^2}}
\]

(Figure 9.3c). For fresh solutions the only conclusion that can be drawn from Figure 9-3 is that zinc enters as an electronegative species in the highest concentration region.

It is proposed that the data conform to three separate electrode reactions, occurring consecutively as the zinc electrode is discharged.

(a) At low [Zn(II)], zinc discharges as the tetrahydroxy zincate anion:

\[
\text{Zn} + 4\text{OH}^{-} \rightarrow \text{Zn(OH)}_{4}^{2-} + 2\text{e}^{-} \quad (9.4)
\]

(b) At intermediate concentrations, zinc discharges as the trihydroxy anion:

\[
\text{Zn} + 3\text{OH}^{-} + \text{H}_2\text{O} \rightarrow [\text{Zn(OH)}_3(\text{H}_2\text{O})]^{-} + 2\text{e}^{-} \quad (9.5)
\]
(c) At high concentrations, zinc discharges as the neutral dihydroxy species which is initially electroinactive. However, on standing the solution species attain equilibrium with the electrode according to

\[ Zn + 2OH^- + 2H_2O \rightleftharpoons [Zn(OH)_2(H_2O)_2] + 2e^- \]  

(9.6)

The precise nature of the electroinactive species in stabilised solutions of highest Zn(II) is difficult to determine. The viscosity measurements (Figure 9-5) are compatible with the zinc species in fresh solutions being considerably larger than in aged solutions, and possibly of colloidal dimensions. The dispersion medium is of complex ionic structure and water molecules would certainly be incorporated in any micelles. The suggestion of colloidal character, originally made by Flerov\textsuperscript{92}, is supported by the fact that in solutions free of suitable stabiliser the electroinactive region is observed only over a very short period. The present data provide the first confirmation that such species can be detected in these solutions by physical methods. The change in viscosity follows the same pattern as does the change in emf of cells (9.2) in the higher concentration region, consistent with the idea that the same process is responsible for both effects.

The formal equations (9.5) and (9.6) may well be written in a number of ways in so far as the mechanistic generation of tri- and di-hydroxy species is concerned. For example, equations of the type

\[ Zn + 3Zn(OH)_4^{2-} + 4H_2O \rightleftharpoons 4 Zn(OH)_3(H_2O)^- + 2e^- \]  

(9.7)

and

\[ Zn + 2 Zn(OH)_3(H_2O)^- + 4H_2O \rightleftharpoons 3 Zn(OH)_2(H_2O)_2^- + 2e^- \]  

(9.8)

may represent reactions at the electrode. In the present study this is immaterial.

9.5. Conclusions

At high zincate the formation of condensed polyzincate species produces anomalies in solution electro-activity, viscosity, and spectral characteristics.
CHAPTER 10

THE DISCHARGE OF THE ZINC/AIR SLURRY CELL

10.1 Introduction

High rates of discharge at high efficiency are required for the commercial exploitation of the zinc/air system. For many applications the cells should be capable of rapid recharge, either mechanically or electrically. Although cells with replaceable anodes can be rapidly recharged, this is not a particularly safe or easy process. A recently introduced device which is both easy to recharge and has high efficiency at high discharge rates is the slurry cell. In this a slurry of electrolyte solution (KOH) and zinc dust is pumped between a conventional air electrode and an electrically conducting "pick-up" grid. When current is taken from the cell, finely divided zinc particles in contact with the grid are converted into a soluble Zn(II) complex; oxygen in the air provides the cathodic counterparts to this anodic reaction through its reduction to either hydroxide ion or oxide in the case of deep discharge to reach the passive condition. Although several patent specifications have appeared dealing with this type of device there is a lack of well established performance data.

A further area in which information is required concerns the effect of extender additives on slurry cell performance. Here interest has been recently revived owing to the discovery that, under ceratin conditions, discharge capacity appears to be boundless when particular mixed solutions of potassium silicate and hydroxide are used (Chapter 5).

In this chapter the results of discharge capacity measurements on slurry cells using electrolytes with and without the addition of capacity extenders are reported.
10.2 Experimental

10.2.(i) Electrolytic Cell and Solution Circuit

The experimental system (Figure 10-1) is similar to that shown in Figure 3-6, however, provision was made for the addition of Zn dust. The cell, Figure 3-3b, was constructed of Perspex and contains an electrode compartment of dimensions 0.75 x 2 x 15 cm. The anode was a silver-plated expanded nickel sheet (250 holes cm$^{-2}$ and 0.02 cm thick supplied by Expanded Metals, Ltd.). The current from the anode was conducted to a rhodium-plated silver sheet in contact with the anode. The cathode was an air electrode, area 30 cm$^2$, which has been described in Section 3.1.(iii). This particular electrode structure is the subject of patents 149 assigned to Shell Research, Limited.

The electrolyte solution is circulated by a centrifugal pump (Charles Austen Pumps, Ltd., Model C25). The solution was pumped up through the cell to ensure uniform flow and to eliminate pockets of trapped air, and was then returned to the reservoir which was purged with nitrogen to remove carbon dioxide.

The electrical circuit and electrolyte system have been described previously in Chapter 3.

10.2.(ii) Procedure

Prior to use the air electrode was impregnated under vacuum with KOH electrolyte solution to ensure that the three-phase interface between the air/catalyst/electrolyte occurs within the catalyst layer. The cell was assembled as shown in Figure 3-3b and the cathode was pressurised with air at 13 kN m$^{-2}$. Zinc powder (AnalaR, B.D.H.) was added to the electrolyte contained in the reservoir and the slurry was circulated through the system. The open-circuit voltage was allowed to stabilise before the experiment was commenced by closing the electrical circuit with the
FIG. 10-1 The zinc-air slurry cell flowing system circuit
current at a pre-set value. The passivation time was determined from the beginning of the experiment to the time when the potential between the zinc anode and the air cathode dropped abruptly; as this drop in potential was of the order of 0.7 V, the point of passivation was unequivocal. The quantity of zinc powder required by the cell at its normal operating current density of 0.033 A cm\(^{-2}\) (based on twice the geometric area of the anode expanded metal) was calculated and this amount was added at half hourly intervals. At the point of passivation no further increase in performance could be obtained by the further addition of zinc powder.

After the zinc electrode had passivated the solution was immediately removed from the cell and analysed for zinc content as described previously.

10.3 Results

Figure 10-2 shows the results of galvanostatic polarisation of the system at a constant current density of 0.033 A cm\(^{-2}\) for a series of KOH concentrations up to 14 mol dm\(^{-3}\). The points on the graph connecting KOH concentration and passivating charge lie close to a straight line passing through the origin. Figure 10-3 shows the analyses of the final electrolytes immediately after the termination of the experiments represented by Figure 10-2. There was no precipitation of Zn(II) species, before the analyses were conducted, even though the solutions were supersaturated with Zn(II) species, compared with thermodynamic solubility data of zinc oxide in KOH electrolyte. Figure 10-4 shows typical open-circuit voltages of 23°C after the potential has stabilised, together with the initial (on-load) potentials measured at a current density of 0.033 A cm\(^{-2}\). It can be seen that generally the potential with an addition of 0.15 mol dm\(^{-3}\) potassium silicate is of the order of 20 - 30 mV lower than without silicate. Both with and without the addition of potassium silicate the on-load
FIG. 10-2 Effect of [KOH] on passivating charge; 0.033 A cm$^{-2}$; 23 °C
FIG. 10-3  Analyses of final solution (Zn(II) species) corresponding to experiments in fig. 10-2.
FIG. 10-4 Effect of [KOH] on cell voltage; 0.033 A cm$^{-2}$
potential tends to rise to a maximum at 10 - 12 mol dm\(^{-3}\) KOH and falls off as the KOH concentration is increased to 14 mol dm\(^{-3}\). Figure 10-5 shows the effect of a 0.15 mol dm\(^{-3}\) addition of potassium silicate on the KOH concentration/discharge characteristics of the cell. The passivation charge is increased by the addition of potassium silicate at all concentrations of KOH. Remarkably, however, at KOH concentrations around 3 mol dm\(^{-3}\) KOH the passivating charge is increased proportionally more than at other concentrations of KOH.

Figure 10-6 shows the analyses of the final electrolytes after termination of the experiments represented by Figure 10-5. The solutions in the region of the localised maximum were centrifuged before analysis. The Zn(II) concentrations for high KOH concentrations with added silicate ions are generally much higher than corresponding ones (Figure 10-3) without silicate. In concentrations of KOH corresponding to the localized maximum region, the Zn(II) concentrations in the centrifuged solutions are almost identical to those in solutions without added silicate ions. Also shown in Figure 10-6 are the calculated faradaic yields of Zn(II) species. It can be seen that the calculated Zn(II) concentrations are much greater than the experimental values in the localized maximum region, corresponding to the production of solid zinc oxide in the electrolyte solution. At high KOH concentrations the two values tend to converge.

Figure 10-7 shows the effect of the addition of 12 g lithium hydroxide dm\(^{-3}\) of electrolyte on the discharge characteristics of the cell at 0.033 A cm\(^{-2}\), from which it can be seen that the passivating charge is increased by the addition of the lithium hydroxide at all concentrations of KOH.

Figure 10-8 shows the effect of discharging the cell in electrolyte of constant hydroxyl ion concentration but substituting the lithium ion
FIG. 10-5 Effect of [KOH] on passivating charge; 0.15 mol dm$^{-3}$ pot. silicate; 0.033 A cm$^{-2}$. 

![Graph showing the effect of KOH concentration on passivating charge. The x-axis represents [KOH] in mol dm$^{-3}$, and the y-axis represents passivating charge in C cm$^{-2}$ (x10$^2$). There is a peak at around 0.5 mol dm$^{-3}$, followed by a decrease and then an increase as the concentration increases.]
Analysis of final solutions (Zn(II) species) and faradaic yields corresponding to experiments in fig. 10-5.
FIG. 10-7 Effect of [KOH] on passivating charge; 0.285 mol dm$^{-3}$ LiOH; 0.033 A cm$^{-2}$; 23°C
FIG. 10-8 Effect of replacing potassium ion by lithium ion on passivating charge; 0.033 A cm\(^{-2}\); 23°c; \([\text{OH}^-]\) = 7 mol dm\(^{-3}\)
for the potassium ion starting from a KOH concentration of 7 mol dm\(^{-3}\) at a constant current density of 0.033 A cm\(^{-2}\). The passivating charge initially increases with the substitution of lithium ion for potassium ion but then a plateau value for passivating charge is reached.

10.4 Discussion

The passivating charge/KOH concentration curve, Figure 10-2, based on 0.10 dm\(^3\) KOH electrolyte is somewhat lower than that obtained from a static vertically orientated electrode in a flowing system (Chapter 5). Thus in a KOH concentration of 7 mol dm\(^{-3}\) the slurry cell gave an output of 396 C cm\(^{-3}\) compared with an output of 420 C cm\(^{-3}\) based on a volume of 0.10 dm\(^3\) of electrolyte with the plate cell of Chapter 5. The increase in the Zn(II) concentration of the electrolyte solution at the end of the discharge period indicated that the whole of the faradaic charge obtained in the anodic reaction could be accounted for by the oxidation of the zinc dust on the pick-up grid. The concentrations of the final electrolyte obtained from discharged cells were considerably higher than the concentration of Zn(II) in solution obtained by shaking zinc oxide with KOH electrolyte. Thus it seems that a considerable degree of supersaturation occurs during the discharge process. This supersaturation is similar to the behaviour observed with experiments on massive zinc in flowing electrolyte. The degree of supersaturation is rather less in the case of the slurry cell than in the case of the massive electrode cell, which indicates that the electrode is operating at a slightly reduced faradaic efficiency with respect to the KOH electrolyte. The efficiency based on zinc-dust utilisation is also rather less than 100% although this efficiency can be made as close to 100% as is desired by the addition of smaller incremental quantities of zinc-dust fuel. A feasible way of optimising this efficiency would be to add incremental
quantities of zinc dust when the potential fell to a predetermined level.

The addition of potassium silicate to the system permits a further extension of discharge capacity (based on electrolyte volume) to be obtained. A comparison of Figures 10-2 and 10-5 shows this to be the case. As with the experiments with massive anodes, in the region of 3 mol dm\(^{-3}\) KOH, a localized maximum in the passivating charge curve was observed. This behaviour differed, however, from that previously reported for massive zinc electrodes in that the passivating charge curves did not apparently go to infinity, rather here a well-defined maximum was obtained at 3 mol dm\(^{-3}\) KOH at a passivating charge of more than three times the value in the same KOH concentration without addition of potassium silicate. It has already been proposed (Chapter 5) that the effect of the silicate ion is to produce a film at the zinc electrode/electrolyte interface through which the reaction occurs. This suggestion was substantiated by galvanostatic pulse and impedance measurements. At a KOH concentration of 3 mol dm\(^{-3}\) the Zn(II) species appear to transfer through this film in such a way that the precipitation of zinc oxide does not occur at the electrode, but occurs in solution so that the anode remains active. In the slurry cell the situation is somewhat different from in the plate cell in that the discharge may be terminated if electrical contact is destroyed between the zinc particle and the pick-up grid. It seems likely that in the slurry cell, the loss of electrical contact between the pick-up grid and the zinc particles arises from the discharge terminating process in the region where zinc oxide is precipitated into the solution. In support of this proposal is the observation that milk-white, two-phase systems of zinc oxide in potassium zincate, so characteristic of the "infinite" region for the plate cell, are not observed to the same extent in the slurry cell. It is possible
that the final structure of the zinc particle is that of a zinc core surrounded by a silicate layer (analogous to a viscous electropolishing layer) insulated from the grid by a layer of precipitated zinc oxide. In the massive anode case this layer would be swept away by the flowing electrolyte. The explanation for the local maximum appears to be substantially the same as given previously. At high KOH concentrations potassium silicate acts as an extender in the classical way.

Since lithium ions are not expected to absorb onto the surface of a zinc electrode, it is difficult to explain the extension of capacity, as seen in Figure 10-7 in terms of adsorption of lithium ions. Experimental results with lithium hydroxide support the hypothesis that lithium ions are not adsorbed, as the electrode capacitance is not significantly diminished in the region of actual dissolution as observed in solutions containing silicate ions. The explanation in this case must lie in the effect of lithium ion increasing the capacity of the electrolyte for electrode products based on Zn(II).

In the classical extender region at high KOH concentrations, the effect of potassium silicate and lithium hydroxide on the discharge characteristics of the slurry cell concentrations can be considered from the point of view of the strength of the hydrate shell around the micelles. In the case of potassium silicate the protection of the Zn(II) species takes place as a result of the chemisorption of the SiO$_2^{2-}$ ions into the inner layer of the micelles. The SiO$_2^{2-}$ ion has a closely bound hydrate shell which, upon penetration into the micelle, imparts extra stability by increasing the strength of the hydration sheath.

It is apparent that lithium hydroxide acts by a similar type of mechanism$^{92}$. The energy of hydration of the lithium ion is greater than that of the potassium ion. The replacement of potassium ion by lithium ion in the inner layer of a micelle gives extra stability to the micelle.
by a greater hydration of the species. The effectiveness of relatively small amounts of lithium ion, as seen in Figure 10-8 indicates that these ions can readily replace the potassium ion from the inner layer of the micelle.

10.5 Conclusions

1. The slurry cell can be operated to give a high faradaic yield.

2. The passivating charge, i.e. discharge capacity, of the slurry cell may be increased by the addition of either potassium silicate or lithium hydroxide to the electrolyte.

3. Of these extenders potassium silicate is by far the more effective.

4. At a potassium hydroxide concentration of 3 mol dm\(^{-3}\) with the 0.15 mol dm\(^{-3}\) addition of potassium silicate solution, an interesting localized maximum occurs in the passivating charge/concentration curve.
CHAPTER 11

APPLICATION OF THE SLURRY REGION TO A COMMERCIAL SYSTEM

11.1 Introduction

It has been shown in Chapter 5 that the addition of small amounts (0.15 - 0.45 mol dm\(^{-3}\)) of potassium silicate to the electrolyte solution used in zinc/air cells creates a narrow range of alkali concentrations where zinc can be galvanostatically polarised, below a critical current density, without passivation occurring.

It was thought of interest to approach a commercial producer of zinc/air cells with this discovery with the objective of obtaining data from commercial zinc/air systems. Such an organisation was Energy Conversion, Limited, (E.C.L.). This chapter records the data obtained from experiments conducted to assess the performance characteristics of zinc/air cells made by E.C.L. using electrolytes based on 3 mol dm\(^{-3}\) KOH solutions containing potassium silicate. Also reported are the results of experiments made to make the electrolyte discovery a more viable commercial proposition in the light of the conclusions of E.C.L.

11.2 Experimental

11.2.(i) E.C.L. Zinc/Air Cell Tests

All cell components used were standard E.C.L. production materials. Potassium silicate solution (B.D.H., S.G.1.33) was added to the cell electrolyte solution when required. The discharges were divided into two parts :-

(a) Discharge of standard "D" cells\(^{150}\): Standard "D" cells were discharged in different environmental conditions with 3 mol dm\(^{-3}\) KOH solution both with and without the addition of potassium silicate.
(b) Discharge of various anode types in flat vertically orientated Perspex cells: Perspex cells were used to discharge various types of anode with an air cathode as the counter electrode. The cathode consisted of a nickel mesh screen (80 - 100 mesh) which carries a catalyst of silver graphite, mixed with a proportion of particulate P.T.F.E. in order to render the catalyst layer hydrophobic and ensure a good interface between catalyst/electrolyte/air which diffuses through the porous structure. The electrode is backed on the air side with a layer of P.T.F.E. (unsintered) tape which acts as an additional hydrophobic barrier whilst still being sufficiently porous to allow air to permeate through to the catalyst layer. The maximum current obtainable from the electrode is normally directly proportional to the permeability of the P.T.F.E. tape. The volume of electrolyte used in the Perspex cell was 0.20 dm$^{-3}$ and the area of the air cathode was 36 cm$^2$.

Three types of anode were investigated in the vertical Perspex cells:

(i) standard E.C.L. "D" size anodes;
(ii) solid zinc rod (99.999% pure) 13 cm long and 0.65 cm diameter;
(iii) anodes made by coiling zinc mesh, 5 cm x 20 cm and weighing about 9g, into a cylinder.

11.2.(ii) Experiments With Added KF

The zinc/air cell (Figure 3-3a) and all ancillary equipment have been described previously in Chapter 3. The working and counter electrodes have been described in Section 3.1.(iii). The operating procedure was the same as that outlined in Chapter 5. Viscosity determinations were made using an Ostwald viscometer (Type B.S.188-1937, No. 0720) at a temperature of 298 ± 0.01K.
When determining the vapour pressure by the Ramsey and Young\textsuperscript{29}, method, a constant pressure is maintained and the temperature at which the liquid boils under that pressure is determined. A diagram of the apparatus is shown in Figure 3-10 and the method has been described previously\textsuperscript{30}. In the present experiments a manostat was used for accurate control of the pressure.

11.3 Results

11.3.(i) E.C.L. Zinc/Air Cell Tests

The data obtained by discharging E.C.L. standard "D" cells under various experimental conditions are given in Table 11.1. The results obtained from the vertically orientated Perspex cell using various anode types are given in Table 11.2.

11.3.(ii) Experiments With Added KF

Figure 11-1 shows vapour pressure data for the electrolyte solutions investigated. The effect of potassium silicate and potassium fluoride additions on the vapour pressure of 3 mol dm\textsuperscript{-3} KOH solution is shown and compared with the vapour pressure data for 8 mol dm\textsuperscript{-3} KOH solution. Table 11.3 summarises the data obtained from vapour pressure determinations.

The effect of varying the KF concentration of zinc/air cell electrolytes solutions, based on 3 mol dm\textsuperscript{-3} KOH solution, on the discharge characteristics is shown in Figure 11-2. Figure 11-3 shows the effect of varying the potassium silicate concentration of the ternary electrolyte solution on the discharge characteristics of the zinc/air cell. The effect of KF on the viscosity of electrolyte solutions based on 3 mol dm\textsuperscript{-3} KOH was investigated and the data obtained is shown in Figure 11-4.
<table>
<thead>
<tr>
<th>[KOH] mol dm⁻³</th>
<th>Potassium silicate addition mol dm⁻³</th>
<th>Relative humidity %</th>
<th>Discharge temperature °C</th>
<th>Discharge current A</th>
<th>Cell capacity A h⁻¹</th>
</tr>
</thead>
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<tr>
<td>3.0</td>
<td>-</td>
<td>20-40</td>
<td>25</td>
<td>2.0</td>
<td>9.4</td>
</tr>
<tr>
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<td>20-40</td>
<td>25</td>
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<td>7.4</td>
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<tr>
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<td>25</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
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<td>25</td>
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<tr>
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<td>-</td>
<td>90</td>
<td>-15</td>
<td>0.25</td>
<td>5.2</td>
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<td>0.15</td>
<td>90</td>
<td>-15</td>
<td>0.25</td>
<td>3.1</td>
</tr>
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<td>[KOH] mol dm$^{-3}$</td>
<td>Potassium silicate addition mol dm$^{-3}$</td>
<td>Anode type</td>
<td>Discharge current A</td>
<td>Theoretical discharge capacity Ah$^{-1}$</td>
<td>Discharge capacity Ah$^{-1}$</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------------------------------</td>
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<td>---------------------</td>
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<td>-------------------------------</td>
</tr>
<tr>
<td>3.0</td>
<td>-</td>
<td>solid zinc rod</td>
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<td>3.5</td>
<td>1.1</td>
</tr>
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<td>0.15</td>
<td>'D' size porous anode</td>
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<td>-</td>
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<td>1.8</td>
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<tr>
<td>3.0</td>
<td>0.15</td>
<td></td>
<td>0.20</td>
<td>5.2</td>
<td>4.0</td>
</tr>
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</table>

Table 11.2
3 mol dm$^{-3}$ KOH + 0.15 mol dm$^{-3}$ pot. silicate
3 mol dm$^{-3}$ KOH + 30 mol dm$^{-3}$ KF
30 mol dm$^{-3}$ KOH + 30 mol dm$^{-3}$ KF
8 mol dm$^{-3}$ KOH

Temperature / $10^3 K$

Log pressure / mmHg

FIG. 11.1: Vapour pressure versus temperature.
Table 11.3

<table>
<thead>
<tr>
<th>[KOH] mol dm⁻³</th>
<th>[KF] mol dm⁻³</th>
<th>Vapour press. at 298 K mm Hg</th>
<th>$\alpha_{\text{H}_2\text{O}}$</th>
<th>Slope of $\log p$ vs $T^{-1}$ K</th>
<th>Latent heat of vaporisation kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>-</td>
<td>22.9</td>
<td>0.967</td>
<td>2.04 x 10³</td>
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<td>3.0</td>
<td>1.0</td>
<td>20.4</td>
<td>0.861</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>2.0</td>
<td>19.5</td>
<td>0.822</td>
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<td>4.49</td>
</tr>
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<td>18.2</td>
<td>0.768</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>4.0</td>
<td>15.9</td>
<td>0.671</td>
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<td>4.21</td>
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<td>5.0</td>
<td>13.8</td>
<td>0.583</td>
<td>2.48 x 10³</td>
<td>4.75</td>
</tr>
<tr>
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<td>-</td>
<td>15.1</td>
<td>0.637</td>
<td>2.26 x 10³</td>
<td>4.34</td>
</tr>
<tr>
<td>WATER</td>
<td></td>
<td>23.7</td>
<td>1.000</td>
<td>-</td>
<td>2.25</td>
</tr>
</tbody>
</table>
FIG. 11-2  Effect of [KF] on passivating charge;
3.0 mol dm$^{-3}$ KOH; 0.15 mol dm$^{-3}$ pot.
silicate; 0.4 cm$^{-1}$; 0.04 A cm$^{-2}$
FIG. 11-3  Effect of [potassium silicate] on passivating charge; 3.0 mol dm$^{-3}$ K$_2$O; 4.0 mol dm$^{-3}$ KF; 0.4 cm$^{-1}$; 0.04 A cm$^{-2}$
FIG. 11-4  Effect of [KF] on the viscosity of alkaline solutions; 3.0 mol dm$^{-3}$ KOH; 25°C
11.4 Discussion

11.4.(i) E.C.L. Zinc/Air Cell Tests

E.C.L. standard "D" cells were filled with 3 mol dm$^{-3}$ KOH solution both with and without the addition of 0.15 mol dm$^{-3}$ potassium silicate. The cells were discharged at 2A until the on-load potential dropped to a predetermined level of 900mV. The time to this potential being regarded as the time of useful discharge. The performance of cells discharged at 25$^\circ$C and 20 - 40% relative humidity are shown in Table 11.1.

A standard "D" cell filled with 8 mol dm$^{-3}$ KOH solutions would be expected to give a performance of between 13 and 16 Ah$^{-1}$ which is superior to the performances of cells filled with electrolyte solutions based on 3 mol dm$^{-3}$ KOH. A post-discharge examination of the cells showed that the electrolyte solution had dried out. The relative humidity above a 3 mol dm$^{-3}$ KOH solution is of the order of 89%, and that of a normal laboratory is of the order of 20 - 40% R.H. Under these conditions standard "D" cells filled with electrolyte solutions based on 3 mol dm$^{-3}$ KOH would rapidly lose water vapour through the permeable air cathode. The loss of water in the cells results in an increase in the electrolyte concentration, which in the case of electrolytes containing potassium silicate would prove to be disastrous because the effectiveness is only over a small range of KOH solution concentration. Therefore, it is important to maintain the concentration of the KOH solution inside the cell constant at low humidities to observe the full effect of additions of potassium silicate.

A humidity cabinet was set to operate at 90% R.H. and a further series of "D" cells were discharged at 2A and 90% R.H. The data obtained from these experiments are given in Table 11.1. Cells, filled with 3 mol dm$^{-3}$ KOH solution both with and without the addition of potassium silicate, discharged at 90% R.H. appeared to retain a constant volume of electrolyte.
An examination of the porous anodes from discharged standard "D" cells indicated that the addition of potassium silicate caused zinc oxide to be precipitated from the electrolyte solution into the pores of the anode, instead of being deposited into the bulk of the electrolyte as occurs in the flowing system (Chapter 5). This precipitation probably caused early passivation of the anode material. A larger addition of potassium silicate aggravated this effect making the discharge characteristics even less attractive (Table 11.1). A lowering of the discharge temperature produced a further reduction in the discharge capacity of standard "D" cells filled with electrolyte solutions based on 3 mol dm$^{-3}$ KOH as can be seen from the data of Table 11.1.

Solid zinc rods were discharged in vertically orientated Perspex cells at 200mA in stationary electrolyte solutions. Confirmation of the effects observed with the flowing system (Chapter 5) was obtained when solid zinc rods were discharged in potassium silicate containing electrolyte solutions based on 3 mol dm$^{-3}$ KOH. A slurry region was detected, the zinc oxide falling away from the electrode even in stationary solutions, and the discharge was only terminated by the utilisation of all the zinc anode. A constant cell potential was observed from just after the start of the slurry region to the time of dissolution of all the anode material. However, the slight fall-off of potential of about 30 - 40 mV obtained previously (Chapter 5), just before the onset of the slurry region, was not observed. Inspection of the anode during discharge revealed that they had an electro-polished appearance similar to that observed in the flowing system.

Experiments with E.C.L. standard "D" cell zinc anodes carried out in the Perspex cell did not reflect the results obtained with the solid zinc rod electrodes (Table 11.2) rather, they were similar to those obtained with standard "D" cells. Here, again premature passivation
of the anode material was caused by the precipitation of zinc oxide into the highly porous structure of the anode. A possibility of premature passivation being caused because "D" cell electrodes are amalgamated with 3% Hg was eliminated by conducting experiments with amalgamated solid zinc rods. Identical results to those of unamalgamated zinc rod electrodes were obtained showing that the amalgamation process does not effect the slurry behaviour.

It is difficult to alter the porosity of standard "D" cell zinc anodes, however, slightly porous anodes were made by coiling pieces of zinc mesh into a cylinder. When discharging these slightly porous anodes in silicate containing 3 mol dm⁻³ KOH solutions a slurry region was observed. However, the discharge did not reach the theoretical capacity for the weight of the anode (Table 11.2) because preferential dissolution at the interface of the electrolyte/air/anode caused the anode to sever at this interface thus terminating the dissolution process. However, before this occurred the cell potential had reached a constant value and, but for this mishap the discharge would presumably only have been terminated by the utilisation of all the zinc mesh. In spite of this unforeseen experimental difficulty the ability of silicate containing 3 mol dm⁻³ KOH solutions to produce a slurry region with slightly porous anodes was demonstrated.

It was concluded by E.C.L. that the major difficulty in using 3 mol dm⁻³ KOH solution with an addition of 0.15 mol dm⁻³ potassium silicate in their zinc/air cells was the rate of water transfer through the cathode. The humidity range under which these cells operate makes the use of electrolyte solutions based on 3 mol dm⁻³ KOH impractical because of the danger of the electrolyte solution drying out. The slurry region is only observed over a very narrow range of KOH concentrations (Chapter 5), therefore, any changes in KOH concentration
caused by water loss through the air cathode would reduce the ability of the system to produce a slurry region. If the operating concentration range could be extended to 7-8 mol dm$^{-3}$ KOH or the solution could be made to have a vapour pressure comparable with that of 7-8 mol dm$^{-3}$ KOH solution, it would be advantageous to use this solution in E.C.L. primary zinc/air cells. The use of this solution would mean that the costly, difficult to fabricate, inconsistent, present porous anodes could be replaced by solid rod or mesh type anodes. However, until these improvements in the solutions properties have been made no advantage can be foreseen in using solutions based on 3 mol dm$^{-3}$ KOH containing potassium silicate.

11.4.(ii) Experiments With Added KF

From the findings and conclusions of E.C.L. it became apparent that solutions based on 3 mol dm$^{-3}$ KOH were unsuitable in their present form for use in zinc/air cells with "air breathing" cathodes. It was, therefore, necessary to lower the vapour pressure of the electrolyte solutions based on 3 mol dm$^{-3}$ KOH. An inert salt like KF, added to the solution would lower the vapour pressure. It was of interest to investigate both the extent of this lowering and the effect of the added salt on the discharge behaviour of the system.

The vapour pressure measurements (Figure 11-1) show that the addition of KF does lower the vapour pressure of 3 mol dm$^{-3}$ KOH solutions indicating a lowering of the activity of water according to

$$a_{H_2O} = \frac{P}{P_o}$$  \hspace{1cm} (11.1)

where $P_o$ is the vapour pressure of pure water at temperature T.

Calculations$^{69}$ show that at about 7.5 mol dm$^{-3}$ KOH solution all the water molecules are incorporated in the hydration sheath of either the potassium ion or the hydroxyl ion. It is to be expected that an
iso electronic ion like flouride would behave in a similar way to hydroxyl ions. It is most convenient to examine the energetics of the hydration process by determining the heat of vaporisation of the water molecules from the system of interest. The ratio of change of vapour pressure with change in temperature is closely related to the latent heat of vaporisation of the liquid by the Clausius-Clapeyron equation:

$$\frac{d \log P}{dT} = \frac{L}{RT^2}$$  \hspace{1cm} (11.2)

where \(L\) is the latent heat. Assuming that over a small temperature range, \((T_2 - T_1)\), the latent heat of vaporisation is constant, equation (11.2) on integration becomes

$$\frac{\log P_2}{P_1} = \frac{L (T_2 - T_1)}{R (T_2 T_1)}$$  \hspace{1cm} (11.3)

where \(L\) is the mean molar heat of vaporisation over the temperature range \((T_2 - T_1)\). Table 11.3 shows the calculated values of \(L\) for the various solutions. With the addition of KF the activity of \(H_2O\) was reduced and the latent heat of vaporisation was increased. It would appear, therefore, that the flouride ion is behaving in a similar manner to the hydroxyl ion in removing free water from the solution by incorporation into the hydration sheath.

The slurry region observed previously, (Chapter 5), was observed in a number of the solutions investigated in these experiments. However, there are characteristic differences between the behaviour of the system both with and without the addition of potassium flouride. A slurry type behaviour was observed with a ternary electrolyte solution of 3 mol dm\(^{-3}\) KOH, 0.15 mol dm\(^{-3}\) potassium silicate and 4 mol dm\(^{-3}\) KF. This solution has similar vapour pressure characteristics to those exhibited by 8 mol dm\(^{-3}\) KOH solution. However, there is a change in the character of the solid phase produced in solution. The lifetime of the
precipitate as a suspension appears to be considerably reduced to such an extent that it could not leave the electrode chamber. Figure 11-2 illustrates this point, where the passivation charge using this solution was less than infinite. The discharge was terminated by physical blocking of the electrode compartment by the slurry and also the coating of the air electrode by a thick layer of precipitate. Concentrations around 0.15 mol dm$^{-3}$ potassium silicate gave optimum discharge capacity (Figure 11-3). At concentrations lower than 0.15 mol dm$^{-3}$ no slurry region was observed and at higher concentrations the physical blocking problem became progressively more prominent. When the discharge had been terminated the anodes were inspected, they had the same electropolished finish observed previously (Chapter 5) and did not appear to be filmed in any way. However, the cathode was covered with a white compact precipitate of ZnO which may have terminated the discharge process.

The addition of potassium fluoride in some way destroys the balance of processes occurring in the slurry region so that a steady state equilibrium is not achieved for solutions with similar vapour pressure characteristics to 8 mol dm$^{-3}$ KOH solutions. A white precipitate was produced but a critical examination of the cell potential versus time curve indicates that a levelling out of potential is never really achieved. Rather, the potential falls continuously making it seem unlikely that steady state conditions can be obtained with the present experimental apparatus. Indeed, even an increase in the solution flow rate or a decrease in the current density did not produce steady state equilibrium conditions. The observation that the electrode compartment contained large amounts of white dense precipitate after the failure of the cell indicated that the ability of the precipitate to flow round with the solution had been reduced. Rather, it tended to agglomerate on the separators and at the back face of the air cathode, thereby blocking
the electrode compartment. A possible reason for this is that the addition of KF has increased the viscosity of the solution (Figure 11-4) and drastically reduced the amount of free dispersion medium (Table 11.3) which is presumably water. Consequently it is easier for the quasi-colloidal particles to coagulate. The reduction in solution free water is confirmed by the vapour pressure measurements of electrolyte solutions based on 3 mol dm$^{-3}$ KOH with added KF (Table 11.3).

The primary application has been improved by the present experiments since a slurry region type behaviour was observed with electrolyte solutions based on 3 mol dm$^{-3}$ KOH with additions of potassium silicate and potassium flouride. These solutions had similar vapour pressure characteristics to those of 8 mol dm$^{-3}$ KOH solutions. The fact that the precipitate formed with added potassium flouride did not form stable suspensions and physically blocked the electrode compartment and the air cathode, in the flowing system, may be a serious disadvantage. However, in a primary zinc/air cell with a stationary electrolyte this may not be of paramount importance, and will have to be determined by actual primary zinc/air cell trials.
CHAPTER 12

FINAL DISCUSSION

Battery systems using zinc electrodes in alkaline solution have been manufactured since the late 19th Century. Since then zinc-in-alkali has been coupled with various positive electrodes ranging from silver oxide to catalysed carbon and other depolarised oxygen electrodes to give batteries which are used for many different purposes. There are several reasons for the interest shown in the zinc/air systems, the main one being that the zinc/air system has a relatively high theoretical energy density (1580 kJ kg\(^{-1}\)).

The initial impetus for this investigation was the desire to improve these high energy density devices. Specifically the use of extenders and the possible advantages they could bestow on existing systems formed the major interest in this work. It has been adequately demonstrated in Chapters 5 and 10 of this thesis that the extenders potassium silicate and lithium hydroxide have a profound beneficial effect on the discharge capacity of zinc in alkaline solution. Such advantages must be of technological importance. Two further aims arise from the initial success. Firstly, the selection of the most satisfactory system for the application of the extenders effects and secondly an investigation into the effect of the extenders on the electrochemistry of the zinc electrode in an alkaline environment.

12.1 Applications of Extender Additives to Commercial Zinc/Air Batteries

From the work in this thesis emerged two possible effects of extender materials which could be used to advantage in commercial zinc/air batteries or cells.

12.1.(i) The use of potassium silicate or lithium hydroxide would be expected to increase the discharge capacity of zinc/air batteries or
cells operating with electrolyte solution of high KOH concentration, 
(7 - 9 mol dm$^{-3}$). Indications from experiments with the plate cells 
and slurry cells, described in this thesis, are that the increase in 
capacity could be of the order of 30%.

Some of the commercially available zinc/air devices are not suit-
able for specific applications because of as yet unresolved technolog-
ical problems. These problems are not connected with the discharge 
capabilities and the use of extenders have no apparent application in 
these devices. However, two systems, wet cells$^{151}$ and the Sony Corp-
oration zinc/air slurry cell$^{152}$, appear to offer the best systems to 
achieve the improvement provided by the application of extenders. The 
discharge capacities of both these devices are governed by the ability 
of the electrolyte solution to dissolve anodic products, therefore, the 
use of extenders would improve the energy storage capacity.

12.1.(ii) The Possible Uses of the Slurry Region Effect

The slurry region effect described in this thesis could theoretically 
be applied to any zinc/air device. The slurry region has been 
observed at current densities conventionally demanded in operation 
(20 - 50 mA cm$^{-2}$). This should, therefore, allow massive zinc to be 
used at high levels of current density without the need to render anodes 
microporous in order to avoid passivation. The production of such porous 
anodes represents a large proportion of the cost of the zinc/air device 
so their replacement by massive zinc would render the zinc/air system 
more economic (and simplify quality control). Better utilisation of 
the zinc anode also results with the use of extenders, thus E.C.L. 
obtained only 80% utilisation$^{150}$ of porous zinc anodes in primary dry 
cells, however, a solid zinc anode completely discharged in the slurry 
region solution.
A serious limitation of the application of the slurry region solutions was the high vapour pressure of the electrolyte solutions based on $3 \text{ mol dm}^{-3}$ KOH. However, as shown in Chapter 11 these solutions can be modified by KF additions to achieve vapour pressure compatible with $8 \text{ mol dm}^{-3}$ KOH (the normal type of zinc/air electrolyte solution), and although there are still vapour pressure problems with $8 \text{ mol dm}^{-3}$ KOH the ternary solutions enable the slurry region effect to be realised under the usual operating conditions. Another advantage from the use of the slurry region is the constant potential obtained. It is disappointing to note that the slurry region effect would be unsuitable for zinc/air system using fluidised zinc electrodes such as the Sony Corporation cell\textsuperscript{152}. As shown in Chapter 10 the discharge is terminated when the zinc particles are coated with precipitated ZnO and this situation would be undesirable in any zinc/air fuel cell.

12.2 Mechanism of the Extender Action

Two major effects on the electrochemistry of zinc have been observed in the present study when extenders are present in the alkaline solution.

12.2.(i) The Mechanism of Additions as Classical Extenders

The results of a study of the nature of concentrated potassium silicate solutions in alkali indicated that data from several independent but complementary techniques (Chapter 9) are mutually consistent and show that electrolytically produced solutions of high Zn(II) concentration are relatively complex. For such solutions, the complexity depends upon the age. Initially, quasi-colloidal particles based on Zn(OH)$_2$ and molecules of solvation are present. The addition of potassium silicate or lithium hydroxide greatly improves the time stability of these solutions. This increase in stability can be considered from the point of view of the strength of the hydrate shell around the quasi-colloidal particle or micelle.
It has been suggested\(^\text{35}\) that the Zn(II) concentration at the electrode surface at the point of passivation is equivalent to the hydroxyl ion concentration of the bulk solution. From the present study it would appear that the maximum solubility of Zn(II) species in alkaline solution occurs when all the available OH\(^-\) ions are involved in the formation of a macromolecule of the type \([\text{Zn(OH)}_2]^n\). Because of the difficulties of solvating such a large molecule this situation is not reached in practice. Rather, the precipitation of this macromolecule onto the electrode surface, as observed by Breiter and Powers\(^\text{75}\), is involved in the initial stages of passivation. However, when extenders are present in alkaline solutions in which zinc is dissolving the electrolyte Zn(II) concentration approaches the equivalent OH\(^-\) concentration. Thus a value of 4.29 mol dm\(^{-3}\) Zn(II) has actually been obtained in solutions of 10 mol dm\(^{-3}\) KOH (Chapter 5). Confirming tentative suggestions\(^\text{92}\) the extra stability imparted to the Zn(II) solution species by potassium silicate takes place as a result of the chemisorption of the SiO\(_2^2^-\) ions into the micelles. The SiO\(_2^2^-\) ion has a closely bound hydration shell which, upon penetration into the micelle, imparts extra stability by increasing the strength of the hydration sheath. The energy of hydration of the lithium ion is greater than that of the potassium ion. Thus the replacement of K\(^+\) ions for Li\(^+\) ions in the inner layer of the micelle would impart extra stability to the micelle as a result of the greater hydration of the species.

12.2.(ii) The Mechanism of Potassium Silicate in the Slurry Region

Several of the experimental techniques used in the present study have indicated the presence of an adsorbed layer of silicate ions at the zinc/electrolyte interphase when potassium silicate is present in the alkaline electrolyte solution.
The characteristic differential capacitance curves observed for zinc in alkaline solution exhibit a pseudocapacitance peak due to the interaction of the OH$^-$ ion with the electrode surface in the region where the electrode undergoes active dissolution. The addition of potassium silicate to the alkali solution markedly suppresses the pseudocapacitance peak and shifts it to more negative values. It appears that the silicate ion is more strongly adsorbed than the OH$^-$ ion. With the addition of potassium silicate the resistive component measured was increased. This was similar to the effect observed using the galvanostatic pulse technique, where the indications of an adsorbed film on the electrode surface were reflected in the high ohmic overpotential. The exchange current density in silicate free systems as measured by galvanostatic pulse experiments agreed generally with previously reported results$^{63,69}$ using this technique. When compared with data from silicate containing systems it is clear that the effect of the silicate species is to reduce the magnitude of the exchange current density. Such a reduction may arise from the adsorption of silicate ions at active sites on the electrode surface.

On inspection the anodes from the flowing system in the slurry region had a finish typical of an electropolished surface. This led to the conclusion that the adsorbed layer of silicate may be a relatively thick layer analogous to the type produced during electropolishing$^{107-109}$ through which the Zn(II) species must pass before entering the bulk electrolyte solution. With the use of the parallel circuit impedance technique it was possible to substantiate this conclusion when it was shown that the adsorbed layer of silicate effects the diffusion rate of species in the close vacinity of the electrode surface. A value of $\sim 1 \times 10^{-8}$ cm$^2$S$^{-1}$ being obtained for $D_0$ in silicate-containing solution compared to $0.7 \times 10^{-5}$ cm$^2$S$^{-1}$ for silicate free systems.
The existence of a slurry region can tentatively be discussed in terms of:

(a) the formation of a relatively thick silicate-rich layer around the anode;
(b) the stabilisation of Zn(II) species in solution by silicate ions.

The first phenomenon is well known in the electropolishing literature and is supported by the results of a number of techniques in this study, and the second factor has been demonstrated by Flerov for bulk solutions.

It can be postulated on the basis of these observations that Zn(II) species have a higher solubility in the silicate-rich layer adjacent to the electrode, than in the rest of the solution. Now considering the electrode, operating in the slurry region where ZnO is being continuously precipitated, it can be seen that, provided the higher solubility limit of Zn(II) in the silicate-rich layer is not exceeded, the Zn(II) will diffuse through this layer as a solution species. When the Zn(II) species reach the outer part of the diffusion layer, where their solubility is lowered, they are precipitated as ZnO at a point remote from the electrode surface.

At higher current densities the surface concentration of Zn(II) species increases and eventually the solubility limit of even the silicate-rich layer is exceeded and precipitation occurs actually at the electrode surface, so causing passivation in the normal way.

12.3 Application of the Extender Region to the Electrochemistry of Zinc

The addition of extender materials to alkaline solutions has enabled solutions of very high zincate concentration to be investigated.
Using the linear sweep potential technique it was possible to estimate the Zn(II) concentration at the electrode surface at the point of passivation. The use of extenders allowed solutions of high Zn(II) concentration to be investigated and thus, more accurate extrapolations could be made. It was possible to estimate that at the point of passivation the Zn(II) concentration was equivalent to the OH\(^-\) concentration of the alkaline solution.

Attempts to investigate concentrated zincate solutions have been severely handicapped by the fact that solutions of 2.0 mol dm\(^{-3}\) Zn(II) become unstable on standing and after 15h solutions with Zn(II) concentrations greater than 2.0 mol dm\(^{-3}\) precipitate. The addition of potassium silicate to these solutions made it possible to prepare solutions with Zn(II) concentrations as high as 4.29 mol dm\(^{-3}\) (in 10 mol dm\(^{-3}\) KOH). Without this facility the intensive study of the nature of concentrated zincate solutions would not have been possible.

12.4 The Nature of the Species Present in Zincate Solutions

It was found that the non-linearity of the e.m.f. versus Zn(II) concentration data for cells of the type:

\[
\text{Zn(Hg)} \mid \text{Zincate solutions} \mid \text{Liquid junction} \mid \text{Reference} \quad (12.1)
\]

could be successfully explained in terms of the different reactions occurring as the discharge of a zinc electrode in alkaline solution progresses.

(a) at low Zn(II) concentrations, zinc discharges as the tetrahydroxy zinceate anion

\[
\text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2e^- \quad (12.2)
\]

(b) at intermediate concentrations, zinc discharges as the trihydroxy anion

\[
\text{Zn} + 3\text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_3(\text{H}_2\text{O}) + 2e^- \quad (12.3)
\]
(c) at high concentration, zinc discharges as the neutral dihydroxy species which is initially electroinactive.

This explanation is a much better suggestion than that of Dirkse\(^96\) and Hampson et al\(^99\) who tried to explain the non-linearity in terms of the formation of the complex anion of the type \([\text{Zn(OH)}_4(\text{H}_2\text{O})]^{2-}\).

Initially on preparing solutions with Zn(II) concentrations 3.0 - 4.29 mol dm\(^{-3}\), a region of unique electroactivity was observed, the e.m.f. of the cell (12.1) was independent of Zn(II) concentration. On standing the potential underwent a first order change and attained an approximately constant value after 14 days. After ageing, it was found that a two electron transfer could be related to the data by considering the zinc electrode reaction as

\[
\text{Zn} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2(\text{H}_2\text{O})_2 + 2\text{e}^- \quad (12.4)
\]

Both viscosity and n.m.r. measurements indicated that the zinc species present in fresh solutions were considerably larger (possibly of colloidal dimensions) than in aged solutions. The suggestion of colloidal nature, originally made by Flerov\(^92\), is justified by the fact that in solutions free of extenders the electroinactive region is observed only over a very short period of time. The particles of colloidal character which are initially electroinactive undergo a first order decay to yield a solution containing the species \([\text{Zn(OH)}_2(\text{H}_2\text{O})]_2\), \([\text{Zn(OH)}_3(\text{H}_2\text{O})]^-\) and \([\text{Zn(OH)}_4]^{2-}\), the actual constitution depending on the concentration.

It has been shown that the previous spectral assignments\(^97,101\) are erroneous, reported bands at 283 and 310 \(\Delta \text{cm}^{-1}\) arising from KOH solution itself. The new data presented here show the non-colloidal zinc species to be tetrahedral and not planar or octahedral. It was found that the \(\nu_1\) band in the Raman spectra occurred at 471.2\(\pm\)0.9 \(\Delta \text{cm}^{-1}\) and not as previously accepted\(^97,101\) at \(\approx 484 \Delta \text{cm}^{-1}\). Also the 430 \(\Delta \text{cm}^{-1}\) value
for $\nu_3$ was confirmed but the expected, weak $\nu_2$ and $\nu_4$ bands were not detectable due to the high background and overlapping KOH solution bands.

12.5 The Zn(II)/Zn Exchange Reaction

12.5.(i) Nature of the Electrode Surface

Gerischer$^59$ identified two steps in the zinc exchange reaction at an amalgam surface in alkaline solution:

$$\text{Zn} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)$_2$} + 2\text{e}^- \quad (12.5)$$

$$\text{Zn(OH)$_2$} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)$_4$}^{2-} \quad (12.6)$$

with reaction (12.5) being rate controlling. For the solid metal, however, further possible steps arise due to the adsorption at the electrode and the additional problems of exchange of metal atoms with the crystal lattice. Incorporation of a metal atom into a metal lattice is thought to occur by either of two mechanisms:

(a) diffusion of metal ion in solution to a point opposite a growth site in the lattice, followed by charge transfer and incorporation into the lattice;

(b) charge transfer and incorporation of the adspecies at a point of low coordination on the metal surface followed by diffusion across the surface to a kink site.

Mechanism (a) requires that the hydration sheath is lost in one stage, whilst in Mechanism (b) the hydration sheath is discarded in stages. It has been reported$^{153}$ that the mechanism involving diffusion in solution, followed by direct incorporation at a growth site, is unlikely for both statistical and energetic reasons. The ratio of the mean free path for diffusion and the mean distance between kink sites, has been reported$^{154}$ to determine whether or not surface diffusion of adspecies can control the overall reaction. Hampson et al$^{155}$ have shown that at the equilibrium
potential the diffusion of adatoms across the electrode surface is important, and may control the rate of the reaction.

12.5.(ii) Choice of Rate Determining Step

The overall reaction occurring at an anodically dissolving zinc electrode has been shown to be

\[
\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad (12.7)
\]

Thus, the simplest possible reaction mechanism must consist of several steps. There exists the possibility that the reaction may proceed via a simultaneous two electron change or a consecutive two step mechanism. Armstrong et al.\textsuperscript{122} has detected the presence of the Zn(I) species using an elegant impedance method, therefore, it would appear that the latter mechanism is the more plausible reaction route.

For the case of a stepwise mechanism the transfer coefficients \( \alpha_a \) and \( \alpha_c \) can be obtained from the Tafel slope of the polarisation curve or the dependence of \( i_0 \) on \( \text{OH}^- \) and \( \text{Zn(II)} \) concentration. In the case of a simple one-step process the ratio \( \frac{\alpha_a}{\alpha_c} \) is usually close to unity. A deviation of this ratio from unity is an indication of a stepwise mechanism and the value of the ratio can indicate which is the limiting step.

In the present study \( \frac{\alpha_a}{\alpha_c} \) is approximately 3 from both Tafel slopes and exchange current measurements. This indicates that the rate of transfer of the second electron (12.8) is the limiting step.

\[
\text{Zn(I)} \rightarrow \text{Zn(II)} + \text{e}^- \quad (12.8)
\]

It is interesting to consider why the transfer of the final electron is the rate determining process. An analysis\textsuperscript{126} of the available kinetic data for reactions of the type

\[
\text{M} \rightarrow \text{M}^{n+} + \text{ne}^- \quad (12.9)
\]
clearly shows that the exchange current density decreases with the increasing valence of the cation. This decrease is accompanied by a considerable increase in the activation energy of the electrode process and in the free energy of hydration of the corresponding cations.

The hydration energy, $\Delta H_s$, is approximately proportional to the square of the ionic charge and, therefore, for a given element in different oxidation states increases as the charge of the cation increases\textsuperscript{156}. Although the activation energy is only a small part of $\Delta H_s$ for the corresponding cation, it is known that the activation energy is largely due to the change in structure of the hydration sheath following the change in the charge of the reacting species\textsuperscript{157,158}. It appears, therefore, that one reason why the transfer of the final electron is the rate determining process is the very large difference in $\Delta H_s$ of the cations taking part in the reaction sequence. Since univalent ions are more weakly hydrated the step

$$M \rightarrow M^+ + e^- \quad (12.10)$$

usually requires only a relatively low energy of activation, thus in comparison with subsequent charge transfer steps this initial step is often a quasi-equilibrium process.

If the last step of the reaction sequence is rate determining the electrode serves only as an electron source or sink for this particular step. Therefore, metallurgical effects involving the electrode surface are of little consequence in this type of reaction. It can be concluded that for the zinc dissolution reaction in alkaline solution the reaction of the type (12.10) is practically reversible and no metallurgical effects are observed because the transfer of the second electron is the rate determining process.
12.6 Further Work

1. The application of both the extender region and the slurry region to commercial zinc/air devices to investigate the extent of the expected advantages.

2. An investigation into the suitability of silicate-rich alkaline solutions as an electropolishing medium for zinc.

3. In this investigation no attempt was made to study the effect of temperature and other environmental variables on the slurry region effect. This could prove a useful study if the slurry region effect was exploited commercially.

4. An investigation into possible collection of the white slurry material and the development of a process whereby this material could be reduced back to massive zinc in a suitable form for further discharge in a mechanically rechargeable battery.
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**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>(a_{H_2O})</td>
<td>Activity of Water</td>
</tr>
<tr>
<td>A</td>
<td>Electrode Area</td>
</tr>
<tr>
<td>C</td>
<td>Total Differential Capacitance</td>
</tr>
<tr>
<td>c</td>
<td>Velocity of Light</td>
</tr>
<tr>
<td>(C_{comp})</td>
<td>Differential Capacitance of Compact Double Layer</td>
</tr>
<tr>
<td>(C_{diff})</td>
<td>Differential Capacitance of Diffuse Double Layer</td>
</tr>
<tr>
<td>(C_{xs}, R_{xs})</td>
<td>Measured Series Capacitance and Resistance</td>
</tr>
<tr>
<td>(C_{dl})</td>
<td>Double Layer Capacitance</td>
</tr>
<tr>
<td>(C_p, R_p)</td>
<td>Parallel Circuit Capacitance and Resistance</td>
</tr>
<tr>
<td>(C_s, R_s)</td>
<td>Series Circuit Capacitance and Resistance</td>
</tr>
<tr>
<td>(C_s^o, C_s^r)</td>
<td>Surface concentrations of the oxidised and reduced species</td>
</tr>
<tr>
<td>(C_o^b, C_R^b)</td>
<td>Bulk concentrations of the oxidised and reduced species</td>
</tr>
<tr>
<td>(C_c)</td>
<td>Critical concentration</td>
</tr>
<tr>
<td>(D_o, D_R)</td>
<td>Diffusion coefficient of the oxidised and reduced species</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential on a suitable reference scale</td>
</tr>
<tr>
<td>(E^0)</td>
<td>Standard electrode potential</td>
</tr>
<tr>
<td>(E_r)</td>
<td>Reversible electrode potential</td>
</tr>
<tr>
<td>(E_{rat})</td>
<td>Rational potential</td>
</tr>
<tr>
<td>f</td>
<td>Bond force constant</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>g</td>
<td>Surface roughness factor</td>
</tr>
<tr>
<td>h</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>H</td>
<td>Magnetic field strength</td>
</tr>
<tr>
<td>i</td>
<td>Current density</td>
</tr>
<tr>
<td>(i_o)</td>
<td>Exchange current density</td>
</tr>
<tr>
<td>(i_a, i_c)</td>
<td>Partial anodic and cathodic current densities</td>
</tr>
<tr>
<td>i_L</td>
<td>Limiting current density</td>
</tr>
<tr>
<td>i</td>
<td>Current density at infinite electrode rotation speed</td>
</tr>
</tbody>
</table>
List of Symbols (Continued) ...

I  Spin quantum number
j  $\sqrt{-1}$
k_c, k_a  Potential dependent rate constants for cathodic and anodic reactions
K^0  Apparent standard rate constant
k_{sh}  Standard heterogeneous rate constant
L  Latent heat
m_A, m_B  Mass of A and B
n  Number of electrons
N  Number of moles diffusing across a given cross-sectional area
P  Vapour Pressure
q  Charge on the electrode, flux of diffusing species
R  Gas constant
R_D, R_{ct}  Charge transfer resistance
R_{sol}  Electrolyte ohmic resistance
T  Temperature
t  Time
t_p  Passivation time
V  Vibrational frequency
W  Warburg impedance
x  Distance
Z  Total cell impedance
Z'  Real part of total impedance
Z''  Imaginary part of total impedance
$\alpha$  Charge transfer coefficient
$\alpha_a$, $\alpha_c$  Anodic and cathodic charge transfer coefficient
List of Symbols (Continued) ...

\( \varepsilon_a, \varepsilon_c \) \hspace{1cm} Anodic and cathodic symmetry coefficients

\( \delta \) \hspace{1cm} Diffusion boundary layer thickness

\( \delta_0 \) \hspace{1cm} Hydrodynamic boundary layer thickness

\( \Delta \delta \) \hspace{1cm} Change in chemical shift

\( \Delta H_s \) \hspace{1cm} Hydration energy

\( \eta \) \hspace{1cm} Charge transfer overpotential

\( \Theta \) \hspace{1cm} Charge transfer resistance

\( \Theta' \) \hspace{1cm} Apparent charge transfer resistance

\( \mu \) \hspace{1cm} Reduced mass

\( \nu \) \hspace{1cm} Kinematic viscosity

\( \nu_1, \nu_4 \) \hspace{1cm} Raman bands

\( \sigma_\lambda \) \hspace{1cm} Polarisability

\( \sigma \) \hspace{1cm} Warburg coefficient

\( \sigma' \) \hspace{1cm} Apparent Warburg coefficient

\( \omega \) \hspace{1cm} Angular velocity, frequency
APPENDIX 1

ANALYSES OF ELECTROLYTES

PREPARATION OF CHARCOAL
A.1.(i) Analysis for Zinc in KOH Electrolyte

A known volume of electrolyte was diluted to 50 ml and buffered to pH 10. The solution was then titrated with a standard solution of E.D.T.A. using eriochrome black indicator. The end point was detected as a colour change from red to blue.

A.1.(ii) Analysis of Chloride, Nitrate and Fluoride Electrolytes

In all cases the potassium content was determined and the anion concentration determined.

A series of standards in the range 5 - 50 p.p.m. were made up. Using a flame photometer (E.E.L.) a calibration graph was constructed. The electrolyte to be analysed was diluted to about 25 p.p.m. and the concentration thus determined.

A.1.(iii) Analysis of KOH Electrolytes

Approximately 4g of sulphamic acid were accurately weighed into a 150ml conical flask and dissolved in 30 - 50 ml of distilled water. 2 - 3 drops of methyl red were added as indicator. The solution was titrated with potassium hydroxide and the end point was determined by the first yellow colour.

A.1.(iv) Preparation of Charcoal

Granular gas adsorption charcoal was extracted in a Soxhlet apparatus with constant boiling hydrochloric acid. The acid was changed weekly and the extraction was continued until the acid remained colourless. Generally this procedure took about three months. The charcoal was then washed with water until the washings showed no positive test for chloride ion.