

A ROTATING-DISK STUDY ON TEFLON-BONDED POROUS ZINC ELECTRODES

A. DUFFIELD, P. J. MITCHELL and N. A. HAMPSON

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

N. KUMAR and D. W. SHIELD

Joseph Lucas Ltd., Group Research Centre, Solihull, West Midlands B90 4JJ (U.K.)

(Received November 2, 1984)

Summary

Microcomputer-controlled, rotating-disk experiments have been carried out on Teflon-bonded porous electrodes fabricated from a 5% PTFE suspension + ZnO. The effect of using 1% mercuric oxide as an additive on this type of electrode has been examined. Plots of i^{-1} vs. $\omega^{-1/2}$ on electrodes containing mercuric oxide show intercepts through the origin for low overpotentials, inferring that quasi-reversible kinetics prevail.

Introduction

The possible use of zinc in a secondary electrode system, particularly if used in conjunction with nickel, is widely recognised as favourable due to its high gravimetric and volumetric energy densities and its relatively low cost.

A recent paper [1] described a microcomputer-controlled rotating-disk electrode (RDE) experiment on solid and porous zinc electrodes which were free from additives. The porous zinc electrode reported was formed from Zn/ZnO paste in a 0.01M KOH solution. Most prototype commercial secondary zinc electrodes incorporate additives to reduce factors such as dendritic growth and shape change, which limit the useful cycle life, and to raise the hydrogen evolution overpotential, thereby reducing zinc corrosion [2 - 5]. Polymeric additives are often used as binders to help control the former factors: a common one in the zinc electrode (as well as other electrode systems) is PTFE [2, 5 - 7]. Amalgamation and incorporation of mercuric oxide is typically encountered to raise the hydrogen evolution overpotential [2 - 6], although under some circumstances this has been shown to have a deleterious effect upon cycle life due to shape change [6].

Many RDE experiments have been carried out on solid planar zinc [8 - 10], but it appears that few equivalent studies on porous zinc, similar to those of McNeil [1], have been performed. Neither have these been

extended to the additive-containing electrode encountered in commercial applications. While McNeil carried out his experiments in 7M KOH electrolyte, a common value for battery use, a large number of electrochemical investigations of zinc have taken place at lower concentrations.

In this preliminary study, the electrochemical effect of mercuric oxide as an additive in Teflon-bonded zinc electrodes has been examined by an automated rotating disk method and some unusual results have been produced. Further investigations of these effects using alternative methods, and the consequences of other additives, will be discussed in future publications.

Experimental

The electrolyte in all experiments, and the electrolytic cell were the same as those described previously [1]. Electrode pastes were fabricated from AR grade materials throughout and were composed of 95% ZnO and 5% PTFE (in suspension) with 1% HgO included when desired. Propan-2-ol was used as a liquid medium for paste mixing. The final rolled sheet was of a tough fibrous nature, qualitative observation revealing the PTFE fibres to be orientated in the direction of the last rolling. These pastes were then pressed into a 3 mm dia. (c.s.a. = 0.0707 cm²) hole in a 0.6 mm thick Teflon sheet with a zinc plate (Koch-Light 99.999%) backing. The electrode was placed in an oven at 90 °C for several hours to dry and the paste mass was then recorded.

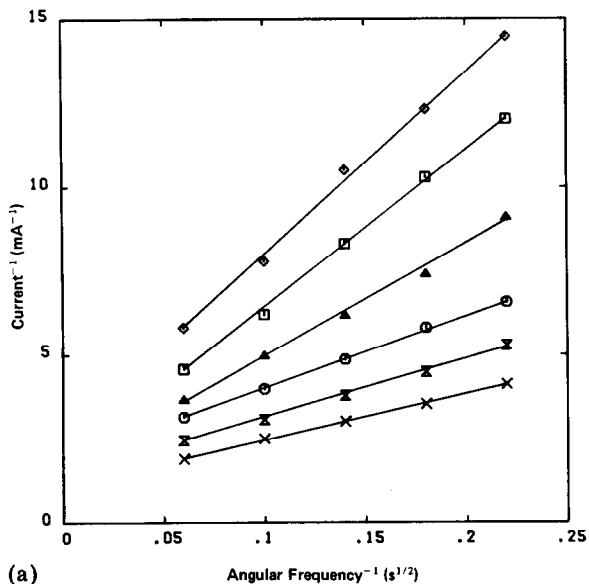
The porous zinc electrodes were formed by galvanostatic reduction at the *C*/3 rate in 7M KOH against a platinum gauze counter and the variation in cell potential with time was noted. The basic shape of these charging curves was similar to those of McNeil, although it was found that pastes containing mercury required nearly the theoretical calculated charge while those free from mercury required 15 - 20% more charge before hydrogen evolution occurred. In both cases the resultant electrode consisted of a porous zinc disc with a convex surface which stood slightly proud of the surrounding Teflon.

All control and data acquisition were performed by a microcomputer with 12-bit D/A and A/D interfaces. The cell current was measured using a differential d.c. amplifier and a 12-bit A/D (0.5 mV/bit) microcomputer interface with zero crossing detector.

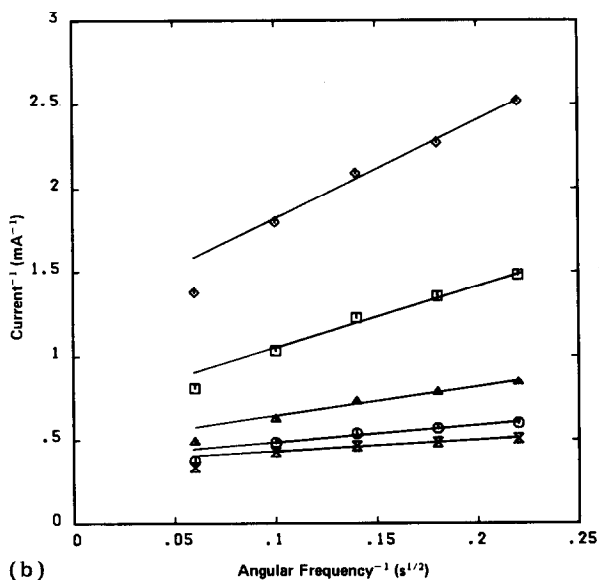
The BASIC algorithm used was the same as described previously [1] with amended software, and the data were stored for later numerical analysis and plotting.

Results and discussion

The discrepancies observed between the degree of charge required for HgO and HgO-free electrodes to reach top of charge can be attributed to



(a)



(b)

Fig. 1. Plots of i^{-1} vs. $\omega^{-1/2}$ for HgO-free electrodes. (a) Low overpotentials: \diamond , 4 mV; \square , 8 mV; \triangle , 12 mV; \circ , 16 mV; \times , 20 mV; \ast , 24 mV anodic of rest potential. (b) Higher overpotentials: \diamond , 30 mV; \square , 40 mV; \triangle , 50 mV; \circ , 60 mV; \times , 70 mV.

hydrogen evolution concurrent with the charging process. This indicates that even this small quantity of mercuric oxide considerably suppresses hydrogen evolution.

Figure 1(a) and (b) shows the rotation speed dependence of the mercury-free electrode. The behaviour of the electrode was similar to that in

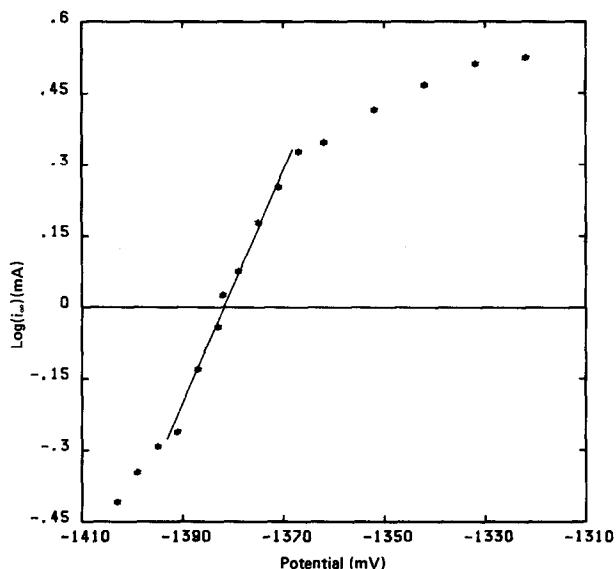


Fig. 2. Tafel line for HgO-free electrode (slope of line = 40 mV/decade).

previous work where linear Levich plots (i^{-1} vs. $\omega^{-1/2}$) were obtained at a lower rotation speed over the whole potential range. Above 30 mV anodic overpotential there is a trend for the current to be higher than expected at the faster rotation speeds. This has been explained by turbulence at the electrode surface due to the rough front face. Such turbulence is likely to change the nature of the conceptual diffusion layer, resulting in the observed higher dissolution of material.

Tafel lines and slope dependence plots were constructed using the linear portions of the Levich lines. The entire potential range could not be covered by a single electrode due to its finite capacity and the necessity of the experimental algorithm to allow the porous electrode to equilibrate at each dissolution potential.

Figure 2 shows the Tafel plot for the HgO-free electrode. In the mid-potential region, -1390 to -1370 mV (with respect to the Hg/HgO reference), a straight line with a slope of about 40 mV/decade can be seen, which is in agreement with Armstrong and other workers [1, 8 - 11]. It is apparent, therefore, that the proposed mechanism for zinc dissolution, involving two, one-electron charge transfer steps, is unchanged. The magnitude of the currents obtained from the electrode, however, is less than previously observed for additive-free porous zinc [1]. The depression of current in this case is probably due to the presence of the PTFE binder in the electrode. It has been shown that polymeric additives have this effect on the polarization curves [12]. The deviations in Fig. 2 at low overpotentials are caused by the significant hydrogen evolution reaction when compared with the small anodic currents seen at these potentials. Above -1370 mV (with respect to Hg/HgO) the Tafel slope increases rapidly with anodic overpotential. These

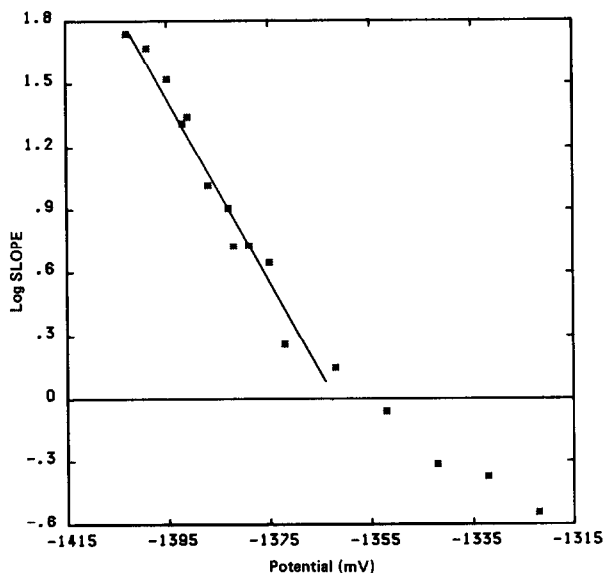


Fig. 3. Slope dependence plot for HgO-free electrode, $\text{SLOPE} = \partial i^{-1} / \partial \omega^{-1/2}$ (slope of line = -30 mV/decade).

larger slopes can be explained by ZnO film formation on the electrode surface, with an increasing ohmic contribution to polarization [13], accompanied by the non-stirring within the porous matrix (non-rotating disk kinetics).

The slope dependence, $\log(\partial i / \partial \omega^{-1/2})$ vs. potential, in Fig. 3, shows the commonly seen [1, 8, 9] -30 mV/decade relationship, indicating that the Zn(II) species are in quasi-equilibrium with the electrode.

Figure 4(a) and (b) shows the i^{-1} vs. $\omega^{-1/2}$ plots for the Teflon-bonded electrode incorporating 1% HgO. As can be seen in Fig. 4(a) the kinetics at low overpotentials are significantly changed. The Levich lines, when extrapolated up to an overpotential of about 24 mV anodic, appear to intercept at the origin. This implies that at these low overpotentials a quasi-reversible system has been created, and marks a significant effect caused by the mercury. If the effect of the mercury is to destroy the structure of the metal surface and result in one from which the atoms can be removed and incorporated at any point, then this effect can be understood. There is evidence that the electron transfer at a Zn/Zn(II) electrode in alkali occurs in two stages, with the second transfer being the rate determining one. If the effect of mercury operates *via* the charge transfer reaction, then it is difficult to see how the reaction could be made more reversible since the mercury would be expected to participate only in the Zn(0)/Zn(I) reaction. The metallurgical argument seems most attractive.

A slope dependence plot, constructed as before, is shown in Fig. 5. In the low overpotential range a -30 mV/decade relationship can be seen, showing that even with these modified kinetics a quasi-equilibrium still

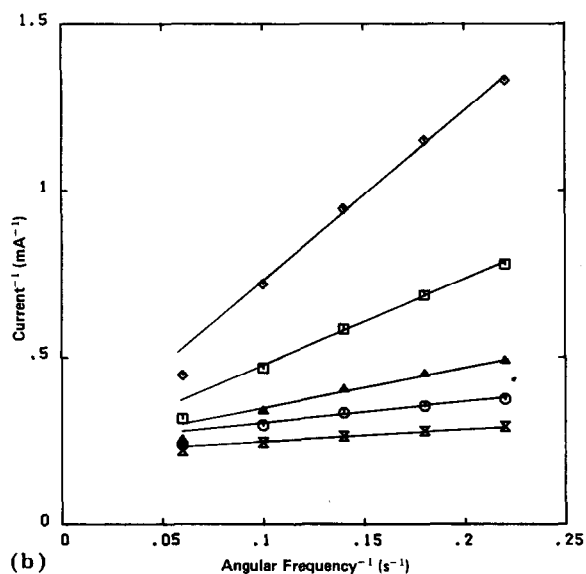
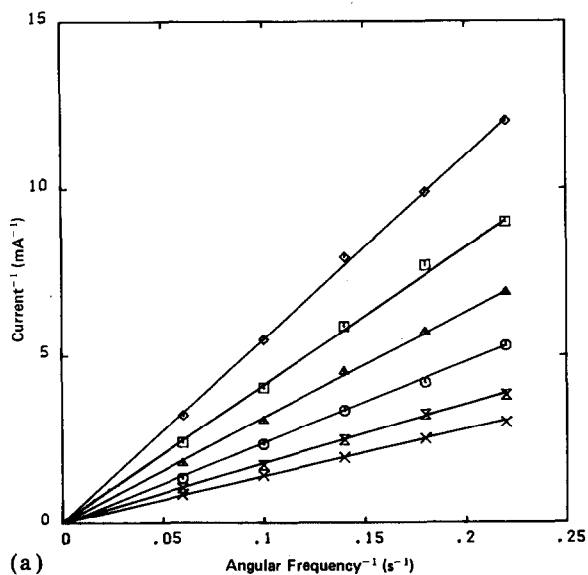


Fig. 4. Plots of i^{-1} vs. $\omega^{-1/2}$ for HgO containing electrodes. (a) Low overpotentials, symbols as in Fig. 1(a). (b) Higher overpotentials, symbols as in Fig. 1(b).

exists between the Zn(II) species in solution and the electrode. As seen also in the HgO-free electrode at more positive overpotentials, the slope $(\partial E / \partial \log \text{SLOPE})_E$ increases markedly. This can be interpreted, in accordance with porous electrode theory [14], as confirming that at higher overpotentials the current rises increasingly from the front of the electrode and thus increases the irreversibility.

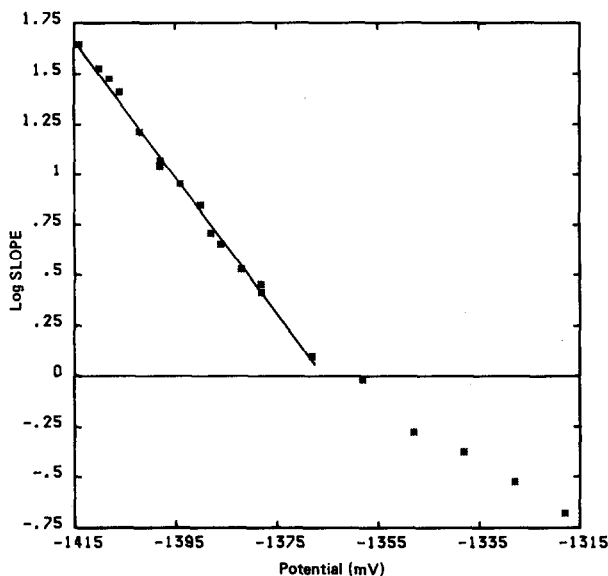


Fig. 5. Slope dependence plot for HgO containing electrodes (slope of line = -30 mV/decade).

In Fig. 4(b) it can be seen that the quasi-reversibility is lost. Though i_{∞} is large it is no longer apparently near infinite, and positive intercepts are obtained when the i^{-1} vs. $\omega^{-1/2}$ at $\eta > 30$ mV are extrapolated. Even at these higher overpotentials, however, the situation is not clear and no logical Tafel lines can be constructed.

Karunathilaka [15] stated that in commercially amalgamated electrodes, where mercury is used to counteract hydrogen evolution, the mercury tends to obscure porosity by providing a more 'liquid-like' surface. Also, amalgamation of commercial, porous zinc electrodes causes them to behave similarly to planar solid zinc electrodes [16]. Hendrix and co-workers [11] pointed out that few studies had been carried out on zinc electrodes amalgamated to the degree found in battery applications, and they managed to form an amalgamated solid zinc electrode. Galvanostatic perturbation investigations enabled Tafel lines to be constructed, though these seemed to taper off to infinity at anodic overpotentials greater than 60 mV. Despic *et al.* [17] carried out studies on solid zinc and amalgam. They derived an equation which fitted their anodic Tafel plots on the basis that the limiting current was due to complete surface coverage by Zn(I) species.

To conclude, it appears that the surface of Teflon-bonded porous zinc is modified by mercury such that, at low overpotentials, a quasi-reversible system exists. Also, the electrodes whose original pastes contained HgO show higher steady state currents than the ones where HgO was absent. Mercury-free, Teflon-bonded porous zinc behaves very similarly to the porous zinc previously reported [1].

Acknowledgement

A. D. acknowledges the financial support of Joseph Lucas Ltd. and the SERC.

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