Short Communication

Effects of Oxalate Ions on the Corrosion of Niobium

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The corrosion behaviour of metals in the presence of organic acids has become more important within recent years, owing to an increased awareness of the possible toxicity of corrosion products from cooking vessels.[1,2] It has been shown that oxalic acid increases the corrosion rate on aluminium significantly.[3] Oxalic acid is also known to be an excellent complexing agent for niobium in aqueous solution.[4] In view of this, the corrosion behaviour of passive niobium in the presence of oxalic acid and oxalate ions has been pursued in the present work.

Experimental

The experiments were performed in the same way as described previously for niobium.[5] In addition, potentiodynamic scans were carried out to obtain information on non-stationary current densities.

The solutions were mixtures of oxalic acid and potassium oxalate at different pH values, using sulfuric acid and potassium sulfate as background electrolytes, keeping the ionic strength nearly constant. One series of measurements, using only potentiodynamic scans, was performed at pH 3 with solutions of 0.02 M CsCl + x M $CsHC_2O_4$ ($0.001 < x < 0.60$ M). Some experiments with lithium hydrogen oxalate were also carried out.

Results

Anodic current density. The anodic current density, whether quasistationary or not, seem to show a half-order dependence on the total concentration of oxalic acid/oxalate below pH 5 (Fig. 1). Above pH 5 no effect on the anodic current density was observed, owing to the instability of the niobium oxalate complexes at higher pH.[4] Use of lithium salts reduced the effect of oxalate ions significantly.

Tafel data and capacitance data. From the quasi-stationary measurements at pH 3, one finds that the Tafel slopes seem independent of the concentration of hydrogen oxalate (Fig. 2), but the inverse current density capacitance de-
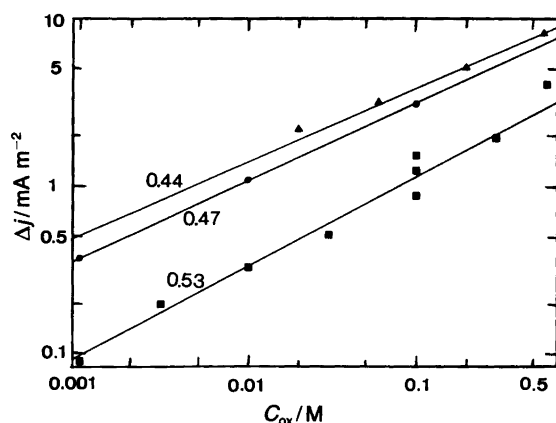

Fig. 1. Increase in anodic current density (Δj) vs. concentration of oxalate (C_{ox}) on passive Nb in air-free, stagnant solutions at 25 °C: ●, 0.50 M H_2SO_4 + x M $H_2C_2O_4$ (pH 0.35) measured during scan (0.04 mV s^{-1}) at 2.5 V(SCE). ▲, 0.30 M K_2SO_4 + x/2 M KHC_2O_4 + x/2 M $K_2C_2O_4$ (pH 4.0) measured during scan (0.04 mV s^{-1}) at 2.5 V(SCE). ■, 0.02 M CsCl + x M $CsHC_2O_4$ (pH 2.7) scan (0.20 mV s^{-1}) to 0.5 V(SCE) and then stabilized for 5000 s before measurement. Values for the reaction orders are shown on the curves.
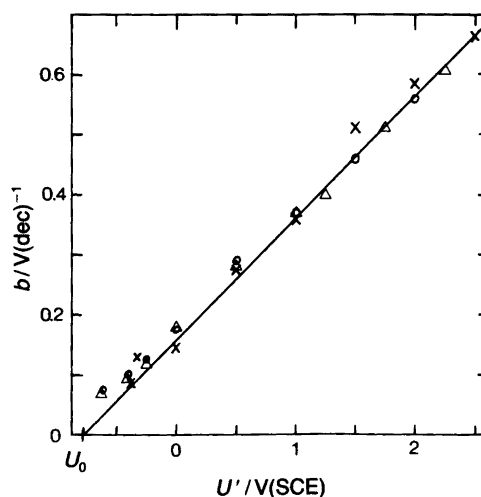

Fig. 2. Tafel slope (b) vs. stabilization potential (U') at pH 2.7 (air-free, stagnant, 25 °C) in: ×, 0.49 M K_2SO_4 + 0.01 M $KHSO_4$; △, 0.45 M K_2SO_4 + 0.03 M KHC_2O_4; ○, 0.35 M K_2SO_4 + 0.30 M KHC_2O_4.
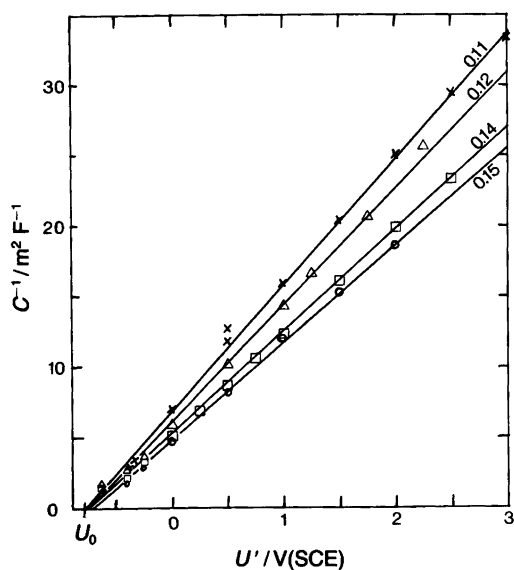
Fig. 3. Inverse electrode capacitance (C^{-1}) vs. stabilization potential (U') at pH 2.7 (air-free, stagnant, 25°C) in: ×, 0.49 M K_2SO_4 + 0.01 M $KHSO_4$; △, 0.45 M K_2SO_4 + 0.03 M KHC_2O_4; □, 0.45 M K_2SO_4 + 0.10 M KHC_2O_4; ○, 0.35 M K_2SO_4 + 0.30 M KHC_2O_4. Values for σ'_m (in C m^{-2}) are shown on the curves.

Conclusions

The experiment shows that the anodic current density of passive niobium has a half-order dependence on the concentration of oxalic acid/oxalate in acid solutions. At higher pH no effect is seen, which argues that oxidation of oxalate does not occur. This is supported by the generally slow anodic electron transfer reactions on passive niobium.[6,7]

The surface charge on the metal increases with increasing concentration of hydrogen oxalate, which suggests that the oxalate and/or the hydrogen oxalate ions are adsorbed on the electrode surface. This seems to be supported by the observed effects of addition of lithium ions. They may inhibit adsorption by forming a lithium oxalate complex in the solution. Data for such a complex formation are at present not known to the author.

Owing to this adsorption, a niobium oxalate complex forms during dissolution of the oxide film. This small decrease of the film thickness will also decrease the inverse electrode capacitance and increase the anodic current density.

creases with increasing concentration of hydrogen oxalate (Fig. 3). However, the extrapolated potential of zero inverse capacitance, U_0, seems constant. This yields an increase of charge at the metal/oxide interface with increasing oxalate concentration, according to eqn. (1),[5] in

$$\sigma'_m = C\,(U' - U_0) \tag{1}$$

which C is the electrode capacitance, U' is the stabilization potential and σ'_m is the charge on the metal/oxide interface. When lithium hydrogen oxalate was used, this effect disappeared.

References

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