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The concentration profiles in solution at dissolving anode surfaces (1) zinc, copper and brasses by the freezing techniques

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Anolytes adjacent to dissolving metal surfaces have been sampled after freezing using liquid nitrogen/isopentane mixtures. Metal ion, anion and pH profiles were obtained after analysis of the samples. The results are discussed in terms of the solution flow rate and of the regimes obtaining at the time of freezing.

Introduction

The properties of the diffusion layer adjacent to a polarized electrode are important because the overall control of the electrode process is related to this layer. Ibl [1] has suggested that the thickness of the layer varies between a few thousandths and a few tenths of a millimetre depending on the hydrodynamic conditions, while Faust [2] quotes a figure of 0·03 mm for nickel anodes dissolving in 'violently agitated hydrochloric acid'. Assuming Fick's Law and a linear concentration gradient, Walton [3] calculated a value of around 0·06 mm for copper dissolving in flowing phosphoric acid.

Brenner [4] has comprehensively surveyed the methods available for investigating cathode layers during metal electrodeposition for which most of the published work has been carried out. The available methods can be divided into optical methods, based on changes in the refractive index of the layers adjacent to the electrode, and sampling methods. The optical methods are not suited to the analysis of complex solutions, and sampling methods based either on a single capillary or on a microporous electrode have the disadvantages of disturbing the equilibrium by drawing off the diffusion layer and of taking an average composition of the diffusion layer as a whole. A final sampling method developed by Brenner [5] is that of very rapidly freezing the cathode layers. Successive fractions of the still frozen layer are removed and analysed by basically traditional techniques.

There is no fundamental reason why the techniques developed for the cathodic case should not be used, after suitable modification, for the investigation of dissolving anodes.

It was decided to use a method based on this last technique to sample the anode layers adjacent to copper, zinc and brass electrodes dissolving in sodium chloride solutions under both static and flowing conditions.

Experimental

The high flow rig, previously described [6, 7] was used with a modified cell containing a hollow anode with replaceable working faces. These faces, of area 12·7 mm × 12·7 mm, were made of copper, zinc and 60/40 and 70/30 brasses. The electrolyte was 20% sodium chloride and the flow rates were zero, i.e. under conditions of natural convection, and 12·09 m/s. As a preliminary, potentiostatic anode polarization curves of the anode facing materials in 20% sodium chloride were obtained and the results are shown in Figs. 1 and 2.

In the freezing cell the electrodes were polarized at a preselected potential and after equili-

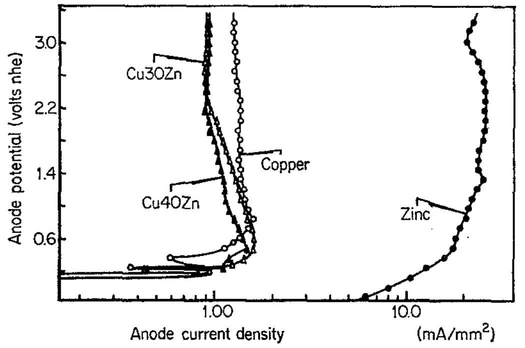


Fig. 1. Polarization of copper, zinc and alloy anodes in 20% w/w NaCl under static flow conditions.

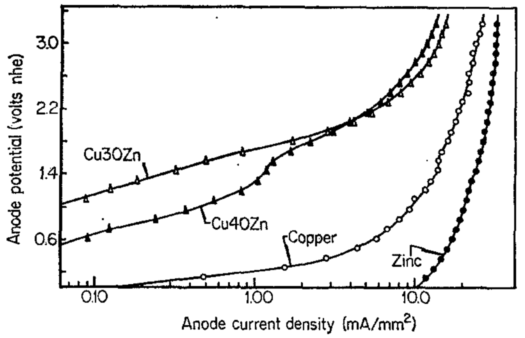


Fig. 2. Polarization of copper, zinc and alloy anodes in 20% w/w NaCl under maximum flow conditions.

brium had been reached, an isopentane/liquid nitrogen slurry, with a temperature of about 110 K, was poured into the hollow anode. The rapid freezing of the electrolyte in the inter-electrode gap caused a decrease in the current, at the first sign of which the circuit was broken. The anode with its adherent frozen anolyte was rapidly removed and placed in a simple microtome for sectioning. The temperature of the layer was maintained by frequent additions of liquid nitrogen. The complete layer, about 0.5 mm thick, was sectioned six times and the samples were examined for pH and metal content.

The pH was measured using a calibrated palladium/hydrogen electrode. Copper was determined using a modification of the spectrophotometric method developed by C.E.R.L. Zinc was determined polarographically using an ammonia/ammonium chloride base electrolyte. Chloride ion concentrations were determined spectrophotometrically.

Details of the apparatus and methods used have been described elsewhere [7].

Results and discussion

The concentration and pH profiles are shown in Figs. 3 to 6, together with the polarization potential, flow conditions and relevant surface regime for each graph.

A general increase of metal ion concentration near to the anode surface is observed, although the magnitude of the increase varies with the conditions, with the greater increases in metal ion concentration occurring when the current densities are highest. The thicknesses of the diffusion layers, of the order of a few tenths of a millimetre, are in the range previously found. As might be expected there is some reduction in the thickness as the flow rate increases, particularly for the copper and zinc anodes.

No profiles for chloride concentrations are given as the values were all close to that of the basic electrolyte and distributed in an apparently random manner. Walton [3] observed an increase in solution anion concentration when copper was anodically polarized in phosphoric acid solutions and work from this laboratory

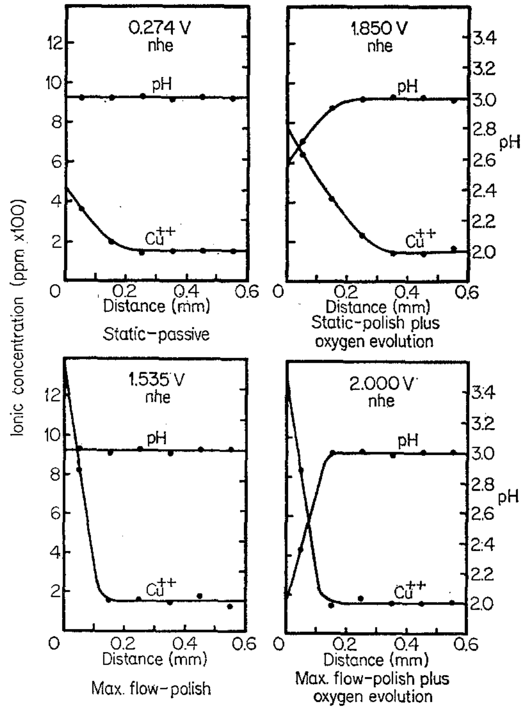
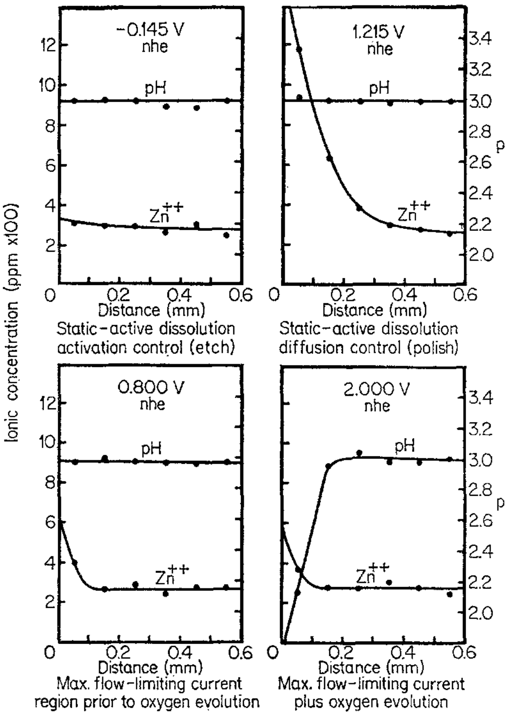


Fig. 3. pH and ionic concentration profiles for copper anodes exhibiting various modes of behaviour.



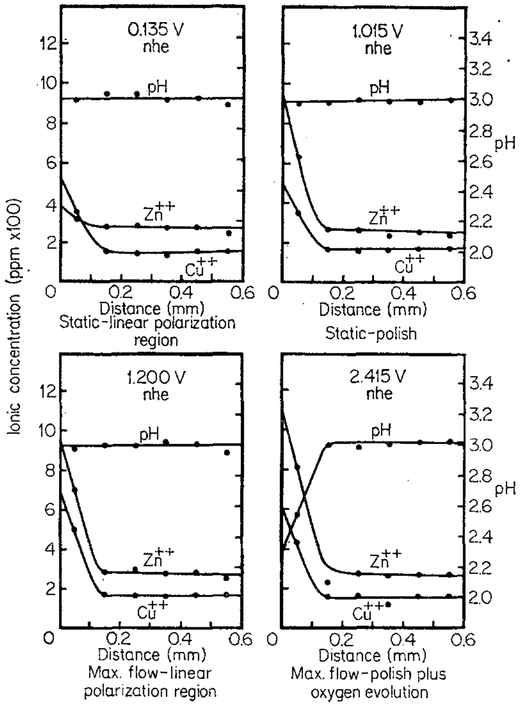
Static-active dissolution activation control (etch)

Static-active dissolution diffusion control (polish)

Max. flow-limiting current region prior to oxygen evolution

Max. flow-limiting current plus oxygen evolution

Fig. 4. pH and ionic concentration profiles for zinc anodes exhibiting various modes of behaviour.



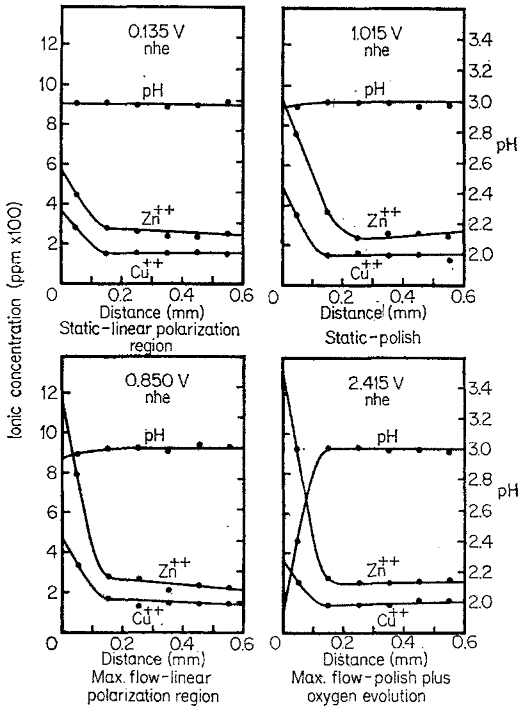
Static-linear polarization region

Static-polish

Max. flow-linear polarization region

Max. flow-polish plus oxygen evolution

Fig. 5. pH and ionic concentration profiles for Cu30Zn alloy anodes exhibiting various modes of behaviour.



Static-linear polarization region

Static-polish

Max. flow-linear polarization region

Max. flow-polish plus oxygen evolution

Fig. 6. pH and ionic concentration profiles for Cu40Zn alloy anodes exhibiting various modes of behaviour.

[8] reports an increase in chloride ion concentration when a microporous nickel electrode was dissolved in chloride solutions. A number of factors could be operative in the systems presently under discussion. Thus the need to maintain electrical neutrality within the diffusion layer could be met by the diffusion of both Cl′ and OH′ and the formation of solid cuprous chloride on the surface, detected on copper [9] and brass [10] anodes, would lead to a consumption of the chloride ions. Increases in chloride ion concentration as previously reported, on the one hand, or decreases due to co-migration of hydroxyl ions and cuprous chloride formation, on the other, were not observed and it may be that the chloride concentration is so great (~120,000 ppm, compared with metal ion concentrations of ~10 ppm) that the experimental technique was unable to detect the changes.

It is possible that the dissolution of a copper anode occurs as a result of a competition between film formation, probably cuprous chloride, and reactions liberating the metal as soluble ions.

Evidence for this is obtained from the cupric ion profiles where the passive mode, when the filming regime predominates, shows a lower metal concentration than the polishing condition. The possibility that the copper anode is under diffusion control is given credence by the occurrence under all conditions investigated of a large concentration gradient, whereas in contrast the condition when zinc is etched and is probably under activation control shows only a small concentration gradient. It may be possible to argue that the magnitude of the rise in the interfacial ionic concentration can be used as a guide to the predominant controlling mechanism at the electrode.

The variation of solution pH within the layer is clearly seen with a large reduction only when solution oxidation is present. Under no other conditions was a significant change in pH observed. This seems to suggest that the pH changes can be related to a release of hydrogen ions by a mechanism such as:

$$H_2O+2e\rightarrow \tfrac{1}{2}O_2+2H^+$$

Comparison of the metal ion profiles for regimes differing only by virtue of oxygen evolution suggests that the increased currents at the higher potentials are solely due to consumption by the solution oxidation reaction with no appreciable increase in the metal removal rate. Although the present results confirm the widely held idea that the pH at a working electrode is different to that in the bulk solution, the nature of the change is not that suggested by some authors. Working on cathode layers Ibl [1] postulated that pH will decrease in the catholyte because of migration of ions under the influence of the field. The reverse of this is that the pH should increase in the anolyte. The present results show that the field induced effect is too small to be detected by the techniques used and is insignificant compared with the increase in hydrogen ion concentration produced by the solution oxidation reactions.

In the dissolution of the two alloy materials the magnitude of the zinc ion increase was greater than or equal to that of the copper ion with the exception of the polarization region of the Cu30Zn anode under static conditions. Since there is evidence [10] that copper anodes dissolving in chloride solutions form films of cuprous chloride while zinc dissolves to the divalent ion, it is not surprising that greater increases in zinc concentration are generally found. This indicates the possibility that the control mechanisms for dissolution of the two metals are essentially independent, even when alloyed. It was also found that the brass with the larger zinc content consistently exhibited a larger differential in the magnitude of the two ionic concentration maxima.

The diffusion layers of the species investigated in the cases of the brasses seem to have the same thickness as indicated in Figs. 5 and 6. This coincidence is more apparent than real because the sampling techiques only allowed the determination of the average analysis over the finite section taken and, while it is probable that the ion with the lowest diffusion coefficient will exhibit the thinnest layer, it seems from the present results that the layers all have the same order of thickness.

Conclusion

A technique has been used which enables the anode layers to be analysed. The anode layers show increases in metallic ion concentration which can be related to the mode of dissolution.

The changes in pH result from solution oxidation.

Acknowledgments

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