

## SHORT COMMUNICATION

### CATHODE CORROSION\*

M. CLARKE

Department of Metallurgy and Materials, Sir John Cass College,  
Whitechapel High Street, London E.1

CASES have been reported recently of corrosion resistant metals or alloys corroding when acting as cathodes in media in which they are quite inert or passive when immersed unpolarized or made anodes. Epstein *et al.*<sup>1</sup> have studied the cathodic corrosion of stainless steel in nitric acid, for which they propose a complicated mechanism. Other examples come from studies in molten salt electrolytes, where corrosion has occurred on cathodes of noble metals as an undesirable side-reaction. Caton and Freund,<sup>2</sup> using a Pt microelectrode for polarography in alkali metaphosphate melts, found the cathode to be severely corroded at high c.d. Bartlett and Johnson,<sup>3</sup> making electrochemical studies on nitrate and nitrite melts noted corrosion on cathodes of Ag, Au, Co, Cu, Pd, Pt, Rh, Ta and stainless steel. None of these metals dissolved unpolarized, and few did so as anodes.

Several examples occur in the field of electrodeposition. Knoedler, Raub and Pfeiffer report the dissolution of gold when made cathodic in aqueous cyanoaurate electrolytes.<sup>4</sup> Brenner, discussing the electrodeposition of manganese and its alloys, from aqueous solution states that the metal initially deposited will sometimes redissolve entirely from the cathode, although the c.d. is unchanged.<sup>5</sup> Te and Po are also said to deposit and redissolve from a cathode.<sup>6</sup>

This communication examines the phenomenon of cathode corrosion, and suggests some general principles involved.

The facts are as follows:

- (a) Metals and alloys do not corrode by a cathodic process.
- (b) Where a metal electrode corrodes when polarized cathodically the measured cathodic current is the algebraic sum of a small partial anodic current and a larger partial cathodic current.

#### DISCUSSION†

##### *Noble metal cathodes*

Taking Pourbaix's criterion for corrosion (metal ion concentration of  $> 10^{-6}M$ ) then for simple aquo cations of the metal, the potential above which corrosion can occur is

$$E_a = E^\circ + (RT/F)n \ln 10^{-6} \quad (1)$$

where  $E^\circ$  is the standard electrode potential, and the other terms have their usual

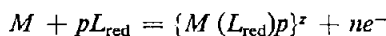
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†In the following argument concentrations are used where rigour demands activities.

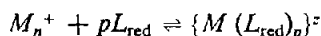
significance. If the potential of the electrode is  $E_i$  when carrying a current  $i$ , the metal is noble if  $E_i < E_a$  for all the currents used, and immune from corrosion. Consider the potential being made negative (electrode a cathode). Then it is possible that the cathode process, or one of them if a number occur, is the reduction of some species to a product  $L_{\text{red}}$  which is a more powerful ligand for metal ions than water. Let  $E_L$  be the potential below which there is appreciable reaction:



The ligand can form a soluble complex ion with the metal by the reaction



where  $p$  is the coordination number of  $M$  in the complex, and  $z$  is the complex ion charge. If  $K$  is the instability constant for the complex:



$$\text{then } K = \frac{[M^{n+}][L_{\text{red}}]^p}{[\{M(L_{\text{red}})_p\}^z]}$$

In the presence of a concentration of  $L_{\text{red}}$  in the cathode layer, the corrosion potential is lowered to  $E_a - D$ , where

$$D = (RT/nF) \{p \ln [L_{\text{red}}] - \ln K\}$$

The metal is no longer immune, and can corrode while acting as a cathode provided

$$E_L > E_i > (E_a - D) \quad (2)$$

This condition may be expressed in terms of the cathode polarization from the steady-state potential  $E_0$ , where

$$\eta_c = E_i - E_0$$

as

$$E_L - E_0 > \eta_c > E_a - (D + E_0) \quad (3)$$

When polarization depresses the potential below the *r.h.* inequality of equation 2, corrosion ceases because the metal is now cathodically protected. Noble metal cathodes which corrode should therefore do so within a range of potential.

#### *Passive metal cathodes*

A passive metal cathode can corrode without the necessity for the production of a ligand by reduction; water or some other species already present in the electrolyte may suffice. Cathode polarization to potentials below the Flade potential  $E_f$ , but

above  $E_a$  will destroy the protective film without establishing full cathodic protection. Corrosion is possible if

$$E_f > E_i > E_a \quad (4)$$

or if

$$E_f - E_0 > \eta_c > E_a - E_0 \quad (5)$$

If, however, the cathode process does produce a suitable ligand, the potential range for cathode corrosion will be extended to

$$E_f > E_i > (E_a - D) \quad (6)$$

or to

$$E_f - E_0 > \eta_c > E_a - (D + E_0) \quad (7)$$

If the potential  $E_L$  is above  $E_f$ , the ligand may exert a solvent action on the protective film, and raise the upper limit for corrosion.

For the reported cases of cathode corrosion the data required to test the above conditions is not available, but an indirect test can be made by examining the effect of the mechanisms proposed on the cathode polarization curve for a metal showing cathode corrosion.

For a noble metal the effects are illustrated in Fig. 1 where the partial cathode polarization current follows  $E_0$ DEGH. At and below the potential  $E_L$  cathodic

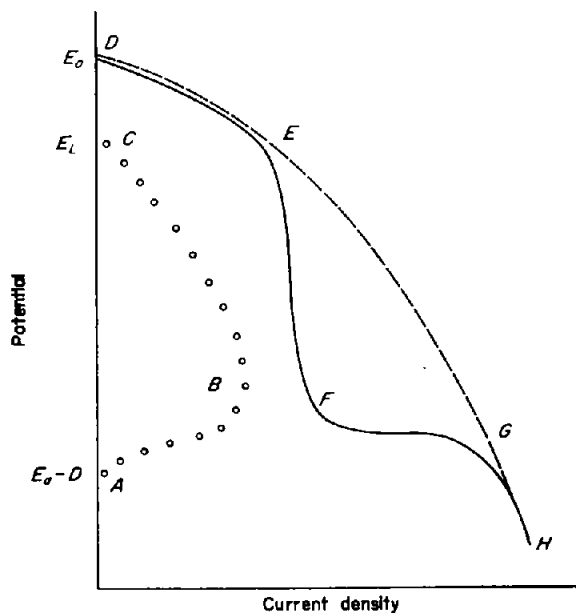


FIG. 1. A noble metal, standing potential  $E_0$ , corroding due to the production of a ligand by cathodic reduction of the electrolyte below potential  $E_L$ , which lowers the potential for immunity to  $E_a - D$ . Curve ABC ( $\circ \circ$ ) is the partial anode curve for metal corrosion, curve DEGH (---) that for the cathode process. The observed curve, potentiostatic conditions, is the sum of these two, DEFGH (—).

production of the ligand commences, and for simplicity it is assumed that its rate of formation is proportional to the depression of the potential below  $E_L$ . Until  $E_i$  approaches  $E_a - D$ , equation 2, the partial anode c.d. for metal corrosion is controlled by ligand availability, and then by anode polarization, giving the curve ABC. The observed polarization of the cathode as a whole, obtained by adding the partial curves, should show a kink in DEFGH, to an extent which will depend on the relative rates of the anode and cathode processes.

For a passive metal, combination of the typical anode curve ABCD (Fig. 2) and the partial cathode curve EFG may give an observed cathode polarization HIJK which shows a re-entrant near  $E_f$ , if the magnitude of the partial anode current at  $B$  is sufficiently large. Ligand formation would lower the value for  $E_a$ .

When corrosion is severe the effects illustrated in Fig. 2 will be most pronounced, whereas slight corrosion might not make a detectable impression on the observed cathode polarization curve.

Of the examples of cathodic corrosion quoted, potentiostatic polarization measurements have been reported only in the case of stainless steel in  $\text{HNO}_3$ . The cathodic reduction of  $\text{HNO}_3$  can give a variety of products in the cathode layer according to conditions, some of which could act as ligands for some or all the components of stainless steel. From such information as is available it is probable that the complexes

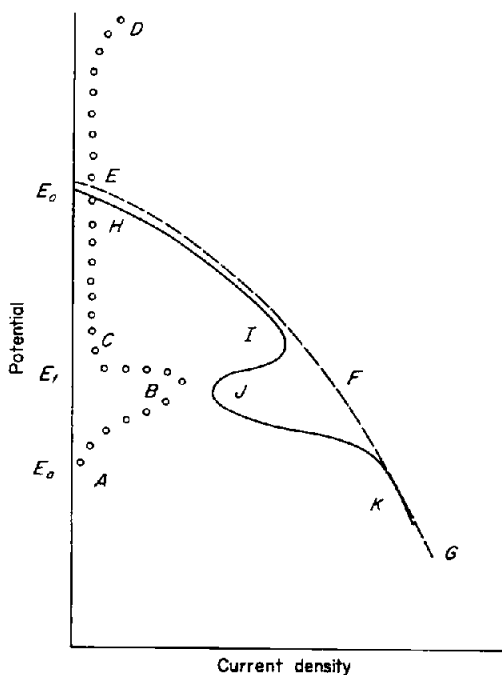


FIG. 2. A passive metal, Flade potential  $E_f$ , corroding when the cathode polarization falls below  $E_f$ . The observed cathode curve, potentiostatic conditions, HIJK (—) may show a re-entrant due to the combination of the partial curves for the anode and cathode processes. Curve ABCD (o o o) is a typical curve for anode passivity, and EFG (---) is the partial cathode curve.

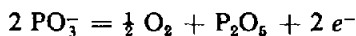
would undergo secondary reactions in the bulk solution. The corrosion rate of stainless steel cathodes<sup>1</sup> reaches a maximum in 2N HNO<sub>3</sub> and there are quite pronounced re-entrants in the polarization curves for 304 steel in 2N and 4N HNO<sub>3</sub>, and for 316 steel in 3N HNO<sub>3</sub>. At very low potentials the rate of attack diminished, as predicted by equations 4 or 6, a result which has been observed by other investigators.<sup>7</sup>

The effect of acid concentration, and of additions of uranyl nitrate or sodium nitrite, both of which decrease the rate of attack, suggest that cathodic ligand formation plays some part, and that these changes reflect a change in the balance of ligand production amongst the various cathode processes. The authors<sup>1</sup> mention that stainless steel cathodes are not corroded in H<sub>2</sub>SO<sub>4</sub>.

These results seem consistent with the mechanism proposed above. In H<sub>2</sub>SO<sub>4</sub> the cathode reaction will be hydrogen discharge, and  $E_0$  will be much lower than in HNO<sub>3</sub>. There seems little scope for ligand formation, so the necessary separation between  $E_i$ ,  $E_f$ , and  $E_a$  needed to fulfil equation 4 is unlikely to be attained. A cathode in H<sub>2</sub>SO<sub>4</sub> will be cathodically protected.

While the results mentioned for fused salt baths do not provide polarization data, they do provide direct evidence for complex formation as a result of cathode processes. Bartlett and Johnson<sup>3</sup> found that in all cases of cathode corrosion, the electrolytes contained coloured complex metal nitro-compounds of high stability. In no case was the corroded metal capable of reducing the melts to these nitro-complexes without cathodic polarization. The evidence also points to stable complex formation in the cases cited by Caton and Freund.<sup>2</sup>

Metal oxides dissolve in fused metaphosphates to give complex phosphates,<sup>8</sup> and in these melts a Pt anode is inert or passive, and the anode process is



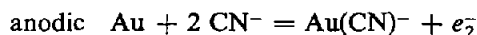
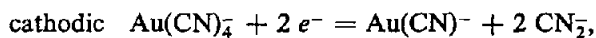
With melts containing dissolved metal oxides, polarographic reduction waves were obtained, but the reduction products were very stable complexes which remained in solution, and no metal deposition was possible within the accessible potential range.

Evidence was obtained of reduction products of the anions at a Pt cathode, including phosphites, phosphides and free P as the potential was lowered. The heaviest attack on Pt cathodes occurred in the potential range where P was one of the products, and the c.d. was high (250 mA/cm<sup>2</sup>). This suggests the Pt corrosion product is so stable that the potential cannot be depressed far enough to re-enter the immune zone.

Knoedler *et al.*<sup>4</sup> have suggested a mechanism, which, with some modification, is the same as that proposed here. They found that gold could be electrodeposited at a cathode from solutions of Au(CN)<sub>4</sub><sup>-</sup> providing that the potential was below -0.8 V (vs. SCE), but above that potential the gold redissolved although a cathodic current was still flowing. The suggested reaction was



which may be expressed as two reactions:



to comply with the principles adopted in the present discussion. These authors also measured the cathode polarization under potentiostatic conditions, and in two examples these show pronounced re-entrant portions like that of Fig. 2.

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