Short Communication

Passive Behaviour of Titanium in the Presence of Carboxylate Ions

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Owing to its excellent corrosion resistance,[1-3] titanium has found increased application in differrent chemical environments. However, an awareness of the possible toxicity of even small amounts of corrosion products from, e.g., dental implants[3] or cooking vessels[4,5] has also increased, and the corrosion behaviour of metals in the presence of carboxylate ions has gained interest.[6,7] In view of this, the passive behaviour of titanium in the presence of some carboxylate ions has been studied, especially the film thickness and dissolution rate. Emphasis has been placed on potentiostatic stabilization (20 h) in the passive range, with sharp potentiostatic and galvanostatic excursions away from the stabilized state to elucidate the electrochemical properties of the titanium electrode.

Experimental

The measurements were performed on high-purity titanium sheet electrodes (4.2 cm²) in a thermostatted (25 °C) pyrex glass cell, with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). The platinum wire entered the solution through an open glass tube, while the reference electrode was immersed directly into the solution. Before use or reuse, the titanium electrode was mechanically polished (1000 mesh SiC), cleaned in acetone, etched for 1 min in aqueous 1 M HF, rinsed in distilled water and washed with a portion of the actual cell solution. Test solutions were made from AR grade acids and salts with water twice distilled in a quarz apparatus. In the cell they were deoxygenated by nitrogen bubbling and kept stagnant under a nitrogen atmosphere during the measurements. The cell was shielded from light and stray fields by a surrounding aluminium foil. The carboxylic acids used were citric, formic, oxalic, phthalic, succinic and tartaric acid in the concentration range from 0.0010 to 0.500 M. The solutions were buffered to pH 4 by KOH solution. As a background electrolyte, 0.10 M KCl was used. In the tartrate solutions, potassium was replaced by sodium owing to the low solubility of potassium hydrogen tartrate. No measurements were performed on mixtures of the acids. As a blank solution (without any carboxylate) a mixture of 10^{-4} M HCl and 0.10 M KCl was used. The measuring procedure has been described in previous contributions from our laboratory.[1,2]

Results

The passive current density in the background solution was just above 10 nA cm⁻² at both 0.5 and 1.0 V. The passive current density in the presence of phtalate or succinate did not differ much from the background, and citrate, formate or tartrate did not increase the passive current density by more than 100 %. Also, the passive current density did not vary significantly with electrode potential or carboxylate concentration. However, in the presence of oxalate, the passive current density increased to 30 nA cm⁻² for 0.0050 M and to 70 nA cm⁻² for 0.500 M concentration. The uncertainty in the measurements is 10–20 %.

From oxalate solutions that had been stabilized for 2 days, titanium ions could be detected by addition of tiron to the solution. A faint yellow colour then appeared. This colour did not appear in the other solution compositions tested.

The Tafel slopes in the background solution are 287 mV decade⁻¹ at 0.5 V and about 370 mV decade⁻¹ at 1.0 V. The Tafel slope decreases to about 270 and 350 mV decade⁻¹, respectively, in the presence of citrate, formate or tartrate. The variation with concentration of these anions is small and irregular. In the presence of oxalate, the Tafel slope decreases regularily at 1.0 V, but not so clearly at 0.5 V (Fig. 1). Phthalate and succinate do not influence the Tafel slopes significantly.

The inverse capacitance measured in the background solution resembles that found previously.[1] Values of 5.5 m² F⁻¹ (0.5 V) and 8.0 m² F⁻¹ (1 V) are found. In the presence of citrate, formate or tartrate, the inverse capacitance decreases to about 4.7 and 7.0 m² F⁻¹, respectively. There is no systematic variation with concentration. Fig. 2 shows
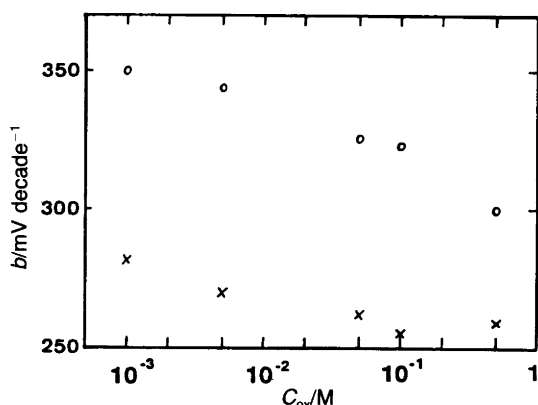
Fig. 1. Anodic Tafel slope, b, at 0.500 V (SCE) ($\times$) and 1.000 V (SCE) ($\circ$) versus concentration of oxalate, C_{ox}, at 25 °C in a deaerated, stagnant solution at pH 4.

that the inverse capacitance decreases rapidly at low concentrations of oxalate, but this decrease slows down at higher concentrations. Again, neither phthalate nor succinate has any measureable influence on the behaviour of the titanium electrode; the inverse capacitance resembles closely the values obtained from the background solution.

Discussion

From eqn. (1)[8] one may calculate the oxide film thickness

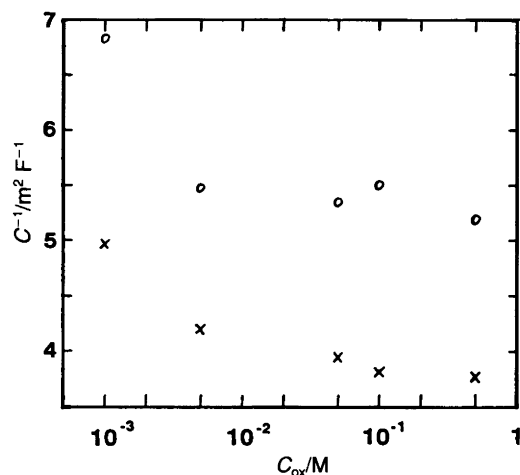$$b = \frac{2.303\, RT\, \delta'}{zF\, \lambda\, fg} \tag{1}$$

Fig. 2. Inverse capacitance, C^{-1}, at 0.500 V (SCE) ($\times$) and 1.000 V (SCE) ($\circ$) versus concentration of oxalate, C_{ox}, at 25 °C in a deaerated, stagnant solution at pH 4.

(δ') at a given stabilization potential. Here, b is the measured Tafel slope, z the charge number of the metal ion ($0= 4$), λ the activation distance for the metal ion to jump between the metal and the oxide film ($= 0.15$ nm), f the field factor ($= 1$)[9] and g the kink site factor ($= 2$).[1,10] R, T and F have their usual meanings. With $b = 287$ mV decade^{-1} (0.5 V) one obtains $\delta' = 5.8$ nm in the background solution. This can be expressed as an anodization ratio by eqn. (2), where a is the anodization ratio, U' the

$$\delta' = a(U' - U_b) \tag{2}$$

stabilization potential and U_b the potential of zero Tafel slope, often found to resemble the reversible reduction potential for the oxide.[1,11,12] This gives an anodization ratio of 2.8 ± 0.1 nm V^{-1}, which is in close agreement with previous findings.[1] From the measurements at 1 V a somewhat larger anodization ratio is obtained.

Turning to the Tafel slope in 0.050 M oxalate solution, 262 mV decade^{-1}, this gives $\delta' = 5.3$ nm and $a = 2.6 \pm 0.1$ nm V^{-1}. The result from 1 V (326 mV decade^{-1}) gives the same value for a. This reduction of the film thickness and anodization ratio is also seen at low pH,[1] where titanium dioxide is more soluble than at pH 4. In the presence of oxalate, oxalatotitanate ions are formed,[13] increasing the solubility of the oxide and hence decreasing the anodization ratio.

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