

THE EFFECT OF ADDITIVES ON THE ANODIC BEHAVIOUR OF CADMIUM IN KOH SOLUTIONS

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Summary

The anodic oxidation of a negative cadmium electrode was studied in an alkaline solution containing organic and inorganic additives. Potential step and cyclic voltammetry techniques were used to evaluate the effect of the additives. Current measurements indicated an increase in the ionic conductivity of the Cd/Cd(OH)₂ film and this resulted in a higher charge content in the case of a beneficial additive. It is established that these techniques can be used to screen the additives.

1. Introduction

In industrial nickel-cadmium pocket plate flooded cells, it is standard practice for the negative active material to contain small amounts of additives such as Fe₂O₃, Ni(OH)₂, polyvinyl alcohol (PVA), cellacol, terphthalic acid, phenol, etc. These additives are generally termed expanders or extenders and are used in the negative electrode to prevent crystal growth, thus retaining capacity.

The porous cadmium electrode has the property of losing capacity in the absence of any expanders. Investigations, particularly on sintered cadmium plates, have suggested that the fall in capacity is related to the growth of cadmium and cadmium hydroxide [1 - 5] crystals and the redistribution of active material [6 - 8]. It has been stated [2] that the effect of this crystal growth is more pronounced at low charge rates and at high temperature, as might be expected. Several researchers [4, 9, 10] found that the cadmium hydroxide crystals, which grow on cycling, are not easily recharged and it has been suggested [1] that the loss in capacity is due solely to this mechanism. Armstrong *et al.* [5], however, prefer the mechanism whereby the failure is credited to the growth of a passivating film on the surface of the active material.

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As the charge-discharge reaction proceeds by a dissolution-precipitation mechanism, and since crystal growth appears to cause early failure of cadmium electrodes, a modification of the crystallographic environment by the addition of a suitable expander material should overcome the problem of crystal growth. Two principal types of crystal growth modifiers (expanders) have been described in the literature; one affecting nucleation and the other depending on the adsorption onto the growing crystal. The action of expanders and a large range of expander materials has received extensive investigation for the lead/lead sulphate systems [11 - 18]. The well-known result of this process is to create a better high discharge rate at low temperatures, and also to effect improvements in the cycle life of the battery. Unfortunately, however, there appears to be no clear consensus as to the mode of action of expander materials for the cadmium electrode. This is probably due to the expander functioning in more than one way and it is, therefore, difficult to assess the effect of organic expanders by using conventional battery negative electrodes because inorganic expanders are included in the negative active material.

Surface morphological effects of organic expanders on the cadmium hydroxide electrode during cycling can easily be monitored using SEM and X-ray crystallographic techniques, but any adsorption phenomenon, changes in conductivity or changes in the electrocrystallization are extremely difficult to infer from surface structures.

The expanders which have been investigated by battery manufacturers in the negative cadmium electrode of a nickel-cadmium battery are PVA, ter-phthalic acid, cellacol and sodium silicates. Impurities that cause detrimental effects are generally calcium or magnesium ions.

At fixed potentials, the equation for the current as a function of time when the driving force for the anodic film formation of cadmium hydroxide is an ionic concentration gradient is given by [19]:

$$i = \left(\frac{kT}{e} \frac{\sigma}{2\Omega} \right)^{1/2} \left(1 - \exp \left\{ - \frac{e\phi}{KT} \right\} \right)^{1/2} t^{-1/2} \quad (1)$$

and if the driving force is a gradient in the electrostatic potential, then the current density is given by:

$$i = \left(\frac{\sigma\phi}{2\Omega} \right)^{1/2} t^{-1/2} \quad (2)$$

where ϕ is the overpotential, Ω the volume of oxide produced per coulomb of electric current, σ the ionic conductivity, e the electric charge, k the Boltzmann constant, T the absolute temperature and t is the time. In either case the resultant gradient will be proportional to the ionic conductivity of the film-solution interface. The effect of the expanders on the current was investigated as a function of time during the potentiostatic oxidation of a planar cadmium electrode, and values of the ionic conductivity at several

electrolyte concentrations were deduced. Cyclic voltammetry measurements were also made and here the electrode potential was scanned at a constant rate between two voltage limits and the current response to the potential sweep monitored.

2. Experimental

Potential step investigations

The cadmium used in this investigation was a 0.283 cm² disc cut from a (99.9% pure) rod supplied by BDH. It was set in an Araldite holder. Measurements were made in a conventional 3-electrode cell using an Hg/HgO reference electrode and a Ni counter electrode.

The solutions used were 1, 5 and 10 M KOH prepared from AnalaR pellets and deionized, distilled water. All solutions were de-oxygenated with nitrogen and the experiment was conducted at room temperature. Prior to the experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol and water, and then polished with 1 μm diamond paste. It was finally cleaned with methanol again and held at a cathodic potential of -1000 V with reference to the Hg/HgO electrode for 0.5 h and stepped anodically to -0.850 V. Current measurements were made using a 0.5 A, 20 V potentiostat. Additives investigated were PVA, sodium silicate and calcium hydroxide.

Cyclic voltammetry measurements

The cadmium electrode was treated as above and cyclic voltammetry measurements were made using the potentiostat in conjunction with a sweep generator and an $x-t$ chart recorder.

Saturated solutions of PVA, and calcium hydroxide in 5 M KOH electrolyte were prepared and three aliquots of 3 ml, 5 ml, and 10 ml of these solutions were added at each stage of the experiments. Prior to each experiment the cadmium electrode was polished and cleaned as above and held cathodically at -1000 V *versus* the Hg/HgO reference electrode for 0.5 h in 600 ml of KOH electrolyte. The sweep speed was 400 mV min⁻¹.

3. Results and discussion

Potential step investigations

Plots of i against $t^{-1/2}$ calculated from the experimental i *versus* t curves for a number of KOH solution concentrations are shown in Fig. 1.

The slopes of the straight lines increase with KOH concentration and are characteristic of the ionic conductivity of the film and approximately proportional to the logarithm of the KOH concentration. Furthermore, an increase in the anodic potential also leads to an increase in the slope of the i *versus* $t^{-1/2}$ curve (Table 1). The substantial effect of potential on the ionic

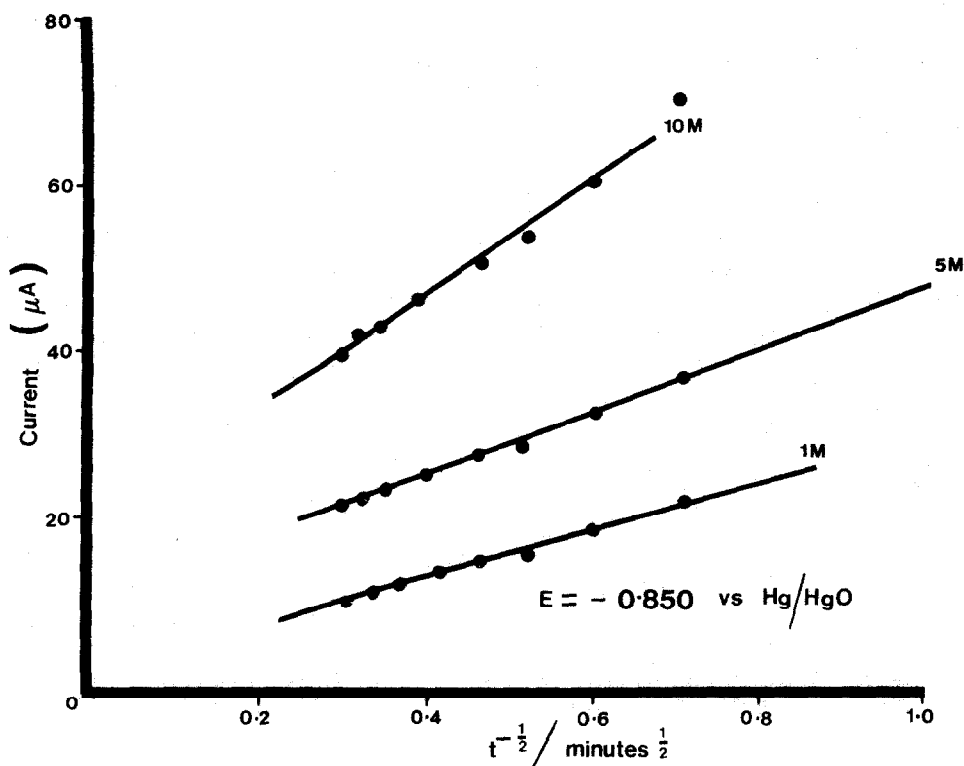


Fig. 1. i vs. $t^{-1/2}$ plots for various concentrations of KOH derived from experimental i vs. t curves.

TABLE 1

Variation in the slope of i vs. $t^{-1/2}$ curves against potential

$-E$ (V)	KOH (M)		
	1	5	10
0.86	23	33.5	66
0.85	22.5	38.5	73
0.84	24.5	41.5	79.5

conductivity and on the rate of film formation is the result of the electrostatic field gradient on these reactions.

The effects of the organic additive PVA, and inorganic additives such as sodium silicate and calcium hydroxide on the current-time relationship and on the ionic conductivity of the cadmium hydroxide layer were investigated.

The addition of calcium hydroxide to the 5 M KOH electrolyte resulted in a decrease in the slope of the i versus $t^{-1/2}$ curve and this caused inhibition

of current flow in the $\text{Cd}(\text{OH})_2$ layer ($E = -0.850$ V). Very low concentrations of the organic (5×10^{-5} M) and sodium silicate additives ($\approx 2 \times 10^{-4}$ M), however, increased the slope and hence caused an increase in the current flow through the $\text{Cd}(\text{OH})_2$ layer (Fig. 2).

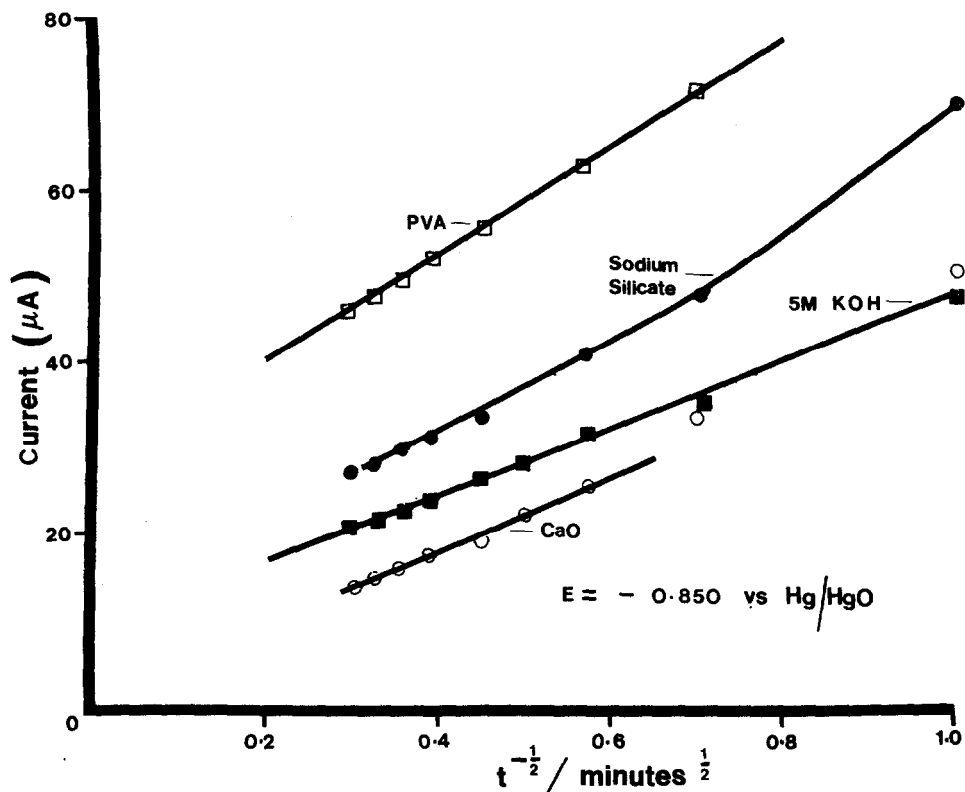


Fig. 2. i vs. $t^{-1/2}$ plots for various additives in 5 M KOH solution.

The fixed potential experiments indicate that after a sufficient time the rate of oxidation follows a parabolic growth law. This law is consistent with at least two hypotheses [19]. The cadmium ions emerging from the metal react with the OH^- ions at the metal-electrolyte interface and deposit on the metal as $\text{Cd}(\text{OH})_2$. The parabolic growth applies when the metal is completely passivated except for small pores. The ability of the cadmium to form the $\text{Cd}(\text{OH})_3^-$ species, as postulated by Okinaka [20], then decreases at the metal-electrolyte surface due to an insufficient supply of electrolyte at the surface of the metal. Therefore, as the cadmium hydroxide layer thickens, the $\text{Cd}(\text{OH})_3^-$ ion path decreases, thus causing a current proportional to $t^{-1/2}$.

The other hypothesis is that the cadmium ion or OH^- ion moves through the cadmium hydroxide layer and electron transfer occurs at the metal-hydroxide-electrolyte interfaces. The parabolic growth law operates

when the exchange currents associated with the metal-hydroxide and hydroxide-electrolyte boundaries are large compared with the rate of growth, so that the rate is limited only by transport through the hydroxide. As the hydroxide layer increases the conductivity decreases and the current required to maintain the imposed potential also decreases, thus yielding a parabolic growth law.

It is thought that the second hypothesis is the more likely, where the cadmium ions emerging during the oxidation probably settle in sites of the $\text{Cd}(\text{OH})_2$ lattice. Under the effect of the concentration and potential gradient, these ions acquire additional activation energy which is sufficient to lift them from these lattice sites and transfer them to interstitial sites where they move via defects or vacancies to the film/solution interface to form the required product.

The increase in the current and also in the ionic conductivity found in the alkaline solution when PVA and sodium silicates are used as expanders, and also when the OH^- ion concentrations are higher, is probably due to the adsorption of these ions in these lattice sites [21]. Studies of impedance [21] have shown that since these additives are predominantly anionic, a decrease in the solution resistance (R_{sol}) and an increase in the double layer capacity of the film solution interface result. Hence, it is more likely that the presence of these beneficial additives will only enhance the dissolution-precipitation mechanism by increasing the anionic atmosphere surrounding the cadmium ions. This would facilitate their transfer to interstitial sites thus leading to a higher concentration of cadmium ions in the interstitial sites, an increase in the concentration-potential gradient, and to a higher ionic conductivity of the film.

Cationic additives such as calcium hydroxide seemed to inhibit the transfer of cadmium ions to the interstitial sites, leading to a lowering in the ionic conductivity.

Cyclic voltammetry

Figure 3 shows linear potential sweep voltammograms for one cycle only between -0.600 V and -1.000 V and back (*versus* the Hg/HgO reference electrode), showing the influence of the addition of various concentrations of PVA to the electrolyte.

In the absence of the expander (curve 3), normal behaviour is exhibited, *i.e.*, the dissolution of cadmium as a $\text{Cd}(\text{OH})_3^-$ ion or $\text{Cd}(\text{OH})_4^{2-}$ ion species followed by reprecipitation, or multilayer formation. The formation of the multilayer results in the passivation of the electrode surface at ≈ -0.860 V *versus* the Hg/HgO reference electrode. The cathodic peak is at ≈ -0.970 V and a long 'tail' is present in all cases.

The addition of the expander to the electrolyte causes a marked change in the polarization curve. In the oxidative process, a greater amount of charge is required to passivate the electrode surface when 5 ml (curve 1) of the saturated solution of PVA is added than when, say, 10 ml or 3 ml are added (curves 2, 4). The anodic and cathodic peaks diminish as they do with

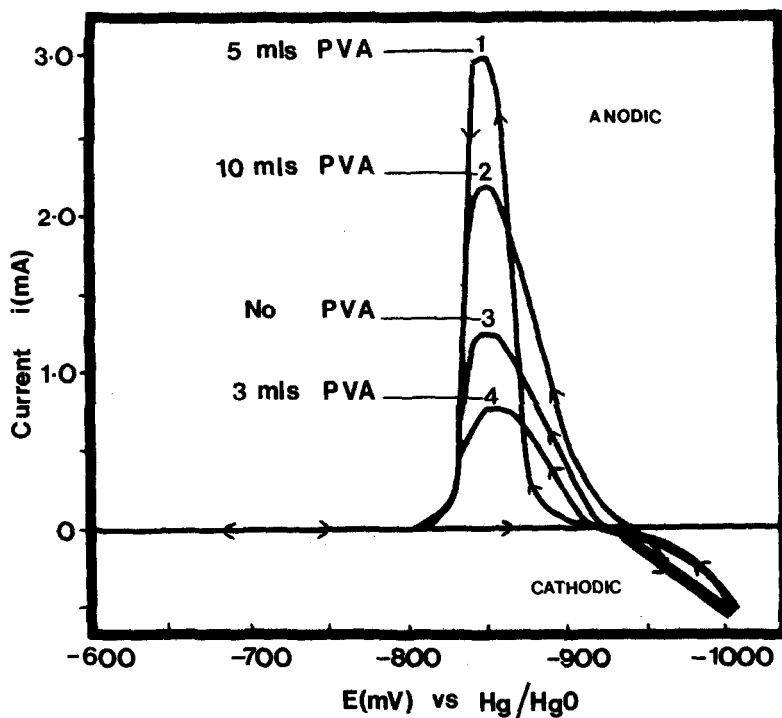


Fig. 3. Cyclic voltammetry of planar cadmium electrode with different concentrations of PVA additive. Scan rate = 400 mV min^{-1} .

the electrode without any expander in the electrolyte. The amount of charge needed to passivate the electrode increases 3-fold with 5 ml of PVA in the electrolyte than in the absence of expander. This is the usual case; too much or too little of an expander can be harmful (or not as efficient) to the electrode performance and an optimum concentration is necessary.

Sodium silicate gave similar results to those obtained with PVA (Fig. 4).

In the case of calcium hydroxide the result is quite catastrophic. Ten millilitres of the aliquot solution almost stops the reaction. The charges under the curve are much lower than is the case without an expander (Fig. 5).

On a planar electrode, the PVA and other beneficial additives probably create a highly porous deposit of cadmium hydroxide on the metal surface, and this porous deposit is a means of migration of OH^- ions to react with the accessible metal, thus resulting in a larger current and high charge density.

In the absence of these additives, the deposit is believed to be relatively non-porous [22] forming large rhombohedral crystallites of cadmium hydroxide on the surface of the metal. This results in a relatively low current and low-charge density.

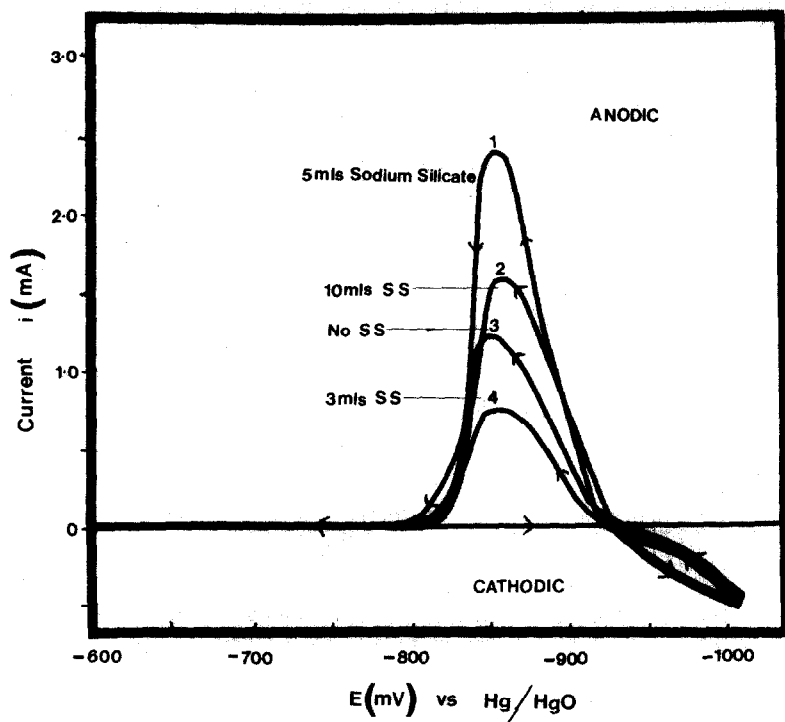


Fig. 4. Cyclic voltammetry of planar cadmium electrode with different concentrations of sodium silicate (ss) additive. Scan rate = 400 mV min^{-1} .

Conclusion

The above techniques can be used as a means of screening expander materials useful in alkaline battery negative electrodes. Beneficial additives resulted in an increased ionic conductivity of the oxidized film and a greater amount of charge being developed, and the reverse effect occurred with harmful additives.

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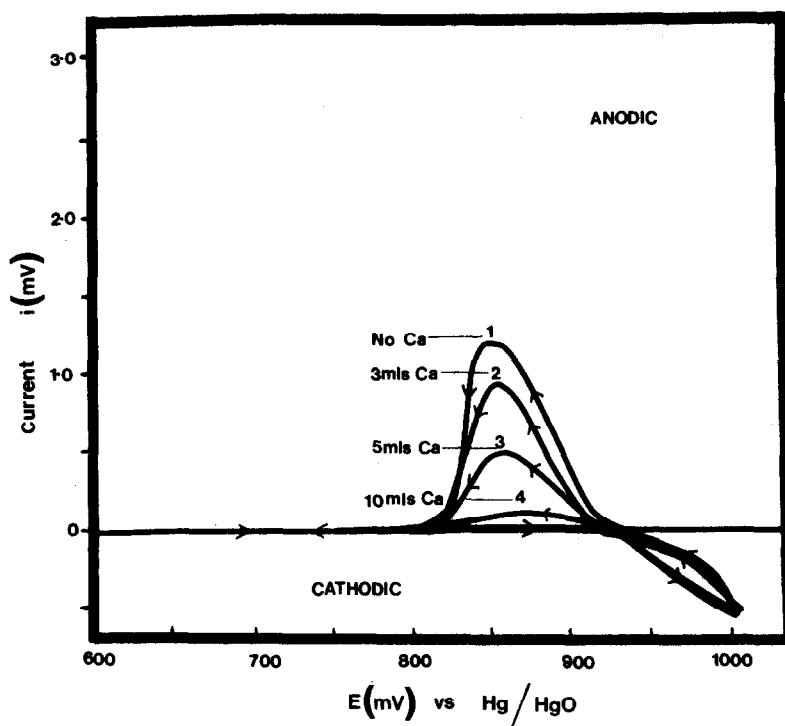


Fig. 5. Cyclic voltammetry of planar cadmium electrode with different concentrations of calcium oxide (Ca) additive. Scan rate = 400 mV min^{-1} .

List of symbols

ϕ	Overpotential
Ω	Volume of oxide produced per coulomb of electric current
σ	Ionic conductivity
e	The electric charge
k	Boltzmann constant
T	Absolute temperature
t	Time

References

- 1 P. Bro and H. Y. Kang, *J. Electrochem. Soc.*, **118** (4) (1971) 519 - 524.
- 2 J. P. Harivel, B. Morignat and J. Migeon, in D. H. Collins (ed.), *Batteries 2 (Proc. 4th Int. Power Sources Symp.)*, Pergamon Press, Oxford, 1964, p. 107.
- 3 A. H. Reed and J. McCallum, *Battelle Tech. Rep. AFAPL-TR-72-20, AD743017*, 1972.
- 4 E. Luksha, D. J. Gordy and G. J. Menard, *J. Electrochem. Soc.*, **120** (1973) 1447.

- 5 R. D. Armstrong, K. Edmondson and J. A. Lee, *J. Electroanal. Chem. Interfacial Electrochem.*, **63** (1975) 287.
- 6 J. L. Weininger and M. W. Breiter, *Power Sources 1966*, Symposium Publication Div., New York, 1967, pp. 269 - 285.
- 7 E. Lifshin and J. L. Weininger, *Electrochem. Technol.*, **5** (1967) 5.
- 8 R. Barnard, J. A. Lee, A. H. Rafinski and F. L. Tye, in D. H. Collins (ed.), *Power Sources 5*, (*Proc. 9th Int. Power Sources Symp.*), Academic Press, London, 1975, p. 183.
- 9 A. J. Salkind and G. W. Bodomer, in D. H. Collins (ed.), *Batteries 2*, (*Proc. 4th Int. Power Sources Symp.*), Pergamon Press, Oxford, 1964, p. 55.
- 10 Y. Okinaka and M. Whitehurst, *J. Electrochem. Soc.*, **117** (1970) 583.
- 11 E. Willihnganz, *Trans. Electrochem. Soc.*, **92** (1947) 281.
- 12 E. J. Ritchie, *Trans. Electrochem. Soc.*, **92** (1947) 227.
- 13 E. J. Ritchie, *Trans. Electrochem. Soc.*, **100** (1953) 53.
- 14 A. C. Zachlin, *J. Electrochem. Soc.*, **98** (1951) 325.
- 15 M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem. Interfacial Electrochem.*, **48** (1973) 465.
- 16 M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem. Interfacial Electrochem.*, **52** (1974) 1.
- 17 M. P. J. Brennan and N. A. Hampson, *J. Electroanal. Chem. Interfacial Electrochem.*, **54** (1974) 263.
- 18 A. C. Simon, S. M. Caulder, J. R. Pierson and P. Gurlusky, *J. Electrochem. Soc.*, **117** (12) (1970) 1463.
- 19 G. T. Croft, *J. Electrochem. Soc.*, **106** (1959) 278.
- 20 Y. Okinaka, *J. Electrochem. Soc.*, **117** (1970) 289 - 295.
- 21 M. Z. A. Munshi, A. C. C. Tseung, J. Parker and J. Dawson, *J. Appl. Electrochem.*, in the press, 1985.
- 22 J. Parker, personal communication.