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Kinetic Parameters of the In(III)/In(I) Electrode Reaction in Bromide Medium

Short Communication

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The electrode kinetic parameters of the In(III)/In(I) couple in acidic 4 *M* bromide solution have been determined by means of the rotating disc electrode technique.

(Keywords: Bromide medium; Electrode kinetics; Indium; Rotating disc electrode)

Die elektrochemisch-kinetischen Parameter des In(III)/In(I)-*Redoxsystems in Bromidlösung (Kurze Mitteilung)*

Die elektrochemisch-kinetischen Parameter am In(III)/In(I)-Redoxsystem wurden in saurer 4-*M*-Bromidlösung mittels der rotierenden Scheibenelektrode bestimmt.

The mechanism of the indium electrodeposition and anodic dissolution has been widely studied by means of several techniques[1]. It is generally accepted that the three-electron process considered occurs in two steps under formation of In(I) ion as an intermediate. However, the kinetics of the particular charge-transfer steps is very little known[2].

In our recent work[3], the In(III) electroreduction on gold from acidic bromide solutions was investigated. The rotating ring-disc technique was successfuly applied to determine conditions under which the only possible reaction is

$$\mathrm{In(III)} + 2\,\mathrm{e} \rightleftharpoons \mathrm{In(I)} \qquad (1)$$

This occurs at low cathodic current densities on the disc surface previously covered with a thin indium passive film.

This communication reports on the preliminary results obtained for the electrode kinetics of the cathodic reaction (1). For this purpose, the rotating gold disc electrode (RDE) was used.

The disc radius of the RDE employed was 0.250 cm. Potential control was maintained by means of a potentiostat EP 20 A (Elpan, Poland). All potentials are referred to the SCE (KCl). Other experimental conditions have been described elsewhere[3]. All measurements were performed at 25 ± 0.2 °C.

The solution studied contained $5 \cdot 10^{-3}\,M$ $InBr_3$, 0.1 M HBr and 3.885 M KBr (total bromide concentration 4 M). Prior to the kinetic measurements, the disc surface was covered cathodically at -660 mV with the primary indium film. For each rotation frequency and potential applied, the cathodic disc current was monitored with time, and then its stationary value was taken into account.

The data obtained were analysed based on the equation derived by *Jahn* and *Vielstich*[4] relating the current, I, to the angular velocity of the RDE, ω, which can be expressed in the following form

$$I^{-1} = I_{\infty}^{-1} + k'\,\omega^{-1/2} \qquad (2)$$

The true activation current, I_{∞}, determined at infinite rotation rate, is given by

$$I_{\infty} = nFA\,(k_{\mathrm{ox}}\,c^{\circ}_{\mathrm{red}} - k_{\mathrm{red}}\,c^{\circ}_{\mathrm{ox}}) \qquad (3)$$

where k_{ox} and k_{red} are anodic and cathodic potential dependent rate constants, c°_{red} and c°_{ox} are the bulk concentrations of the reduced and oxidized form of the depolarizer, respectively, other symbols have their usual significance. If only the oxidized form is present in the bulk of solution, eqn. (3) simplifies to give

$$|I_{\infty}| = nFA\,k_{\mathrm{red}}\,c^{\circ}_{\mathrm{ox}} \qquad (4)$$

Reciprocal stationary disc currents at constant potentials in the range from -660 mV to -700 mV which corresponds to the reaction (1) were plotted against the reciprocals of the square roots of the angular velocity (Fig. 1). Linear relationships, expected from eqn. (2), were found in the range of relatively high rotation velocity of the RDE. Deviation from linearity was observed at $\omega^{-1/2} \to \infty$ particularly when the potential becomes more negative. The reason of this can be attributed to some contribution of the successive reaction step, i.e. $\mathrm{In(I)} + e \to \mathrm{In}$. An increase of the transport rate of the In(I) ions from the disc surface prevents the occurence of this reaction.

Assuming $n = 2$, the cathodic rate constants were calculated according to eqn. (4) from the activation currents determined by extrapolation the linear parts of the plots in Fig. 1 to zero value of $\omega^{-1/2}$. The variation of $\log k_{\mathrm{red}}$ with the electrode potential is shown in Fig. 2. From this plot, a value of the apparent standard rate constant, $k^{\ominus} = 3.5 \cdot 10^{-4}\,\mathrm{cm\,s^{-1}}$, was evaluated by extrapolation to the formal potential of the In(III)/In(I)

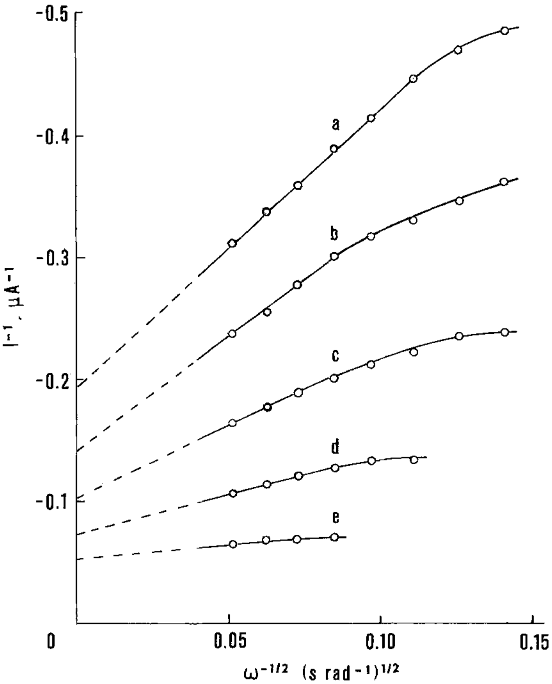

Fig. 1. Plots of I^{-1} vs. $\omega^{-1/2}$ for the reduction of indium(III) at various potentials: *a* −660; *b* −670; *c* −680; *d* −690; *e* −700 mV vs. SCE

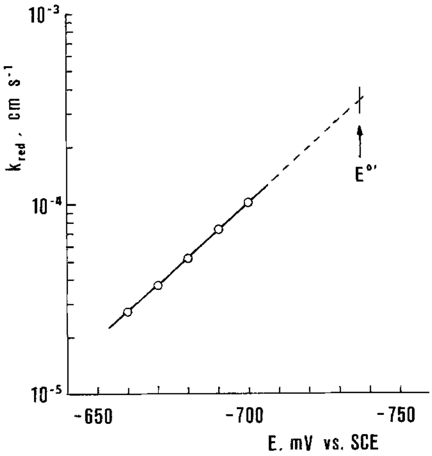

Fig. 2. Potential dependence of the cathodic rate constant for the In(III)/In(I) redox system

couple, $E^{\circ\prime}$, which is -737 mV vs. SCE[5]. The cathodic apparent transfer coefficient was calculated from the slope to be $n\alpha_c = 0.86$.

It is known that two-electron transfer reactions will in most cases proceed by successive single-electron steps, although only one reduction or oxidation stage is observed. According to the theory of *Bockris* and *Reddy*[6], the $n\alpha_c$ value obtained may suggest that the electrode reaction (1) is controlled by the slow transfer of the first electron to the In(III) ion, In(III) + e → In(II), while the second step, i.e. In(II) + e → In(I), is relatively fast.

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