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ELECTROCHEMICAL SYNTHESIS OF LEAD FLUOROBORATE BY ANODIC DISSOLUTION OF LEAD IN FLUOROBORIC ACID SOLUTION

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SUMMARY

Lead fluoroborate solution was prepared by anodic dissolution of lead in fluoroboric acid solution. The optimal current density could reach 2 A/dm^2 with a current efficiency over 90%. The exchange current density of this system was found to be 0.649 A/dm^2 and to follow the Tafel Equation.

Polarography shows that the cathodic reaction of lead fluoroborate involves only free lead ions with a charge transfer number equal to 2.

INTRODUCTION

Lead fluoroborate is an important ingredient in the electrolyte for solder plating. The fluoroborate system is easily controlled and can sustain high current density. However, relatively few publications have discussed the processes of synthesizing lead fluoroborate. Since lead is not readily dissolved in fluoroboric acid chemically, anodic dissolution can lead to faster reaction and few by-products [1,2]. In our study, we used an anion exchange membrane to separate the anolyte and catholyte. The optimal operation conditions of this process were determined and its electro-chemical kinetic properties were also explored by means of galvanostatic methods and polarography.

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THEORY

The electrochemical cell for this synthesis reaction was separated into two compartments with an anion exchange membrane. This membrane prevents the dissolved lead ion in the anolyte migrating into the cathode compartment and allows the fluoroborate ions in the catholyte to migrate into the anode compartment.

The main reactions are

$$\text{Anode } Pb \longrightarrow Pb^{++} + 2e^{-} \quad (1)$$

$$\text{Cathode } 2HBF_4 + 2e^{-} \longrightarrow H_{2(g)} + 2BF_4^{-} \quad (2)$$

$$2BF_4^{-} \text{ (catholyte)} \xrightarrow{\text{migration}} 2BF_4^{-} \text{ (anolyte)} \quad (3)$$

The net result is the generation of $Pb(BF_4)_2$ in the anolyte until it reaches the desired concentration and is taken out as a liquid product.

The kinetic relation of this dissolution reaction was assumed to follow the Tafel Equation.

$$\eta = (-2.303\ RT/z\ F) \log i_o + (3.03\ RT/z\ F) \log i \quad (4)$$

$$\eta = a = b \log i_o \quad (5)$$

The parameters a,b can be evaluated from η vs i data.

Polarography was used to study the mechanism of this reaction

$$Pb^{++} + 2e^{-} \longrightarrow Pb \quad (6)$$

For the lead ion - lead system, if the limiting step is

$$Pd(BF_4)_n^{2-n} \xrightarrow{ze^{-}} Pb^{2-z} + n(BF_4)^{-} \quad (7)$$

where n is the number of BF_4^{-} ions which may be attached to the lead ion in the reactant species, then polarography can give us information about the identity of $Pb(BF_4)_n^{2-n}$ and the effect of BF_4^{-} on the reaction mechanism as well as the charge transfer number z.

EXPERIMENTAL

Synthesis of lead fluoroborate

50% fluoroboric acid (by weight) was used as catholyte. The concentration gradually decreased as the fluoroborate ions migrated

through the ion exchange membrane during the electrolysis. The anolyte was prepared with dilute fluoroboric acid (0.5% to 4.5%) and boric acid as stabilizer [3]. The ion exchange membrane (Ionac MA 3457) was pretreated with fluoroboric acid for 6 h at 50 ^{o}C. A lucite container was used as reactor with both compartments containing 500 ml of electrolytes. Graphite panels were used as cathode and pure lead panels (99.97%) were used as anode.

A constant current was applied to the system for about 30 h until the anolyte reached the desired concentration. The yield and current efficiency were calculated as follows:

Assume that the concentration of lead in the anolyte (V_1 ml) is X_1 ppm, the lead deposited on the cathode is W g, the concentration of the lead in the catholyte (V_2 ml) is X_2 ppm, the molecular weight of lead is M and t is the duration of electrolysis in sec, then the anodic current efficiency (C.E.) is

$$C.E. = \left(\frac{X_1V_1 + X_2V_2 + W}{M}\right)\left(\frac{2F}{It}\right) \times 100 \qquad (8)$$

Analysis of products

The metal content of the solution was analyzed quantitatively by polarography (Priceton Applied Research Model 384). The total BF_4^- and boric acid concentrations were also measured polarographically at -1.68 v and -1.94 v with 0.1N KNO_3 plus 10% mannitol as supporting electrolyte

The free fluoroboric acid can be analyzed by titration. The electrolyte was first treated with excess KCl to precipitate the $Pb(BF_4)_2$ as $PbCl_2$ and KBF_4. Then the solution was titrated with 0.05M $NaHCO_3$ with methyl orange as indicator. Other metal impurities were measured by atomic absorption and anions such as Cl^-, $SO_4^=$ were determined by ion chromatography (Dionex Model 10).

Electrochemical kinetic studies

The polarization data of the anodic dissolution reaction were studied by a galvanostatic technique using a saturated calomel electrode as reference electrode. The transient response was recorded on an oscilloscope 6 .

A D.C. polarography method was also used to measure $E_{3/4}$, $E_{1/4}$ and $E_{1/2}$ for the evaluation of reaction mechanisms.

RESULTS AND DISCUSSION

Process conditions

The applied voltage is strongly influenced by the fluoroboric acid content in the electrolyte, as shown in Fig. 1

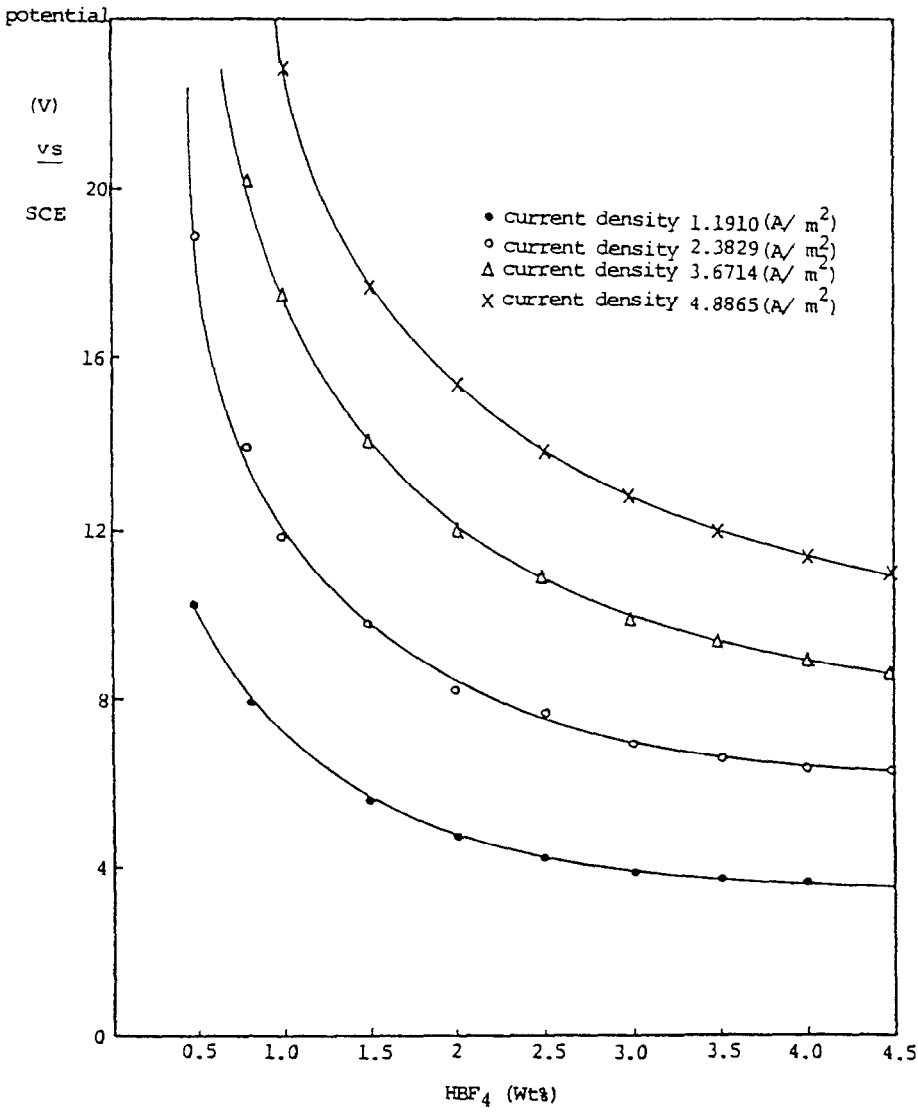

Fig. 1. Applied voltage as a function of HBF_4 concentration at four different anodic current densities.

Presumably, in the initial electrolysis period, the fluoroboric acid accounts solely for the conductivity of the electrolyte. However as the electrolysis continues, the lead fluoroborate concentration increases. Subsequently the effect of fluoroboric acid becomes more complex. In Fig. 2, the conductivity actually decreases when we increase the fluoroboric acid concentration from 1M to 3M in the presence of concentrated lead fluoroborate. Therefore the recommended fluoroboric acid content in the final lead fluoroborate solution is 0.6%.

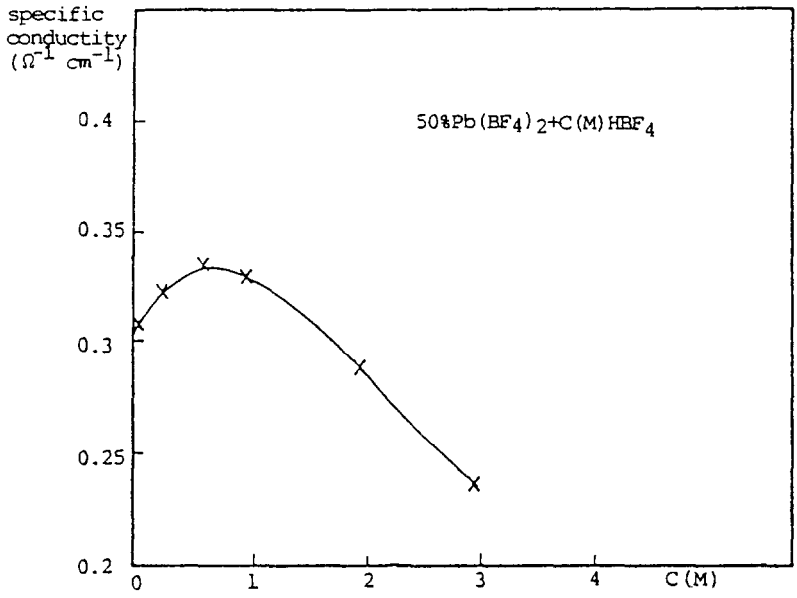

Fig. 2. Specific conductivities of aqueous $Pb(BF_4)_2$ solution 50% $Pb(BF_4)_2$ + C(M) HBF_4.

The effect of current density on the yield and current efficiency is shown in Fig. 3. From the production point of view, high current density is certainly preferred. However a compromise must be reached so that we can maintain a high production rate without generating excess by-products. Part of the yield and current efficiency data are

over 100% in the low current density range. This is because the lead anode also dissolves chemically in addition to the anodic dissolution. It is found that this chemical dissolution becomes significant only in the presence of an applied electric field.

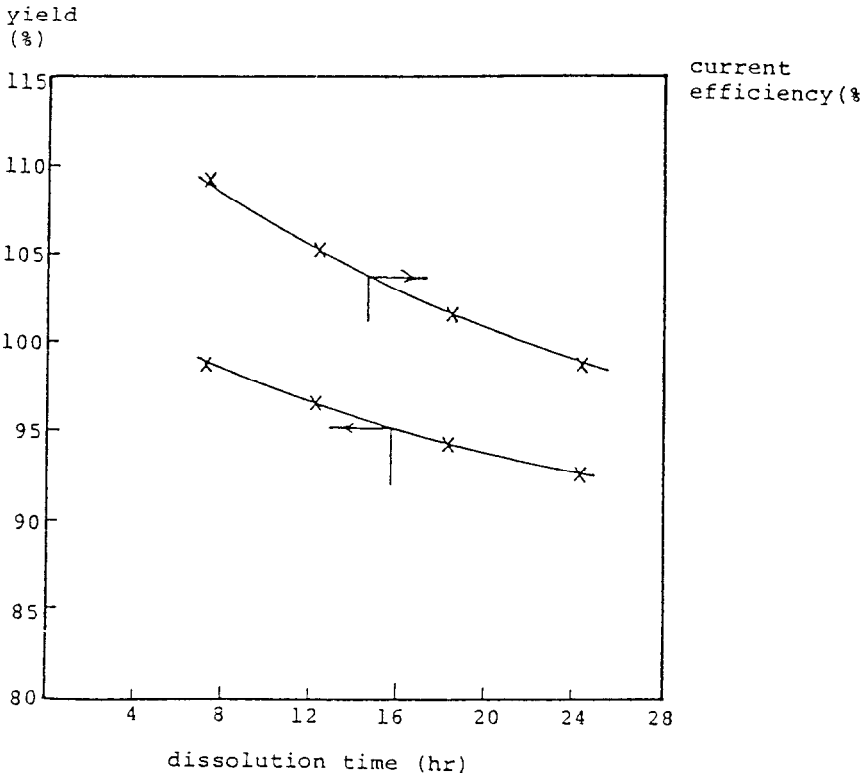

Fig. 3. The yield and current efficiency of anodic dissolution of lead in 1% HBF_4 solution.

Two major by-products were found in the system. Some cloudy white precipitate was formed in the electrolyte. It was identified as lead fluoride. This reaction can be controlled by the addition of boric acid using the following reaction.

$$4F^- + H_3BO_3 \longrightarrow BF_4^- + 3OH^- \qquad (9)$$

However boric acid is only soluble in lead fluoroborate solution to a rather limited extent and it will also increase the resistance. Therefore it is recommended that the boric acid content is between 0.6% and 1%.

Another by-product occurs on the ion-exchange membrane. When the current density was raised over 2 A/dm^2, a black substance was produced on the membrane. In addition, oxygen generated on the side of the membrane facing the cathode, and lead was deposited on the side of the membrane facing the anode. In other words, fluoroborate ions stop migrating through the membrane to neutralize the newly generated lead ions in the anolyte. The anode compartment functions at this stage as in the electrorefining of lead and the cathode compartment becomes a water electrolyzer with the membrane being a bipolar electrode. The black substance was identified by X-ray diffraction as PbO_2. In order to avoid this side-reaction, the anodic current density was limited to 2 A/dm^2.

Kinetic studies

Galvanometry was used to study the polarization of the anodic dissolution of lead in fluoroboric acid. Fig. 4 shows that that the process is highly reversible. The activation overpotential was significantly reduced as the concentration of fluoroboric acid was increased from 0.25M to 1M. The polarization behavior follows the Tafel Equation and the transfer coefficient and exchange current density were evaluated to be 0.66 and 0.492 mA/dm^2, respectively, for the lead/0.25M HBF_4 system.

D.C. Polarography was used to study the reduction of lead fluoroborate. When the lead ion concentration was fixed at 100 ppm, the following results were recorded.

Concentration of BF_4^- (M)	$E_{1/2}$ (V)	$E_{3/4}-E_{1/4}$ (mV)
0	-0.395	31.9
10^{-5}	-9,387	31.5
$5x10^{-5}$	-9,385	30
10^{-4}	-0.396	31
$5x10^{-4}$	-0.395	32.5
10^{-3}	-0.395	30
$5x10^{-3}$	-0.395	30

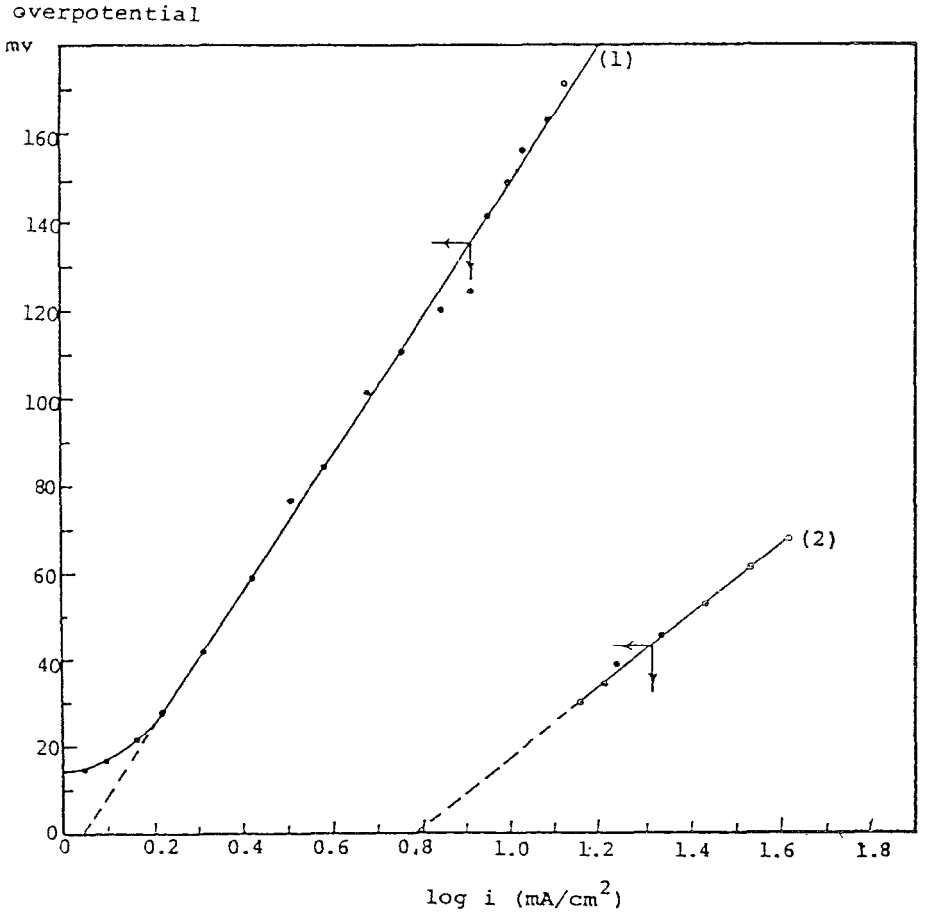

Fig. 4. Anodic polarization curves of lead in 0.25M and 1M HBF_4 solutions, (1) Pb in 0.25M HBF_4 solution; (2) Pb in 1M HBF_4 solution.

It is obvious that $E_{1/2}$ and $E_{3/4} - E_{1/4}$ are independent of the concentration of fluoroborate ions. The value of $E_{3/4} - E_{1/4}$ shows the charge transfer number of the rate determining step to be 2. In addition, since $E_{1/2}$ is partically constant $\Delta E_{1/2}/\Delta \log BF_4^- = 0$. Hence there are no fluoroborate ions involved in the charge transfer reaction. Then the lead ions exist in a completely dissociated state in eqn. (7).

CONCLUSIONS

The polarization data of the Pb/HBF_4 system follow the Tafel Equation. The exchange current density and the transfer coefficient were evaluated to be 9,492 mA/dm^2 and 0.66, respectively.

Polarography also shows that the rate controlling step is

$$Pb^{++} + 2e \rightleftharpoons Pb \qquad (10)$$

and there are no fluoroborate ions involved in this step.

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