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The effect of electro-osmosis on the synthesis of lead and tin fluoroborates

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Pronounced electro-osmosis phenomena were observed during the anodic dissolution of lead and tin in fluoroboric acid with an anionic exchange membrane separating the anode compartment from the cathode compartment. The consequent volumetric increment of anolyte was influenced by the current density and the initial volume and concentration of catholyte.The selectivities (S_i) of the given membrane were found to be

50% $Sn(BF_4)_2$ solution: $S_{BF4-} = 0.952$; $S_{Sn^{2+}} = 0.048$
50% $Pb(BF_4)_2$ solution: $S_{BF4-} = 0.887$; $S_{Pb^{2+}} = 0.113$

1. Introduction

Tin fluoroborate, $Sn(BF_4)_2$, and lead fluoroborate, $Pb(BF_4)_2$, are two major constituents in the acidic solder plating bath, which finds wide application in the printed circuit board and the cable industries. There are generally two approaches to the synthesis of these fluoroborates: one is the chemical method whereby lead or tin salt is dissolved in fluoroboric acid and further concentrated [1–3]; the other is the dissolution of lead or tin metal into fluoroboric acid via an electrochemical method [4–6]. The second method, which is preferred by industry, usually involves separation of the fluoroborate product and reacting acid by means of the density difference. With the introduction of ion-exchange membranes, many traditional electrochemical processes have been modified to achieve better yield and separation. The second method has proved successful in this laboratory [7] for the electrochemical synthesis of lead and tin fluoroborates.

Electro-osmosis through an ion-exchange membrane results in a net transfer of solvent (the water molecule in the present case) across the membrane. This is because there are fixed-charge groups attached to the pores inside the membrane which facilitate the passage of counter-ions due to charge attraction and hinder the passage of co-ions [8]. This unequal transfer of counter-ions and co-ions results in the net movement of water molecules along with the net transfer of counter-ions. Therefore in an electrochemical process using an ion-exchange membrane, aside from the major transfer process, i.e. the passage of the counter-ion, the passage of co-ions and water molecules has to be considered.

2. Experimental details

The electrochemical cell was made of Lucite with an anion-exchange membrane (Ionac MA 3475) dividing it into two equal compartments (14 × 10 × 6 cm). The membrane was treated with 50% fluoroboric acid for 24 h before assembly. All chemicals were of reagent grade. The lead or tin anodes were of 99.9% purity; pure lead or tin sheets were used as cathodes.

Polypropylene was used as the anode bag material to collect the anode slime. HBF_4 solution (50%) was used as initial catholyte while 2–3.5% HBF_4 solution was used as initial anolyte. A constant current electrolysis was conducted until the anolyte reached a 50% lead or tin fluoroborate concentration with some free fluoroboric acid remaining in the catholyte. Standard operation conditions were as shown in Table 1 unless otherwise specified.

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Table 1. Standard operation conditions

System	*Initial anolyte (ml)*	*Initial catholyte (ml)*	*Anodic current density ($A\,m^{-2}$)*
Tin fluoroborate	523	350	520
Lead fluoroborate	515	400	500

The major constituents were analysed by titration and an atomic absorption spectrophotometer was used to measure the concentration of metal impurities.

3. Results and discussion

3.1. *The effect of catholyte volume and concentration on electro-osmosis*

In the electrolysis, if the anolyte volume (V_1) is kept constant then the anolyte density (d_1) is proportional to the fluoroborate content (W_1) in the anolyte, i.e.

$$d_1 = \frac{W_1}{V_1} + d_0 \qquad (1)$$

where d_0 is the initial anolyte density. However, the actual process deviates from the ideal case due to electro-osmosis. If V_1 and W_1 were changed by ΔV_1 and ΔW_1, then the density d_2 is also different from d_1

$$d_2 = \frac{W_1 + \Delta W_1}{V_1 + \Delta V_1} = \frac{W_2}{V_2} \qquad (2)$$

It is shown in Figs 1 and 2 that for both the tin fluoroborate and lead fluoroborate systems, the actual anolyte density is less than the theoretical prediction because of the volumetric increase of anolyte due to electro-osmosis. A corresponding decrease of catholyte volume also takes place.

The extent of electro-osmosis is influenced by the water content (C_3) and the counter-ion concentration (C_1) inside the membrane. Spiegler [8] proposed a relation

$$\frac{J_3}{J_1} = \frac{C_3}{[C_1 + C_3(X_{34}/X_{13})]} \qquad (3)$$

where J_3 and J_1 are the water flux and counter-ion flux and X_{34} and X_{13} are the friction coefficients between the water molecules and membrane and between the water molecules and the counter-ions, respectively. The water content (C_3) is found to decrease when the solution concentration is increased, as shown in Fig. 3. Increase of catholyte quantity (Figs 1, 2), in fact increases the amount of fluoroboric acid available and the fluoroborate concentration inside the membrane (C_1). The water content C_3 is inversely affected (Fig. 3). An increase of C_1 and a decrease of C_3 reduces the extent of electro-osmosis based on Equation 3. This explains why the results approach the theoretical values as the amounts of catholyte are increased. Fig. 4 shows that the electro-osmosis phenomenon becomes more significant with decreased catholyte concentration. This is also consistent with the above reasoning.

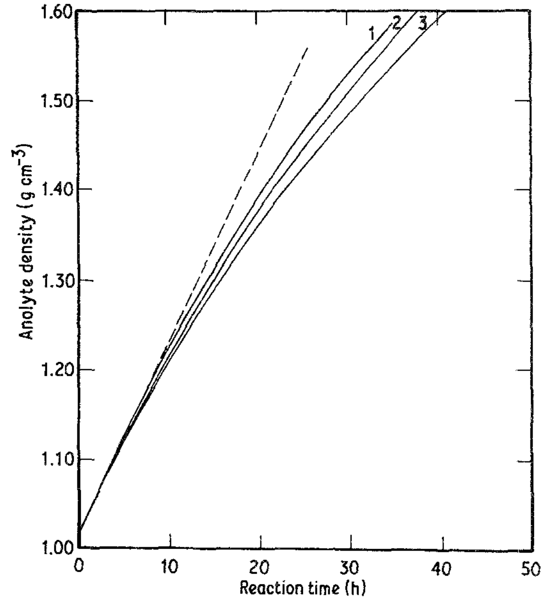

Fig. 1. The effect of initial catholyte quantity and reaction time on the anolyte density in the $Sn(BF_4)_2$ system. Dotted line, theoretical value; solid lines, experimental values. $i_a = 500\,A\,m^{-2}$. Initial anolyte: 3.5% HBF_4, 523 ml. Initial catholyte: 1, 50% HBF_4, 700 ml; 2, 50% HBF_4, 650 ml; 3, 50% HBF_4, 500 ml.

3.2. *Selectivity of the membrane*

The selectivity of an anion exchange membrane is measured by its permeability to cations (Pb^{2+} and Sn^{2+} in this case). Those cations which pass through will either deposit on the cathode or

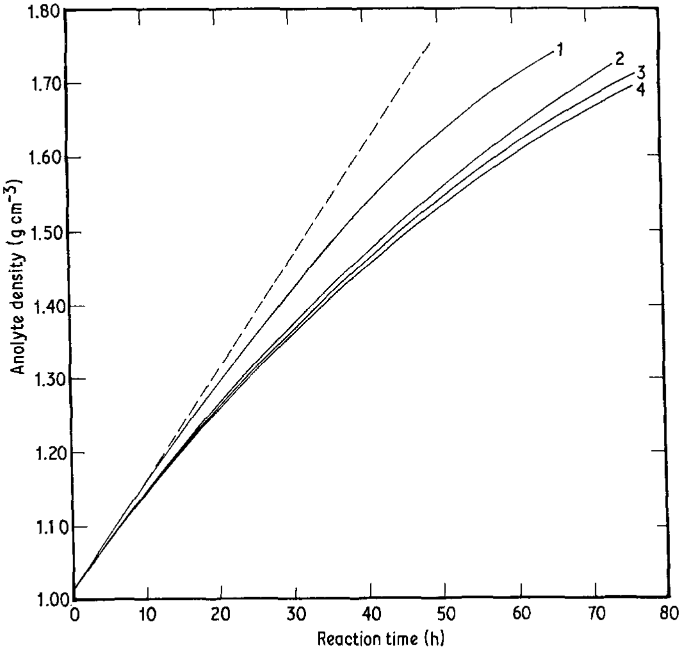

Fig. 2. The effect of initial catholyte quantity and reaction time on the anolyte density in the $Pb(BF_4)_2$ system. Dotted line, theoretical value; solid lines, experimental values. $i_a = 260\,A\,m^{-2}$. Initial anolyte: 2% HBF_4, 515 ml. Initial catholyte: 1, 50% HBF_4, 650 ml; 2, 50% HBF_4, 500 ml; 3, 50% HBF_4, 400 ml; 4, 50% HBF_4, 300 ml.

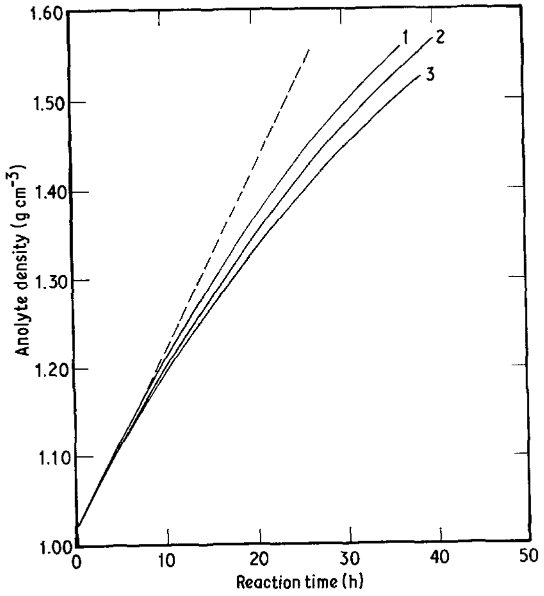

Fig. 3. The effect of initial catholyte quantity and reaction time on the anolyte density in the $Sn(BF_4)_2$ system. $i_a = 520\,A\,m^{-2}$. Initial anolyte: 3.5% HBF_4, 523 ml. Initial catholyte: 1, 50% HBF_4, 500 ml; 2, 43% HBF_4, 500 ml; 3, 39% HBF_4, 500 ml. Dotted line, theoretical value; solid lines, experimental values.

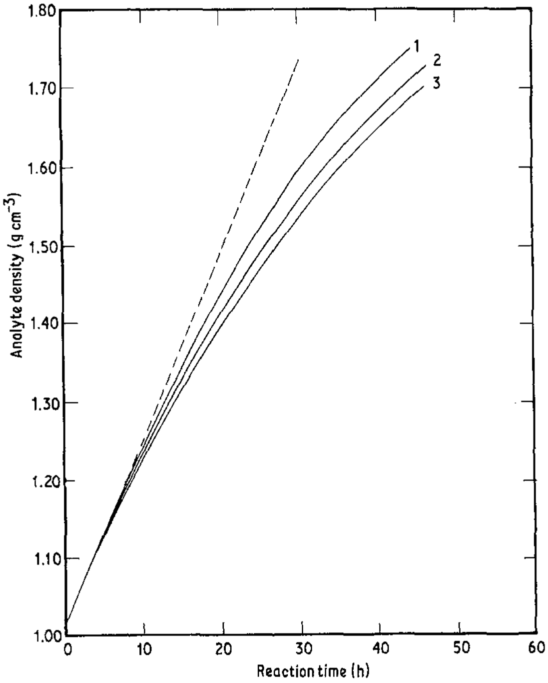

Fig. 4. The effect of initial catholyte quantity and reaction time on the anolyte density in the $Pb(BF_4)_2$ system. $i_a = 500\,A\,m^{-2}$. Initial anolyte: 2% HBF_4, 515 ml. Initial catholyte: 1, 50% HBF_4, 400 ml; 2, 46% HBF_4, 400 ml; 3, 43% HBF_4, 400 ml. Dotted line, theoretical value; solid lines, experimental values.

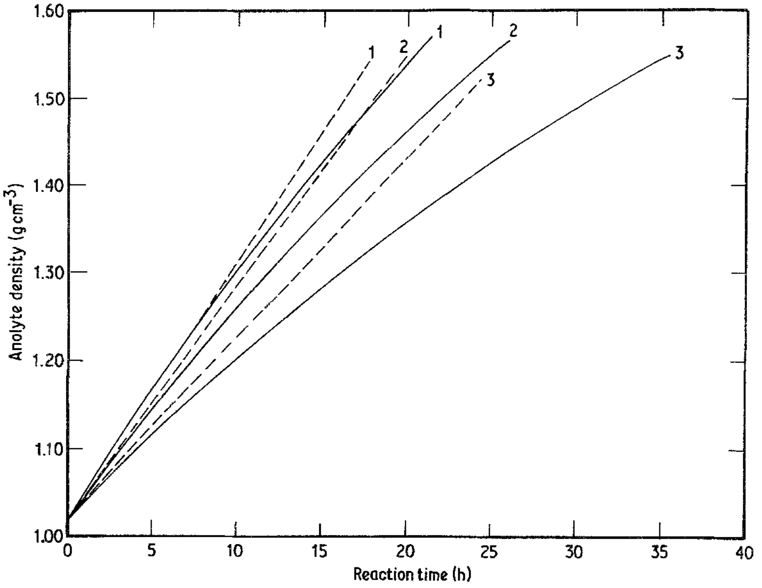

Fig. 5. The effect of anodic current density and reaction time on the anolyte density in the $Sn(BF_4)_2$ system. Initial anolyte: 3.5% HBF_4, 523 ml; initial catholyte: 50%, HBF_4, 350 ml. Anodic current density: 1, 750 A m^{-2}; 2, 666 A m^{-2}; 3, 520 A m^{-2}. Dotted lines, theoretical values; solid lines, experimental values.

remain in the catholyte. The selectivity of this membrane with respect to cations, S_+, is therefore defined by

$$S_+ = \frac{\text{Equivalents of cations passing through the membrane}}{\text{Number of faradays}} \qquad (4)$$

and

$$S_- = 1 - S_+ \qquad (5)$$

It is found that the selectivity quickly reaches a constant value after four or five runs. In our case, for the 50% $Sn(BF_4)_2$ system: $S_{\mathrm{BF}^-} = 0.952$; $S_{\mathrm{Sn}^{2+}} = 0.048$. For the 50% $Pb(BF_4)_2$ system: $S_{\mathrm{BF4}^-} = 0.887$; $S_{\mathrm{Pb}^{2+}} = 0.113$.

The lead ions apparently have stronger penetrating power than the tin ions. This can be accounted for by the fact that the charge density of lead ions is smaller and hence they attract few water molecules. In addition, they suffer less repulsive force from the fixed-charge group inside the membrane.

3.3. *The effect of anodic current density on electro-osmosis*

Figs 5 and 6 show that the experimental results approach the theoretical value as the current density is increased, which implies a reduction in electro-osmosis. This result is noteworthy since previous findings made by George and Courant [9] showed little correlation between current density and electro-osmosis. Lakshminarayanaiah [10, 11] derived a relation which showed electro-osmosis to be inversely proportional to the surface charge density of the liquid in the membrane pore. It is probable that increasing current density draws in more anions from the catholyte which increase the surface charge density and membrane conductance and thus leads to the reduction of electro-osmosis. This can also be

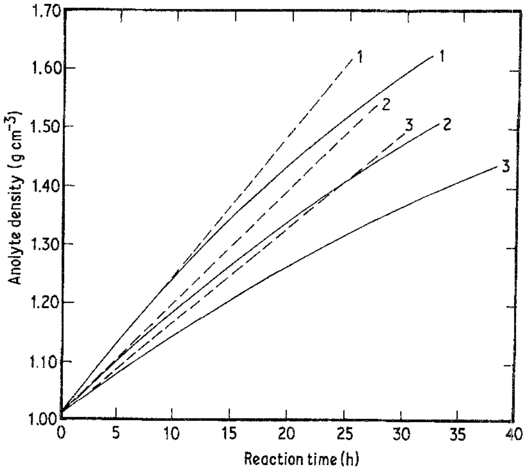

Fig. 6. The effect of anodic current density and reaction time on the anolyte density in the $Pb(BF_4)_2$ system. Initial anolyte, 2% HBF_4, 515 ml; initial catholyte, 50% HBF_4, 400 ml. Anodic current density: 1, 500 A m^{-2}; 2, 390 A m^{-2}; 3, 260 A m^{-2}. Dotted lines, theoretical values; solid lines, experimental values.

explained by Equation 3. When the current density is increased, the counter-ions are accelerated and are less obstructed by the water molecules. A drop in X_{13} in Equation 3 also results in a smaller J_3, which is the extent of electro-osmosis.

4. Conclusions

The electro-osmosis phenomenon is a very serious side-process in the operation of an electrochemical cell incorporationg an ion-exchange membrane. Its significance and quantitative relation with other process variables must be carefully evaluated before any realistic process design can be initiated. In the present case, the anolyte volumetric increment due to electro-osmosis is inversely proportional to the current density, initial catholyte quantity and concentration.

Acknowledgement

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