

Preparation of Dendrite lead by Constant Current Extractive Electrolysis Using Isoamylalcohol.

Yasumasa Shigetomi.

Department of Chemistry, Okayama College of Science, Shuku Okayama-shi.

Introduction

A number of reports are already found in a hand book (1) and a few other publications (2~4) on the electrolysis of various metals in dielectric organic solvent, but most of reporters used hydrophilic organic solvents such as formamide and acetonitrile, and a few have ever conducted electrolysis using hydrophobic organic solvent which does not mix with water.

The author who once studied the chronopotentiometry of uranium (VI) carried out the same study with regard to nonaqueous organic solvent, especially hydrophobic organic solvent only to fail to obtain the expected results. After these experiments, we had interest in the extractive electrolysis in which an aqueous solution of metallic salt and a hydrophobic organic solvent are brought in contact, and metallic salt electrolysed under this condition. Few instances of such electrolysis can be seen. As results of our experiment, it seems that the said extractive electrolysis may have the following characteristics; (1) It requires comparatively high voltage, but as catholyte does not mix readily with anolyte, diaphragmic effects are expected.

(2) The solubility of inorganic salt in an organic solvent is generally low. Consequently product of the electrolysis which is hard to crystallize in the electrolysis of aqueous solution can often be obtainable as crystalline by the extractive electrolysis.

(3) As it is possible to supply ion continuously from aqueous phase to organic phase, it helps the less solubility of inorganic electrolyte in organic solvent and thus the electrolysis continuously effectively performed.

This report is on the extractive electrolysis of lead salts using isoamylalcohol. The product at cathode is identified to be dendrite lead and the one at anode to be lead dioxide. by X-ray analysis.

Experimental

Apparatus-As for the current source, BA-8-2 type the high voltage current supplier for electrophoresis made by Toyo Kagaku Sangyo Co., Ltd. was used. The cell was of fraction funnel type measuring 5 cm in diameter and 8 cm in depth, as shown in Fig. 1. A platinum wire, sealed in glass tube was used as anode. As for the cathode stainless steel plate (18/8) with a diameter of 35 mm was used.

Furthermore, in order to prevent the mixing of the gases produced at both poles, the anode was surrounded with a little bigger size of glass tube so that produced gas at the anode might be directly be let out of the cell. The cell was enclosed in a plastic film and immersed in a themounit kept at 20°C. Electrolysis-In order to prepare for the electrolysis, 25 ml of

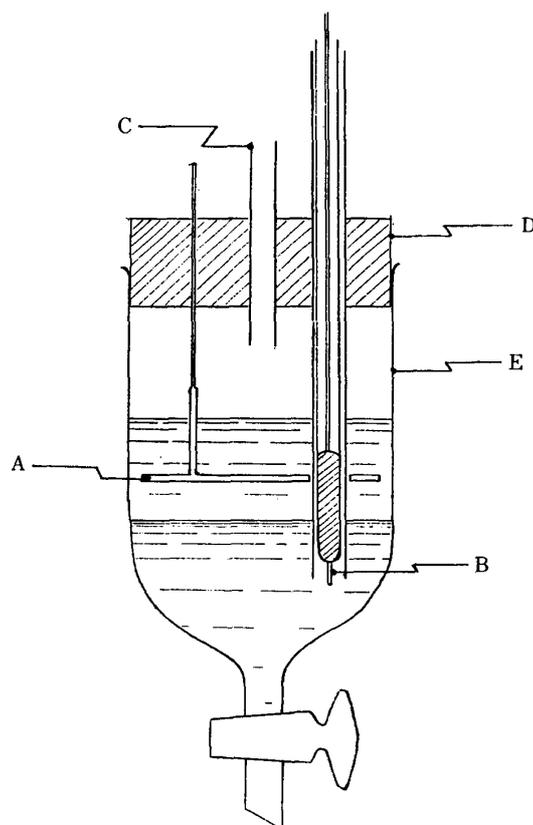


Fig. 1 Cell diagram

- A : Anode
- B : Cathode
- C : Glass tube
- D : Rubber stopper
- E : Electric cell

aqueous solution was poured into the cell and the anode was let in. Then 25 ml of isoamylalcohol was poured into the cell and the cathode was let in. Thus prepared, the electrolysis was carried out at a constant current.

Determination of lead in aqueous phase- the quantity of lead in aqueous solution was determined by chelatometric titration. The decrease of lead contents in aqueous solution during the electrolysis was determined by comparing content of lead in aqueous solution before and after the electrolysis.

Reagent-The reagents used were all of special grade. The organic solvent was used without distilling.

Results and Discussion

Extractive electrolysis at various current densities-with the object of examining how the current density affects the extractive electrolysis, 25 ml of the aqueous solution of 0.6 M lead nitrate was brought in touch with the same amount of isoamylalcohol. The anode was put in the aqueous solution and the cathode, in isoamylalcohol. The time-voltage curves during the electrolysis were obtained and the results are shown in Fig. 2. The voltage is very high immediately after the current is applied in every case, but it gradually falls with the progress of the electrolysis until it reaches a certain degree of value. Quantities of lead and acid in the aqueous solution were determined separately before and after the electrolysis. The amount, electrolysed, was determined from the difference of the absolute amount of lead in

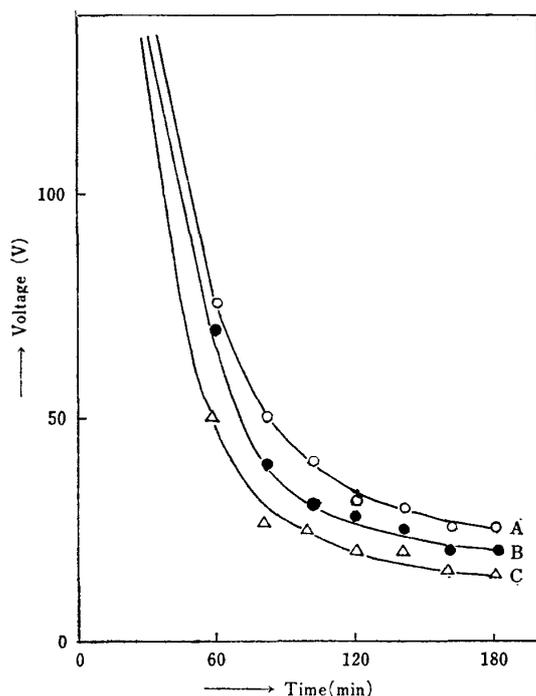


Fig. 2. Relation between time and voltage at various current densities (0.6 M $\text{Pb}(\text{NO}_3)_2$)
A: 3.8 mA/cm² B: 2.8 mA/cm² C: 1.9 mA/cm²

aqueous solution before and after the electrolysis. Also, the amount of acid, produced by the electrolysis, was determined by the same method.

In this electrolysis, dendritic crystal of lead, and lead dioxide were formed at the cathode and the anode respectively. quantities of them were shown in Table 1. As the table shows,

Table 1 Relation between amounts, electrolysed and current density

current density (mA/cm ²)	produced amount of acid (mole)	decreased amount of lead (mole)	amount of PbO ₂ (g)	amount of lead (g)
1.9	0.0013	0.0013	0.258	0.0272
2.8	0.0013	0.0021	0.3864	0.0650
3.8	0.0024	0.0030	0.5285	0.0882

the higher is the density of current, the more deposits are obtained. The amount of lead, crystallized at cathode and the amount of lead dioxide at anode per farady are shown in Table 2, which indicates, the amount of lead dioxide is in exact accordance with the law

Table 2 Deposited amount per farady at various current density

current density	quantity of current (C)	amount of PbO ₂ (mole/farady)	amount of lead (mole/farady)
1.9	219	0.5	0.06
2.8	324	0.48	0.09
3.8	432	0.49	0.10

of Faraday, but that of lead metal is so low as $0.06\sim 0.1$ mole per faraday. It seems that the amount of the metal crystallized at the cathode is small because the acid, hydronium ion drawn in isoamylalcohol is reduced. When lead nitrate is electrolysed according to the conventional method, hydrogen gas is evolved at the cathode, while lead dioxide is produced at the anode. In this case 2 M of acid ought to be produced for the production of 1 M of lead dioxide in net work. In this electrolysis, however, when the extractive electrolysis was carried out at current densities of 1.9, 2.8 and 3.8 mA/cm²; 1.5, 0.7 and 0.004 M of acid were produced respectively for 1 M of lead dioxide. In this case, hydrogen ion is reduced at the cathode evolving hydrogen gas but at the same time lead ion also is reduced.

So different from the conventional electrolysis, it can be expected that a larger amount of acid is produced for the production of 1 M of lead dioxide in this case. As a matter of fact, however, the production of acid was much less in this experiment than in the conventional electrolysis. It is considered that this was due to the fact that isoamylalcohol dissolved in the aqueous solution was oxidized and dissolved by nitric acid so that nitric acid produced at the anode was consumed. The amount of gas produced at the cathode was measured, but a systematic value was unobtainable. In every case, yellow thin film of lead oxide was formed on the surface of the stainless steel cathode.

Relation between concentration and the amount electrolysed. In order to find out how the concentration of the aqueous solution of lead nitrate affects electrolysis, the aqueous solutions of lead nitrate of various concentration were prepared, 25 ml of this solution was brought in touch with the same quantity of isoamylalcohol and it was electrolysed for three hours. Then lead in the aqueous solution was determined. In this way how the concentration affects the quantity of lead to be deposited was examined.

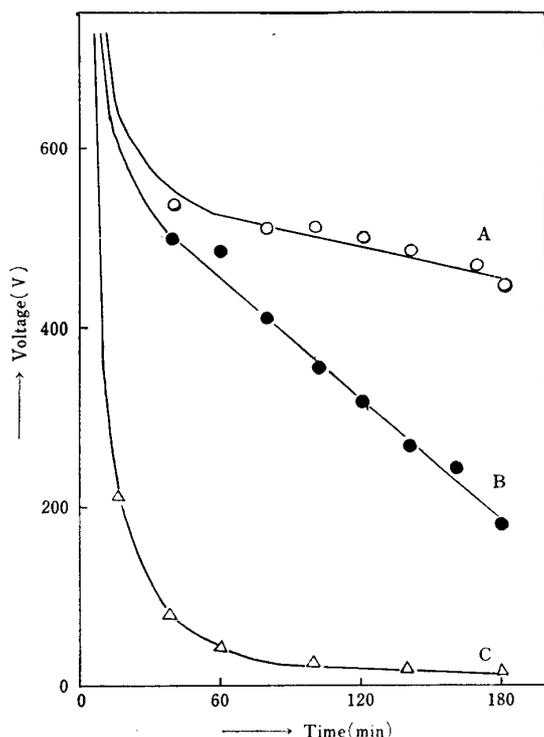


Fig. 3. Relation between time and voltage at various concentration
(30 mA constant current)
A : 0.01 M B : 0.1 M C : 1.0 M

1 M, 0.1 M and 0.01 M of the aqueous solution of lead nitrate were electrolysed and how the voltage-time curves changes with the concentration was examined. The results are shown in Fig. 3. As you can see from the fig, in every case the voltage falls with the progress of electrolysis. The voltage at the beginning was irregular and it was very high. They fell in inverse proportion to the concentration.

The relation between the concentration of aqueous solution and the amounts electrolysed in every case are shown in table 3. The table shows that the amount electrolysed increases

Tabl 3 Relation between concentration and electrolysed amount

concentration (mole/l)	decreased amount of lead (mole)	amount of PbO ₂ (g)	amount of lead (g)
0.01	0.0002	—	—
0.1	0.0005	0.0657	—
1.0	0.0021	0.2677	0.0288

in proportion to the concentration. In other words, the higher is the concentration, the larger amount is to be electrolysed. The blank part in the table explains that the amount was too small to be weighed.

Table 4 shows how much product is deposited at both electrodes per farady. As may be

Table 4 deposited amount per farady at various concentration

concentration (mole/l)	quantity of current (C)	amount of PbO ₂ (mol/farady)	amount of lead (mol/farady)
0.01	216	—	—
0.1	216	0.12	—
1.0	216	0.50	0.06

seen in the table, the amount rises with the rise of the concentration. As mentioned already, it seems that the amount of lead deposited per unit farady is low because hydrogen ion is reduced and produces hydrogen gas.

Relation between time and the amount, electrolysed. - For the purpose of determining how the amount electrolysed varies with the time, 25 ml of the aqueous solution of 0.6 M lead nitrate was brought in contact with the same amount of isoamylalcohol, and it was electrolysed for a certain period of time. Then lead in the aqueous solution was analysed in order to find out the relation between the time and the amount electrolysed. The results are shown in Fig. 4, 5 and 6. Fig. 4 shows the relation between the time and the amount of lead dioxide which was deposited at the anode. As the figure indicates, the amount of lead dioxide deposited rises in proportion to the time electrolysed. Also the relation between the time and the amount of dendrite of lead, crystallized at the anode, is shown in Fig.5. The figure

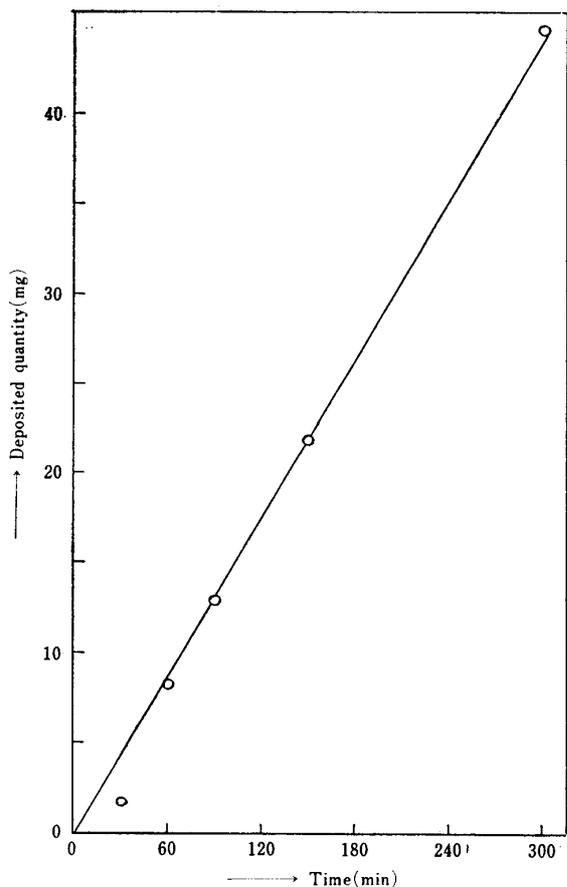


Fig. 4 Relation between time and deposited quantity at anode (30 mA constant current)

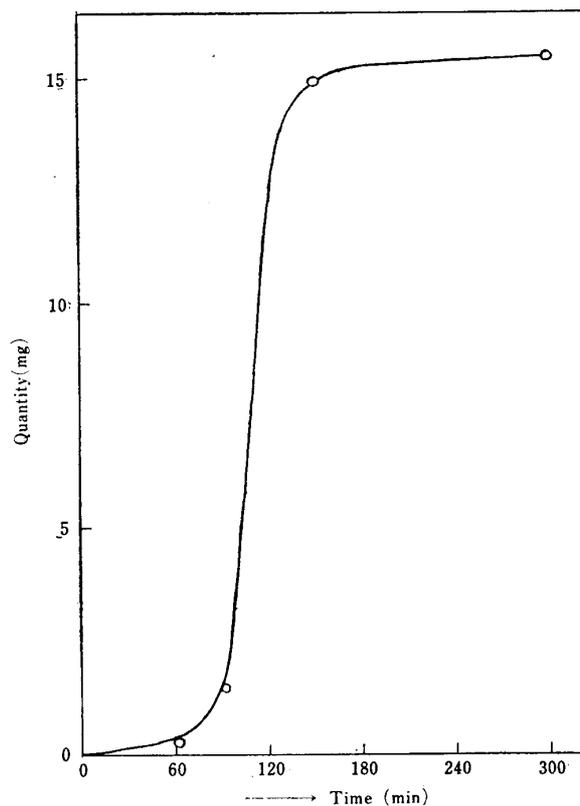
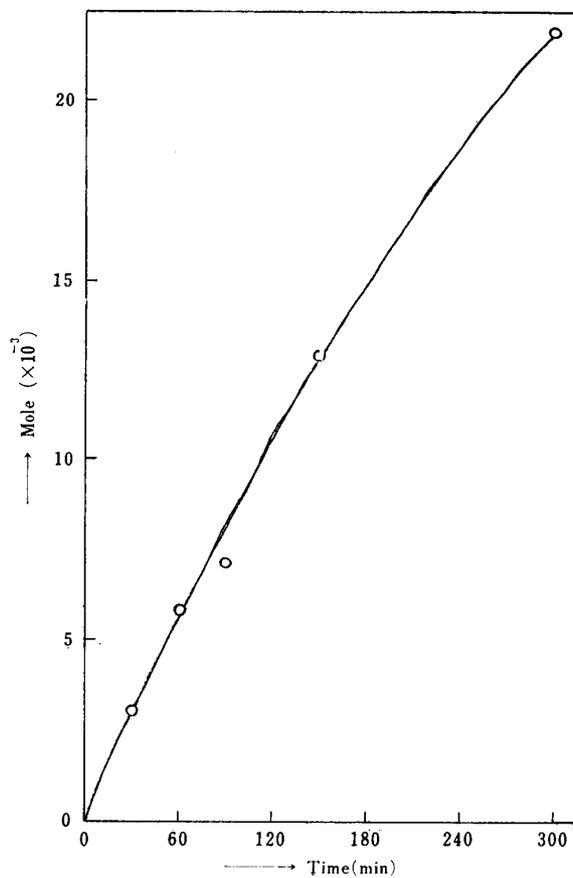


Fig. 5 Relation between time and deposited quantity at cathode (30 mA constant current)

Fig. 6 Relation between time and decreased quantity of lead in aqueous solution (30 mA constant current)



tells that the deposition of lead progresses for two hours, but that it stops after that.

Furthermor, fig. 6 shows the relation between the time and the decrease of lead ion in the aqueous solution. As may be seen in the figure, the curvature of the curved line changes suddenly toward its end. This means that the formation of both lead dioxide and lead continues for two hours but that the formation of the latter almost stops after that.

Identification of products-In order to identify the products at both poles, they were subjected to X-ray diffraction analysis. The data obtained were compared with those of the corresponding compound on A. S. T. M card. The results are shown in Fig. 7 and 8.

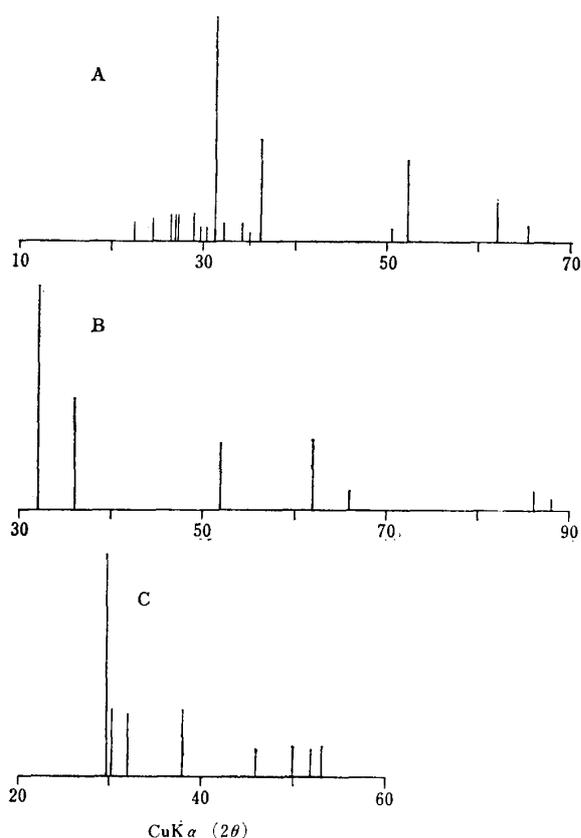


Fig. 7 X-ray diffraction putton

- A : deposit at cathode
- B : A. S. T. M. data of lead metal
- C : A. S. T. M. data of PbO.

The product at the cathode crresponds with those of lead on A. S. T. M card, which tells that the greater part of products are lead though it contains a very small amount of lead (II) oxide. As the data of the product at the anode crresponds exactly with those of lead dioxide on the A. S. T. M card, there is no doubt that the product is lead (VI) dioxide.

Conclusion

The authors' experiment to elctrolyse the aqueous solution of lead nitrate extractively using isoamylalcohol found that it is different from the conventional electrolysis in that lead metal crystal is obtained as the product at the cathode, because the covering of the cathode

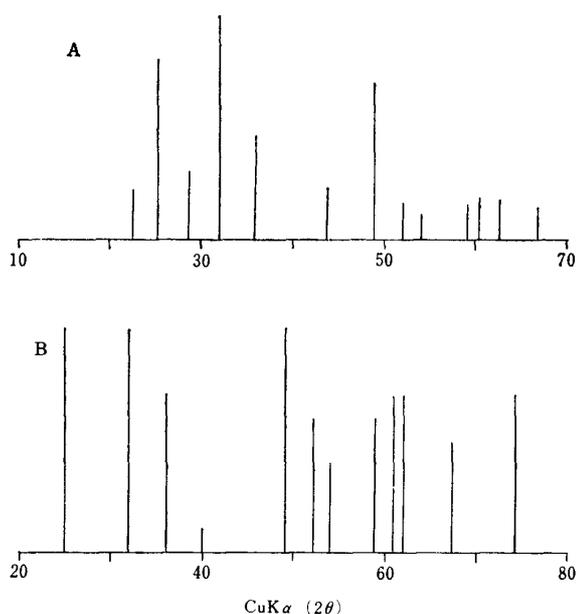


Fig. 8 X-ray diffraction pattarn

- A : deposit at anode
- B : A. S. T. M data of PbO₂

by isoamylalcohol causes lead (11) to be reduced and hydrogen ion to be less reduced.

With regard to this study, the authors wish to express their thanks to Mr Shiro Kishi of Okayama Prefectural Industrial Laboratory and Mr Shiro Kimura of Nippon Denshi Co., Ltd. who took up the X-ray analysis of lead and lead compound, professor of our Okayama College of Science, Kouichi Emi and Tatsuo Yokoyama who helped the study in various ways, and Miss Maso Hamada who helped the experiment.

References

- (1) The Electrochemical Society of Japan, Hand Book of Electrochemistry, Maruzen, Tokyo (1964) p 257
- (2) T, Hayashi and T, Ishida *Denki Kagaku* 30, 552 (1962)
- (3) H, Schmidt and T, Noock *Z, anorg, allgem, Chem* 263 (1958)
- (4) M, Sato *Denki Kagaku* 39, 756 (1971)