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Electrochemical Behavior of Er(III) In N, N-dimethylformamide^①

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[Abstract] The cyclic voltammetry, current-time curve at potential step and potential-time curve of galvanostatic method were used to investigate the electrochemical behavior of Er(III) in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ (N, N-dimethylformamide) system on Pt and Cu electrodes. Results indicate that the electroreduction of Er(III) to Er(0) is irreversible on Pt and Cu electrodes, the diffusion coefficient and electron transfer coefficient of Er(III) in 0.01 mol/L $\text{ErCl}_3\text{-0.1 mol/L LiClO}_4\text{-DMF}$ system at 303 K are $1.96 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ and 0.081 respectively. The Er metal film was prepared by galvanostatic electrolysis on Cu electrode in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ system at $40 \text{ A} \cdot \text{m}^{-2}$ (current density). The deposits composed of Er over 95% (mass fraction) were obtained.

[Key words] Er(III); N, N-dimethylformamide(DMF); diffusion coefficient; electron transfer coefficient; electrodeposition

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1 INTRODUCTION

Rare earths and their alloys are widely used in magnetic, optical and electric materials. But it is difficult to electrodeposite rare earths and their alloys in aqueous solutions due to the activity of rare earths. If the rare earths and their alloys can be prepared in organic solvent at room temperature by electrodeposition, the temperature of electrodepositing in molten salts system would be high, which will greatly enhance their application as functional materials^[1~6]. In the paper, the electrochemical behavior of Er(III) in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ system are investigated by cyclic voltammetry, current time curve at potential step, potential-time curve of galvanostatic method, and some kinetic parameters are determined. At last, the electrodeposition of Er(III) in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ system are studied.

2 EXPERIMENTAL

The dehydrated ErCl_3 was obtained by the reaction of Er_2O_3 (99.99%) with HCl(AR) and dehydrating in vacuum at 393 K, and the supporting electrolyte LiClO_4 (AR) was dehydrated in vacuum at 453 K^[7, 8]. Before use, DMF(AR) was dehydrated with 0.4 nm molecular sieves and distilled at reduced pressure to remove impurities^[9].

A simple three electrodes cell was used for the experiment. The working electrode was Pt wire(99.9%, 0.05 cm^2) and Cu wire(99.9%, 0.08 cm^2), a Pt foil

was used as an auxiliary electrode, a saturated calomel electrode(SCE) was used as the reference electrode which was connected to the cell with a double salt bridge system, all potential values determined were converted to those versus SCE. All experiments were carried out under argon atmosphere at room temperature. HD-1A low frequency super low frequency functional generator, HDV-7C transistor potentiostatic instrument and 3086 X-Y recorder were used for electrochemical measurement. The product was analyzed by EDAX method to determine the content of Er in deposits and by X-ray diffraction to determine the phase composition of electrolytic product. The morphology of the plated film was observed by scanning electron microscope(SEM), the ErCl_3 content in solution was measured by EDTA titration.

3 RESULTS AND DISCUSSION

3.1 Electrode process of Er(III) on Pt electrode

Fig. 1(a) is the cyclic voltammogram of Pt electrode in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4\text{-DMF}$ at 303 K. The potential sweep ranges and the window of electrochemistry are from -3.40 V to 1.37 V and 4.77 V respectively, so the window of electrochemistry is fit to this experiment. Fig. 1(b) is the cyclic voltammogram of Pt electrode in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3\text{-0.1 mol} \cdot \text{L}^{-1} \text{LiClO}_4\text{-DMF}$ at 303 K, one cathode peak appears at -1.65 V , compared with Fig. 1(a), the peak at -1.65 V corresponds to the reduction of Er(III), namely: $\text{Er(III)} + 3\text{e}^- \rightarrow \text{Er(0)}$. The voltammogram curve was shown in Fig. 2 at

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different sweep rate (ν). The peak potential (φ_p) changed with the sweep rates (ν). The peak potential (φ_p) versus the natural logarithm ($\ln \nu$) of sweep rate shows a linear variation, it is further proved that the reduction of Er(III) is an irreversible electrode process. The result is similar to the result of Ref[10].

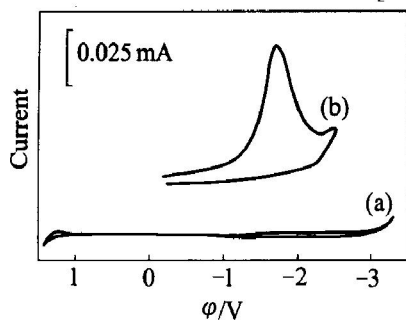


Fig. 1 Cyclic voltammogram of on Pt electrode
($S = 0.05 \text{ cm}^2$, $T = 303 \text{ K}$, $\nu = 60 \text{ mV} \cdot \text{s}^{-1}$)
(a) $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4 \text{ DMF}$;
(b) $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3 - 0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4 \text{ DMF}$

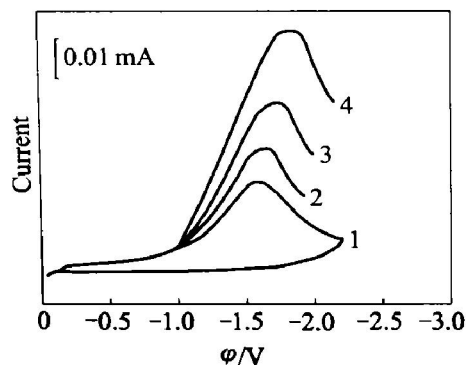


Fig. 2 Cyclic voltammogram of $0.01 \text{ mol} \cdot \text{L}^{-1}$
 $\text{ErCl}_3 - 0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4 \text{ DMF}$ at
different sweep rates
(1) -20 mV/s ; (2) -40 mV/s ;
(3) -60 mV/s ; (4) -100 mV/s

For an irreversible charge transfer electrode process,

$$5 \varphi_{p/2} - \varphi_p = 1.857 RT / (\alpha n F) \quad (1)$$

The plot of $\varphi_p - \ln \nu$ is a straight line with a slope of

$$k = RT / (2 \alpha n F) \quad (2)$$

where $\varphi_{p/2}$ and α are the half peak potential and electron transfer coefficient respectively. From $|\varphi_{p/2} - \varphi_p| = 0.20 \text{ V}$ of the cathodic wave in Fig. 1(b), the electron transfer number (n) is 3.0, hence $\alpha = 0.081$. The plot of φ_p versus $\ln \nu$ for the reduction peak is linear (as shown in Fig. 3), so the electron transfer coefficient can be calculated from

$$k = RT / (2 \alpha n F) \quad (3)$$

From the slope of the plot of $\varphi_p - \ln \nu$ and $\alpha = 0.085$, the value is very close to the value above.

According to the relationship between peak current (i_p) and potential sweep rate (ν) [11]:

$$i_p = 2.99 \times 10^5 n^{2/3} \alpha^{1/2} A c D^{1/2} \nu^{1/2} \quad (4)$$

where i_p , A and D are peak current, electrode area and diffusion coefficient respectively, $D = 1.96 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ can be calculated from the plot of i_p versus $\nu^{1/2}$ for the reduction peak (as shown in Fig. 4).

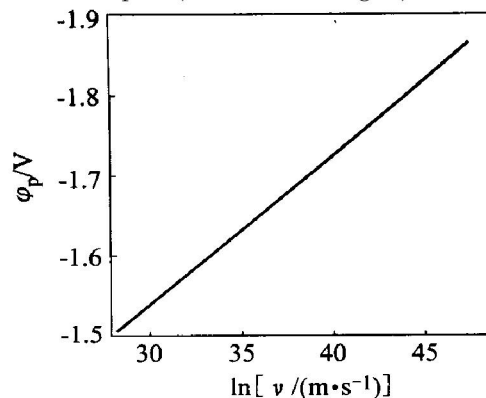


Fig. 3 Curve of φ_p vs $\ln \nu$ of Er(III)
in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3 - 0.1 \text{ mol} \cdot \text{L}^{-1}$
 $\text{LiClO}_4 \text{ DMF}$ system

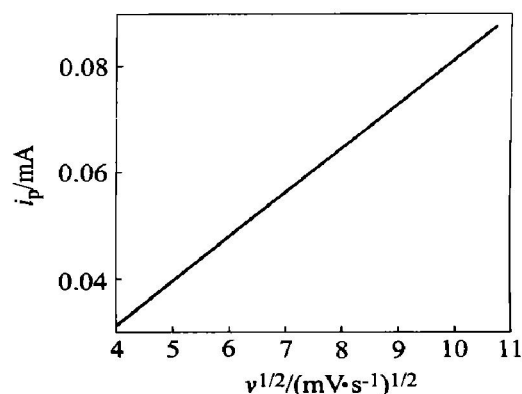


Fig. 4 Curve of i_p vs $\nu^{1/2}$ of Er(III)
in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3 - 0.1 \text{ mol} \cdot \text{L}^{-1}$
 $\text{LiClO}_4 \text{ DMF}$ system

3.2 Current—time curve of potential step

When the potential step ranges from 0.008 V to -2.500 V , the current—time curve of Pt electrode in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ is shown in Fig. 5(a). From it we can find that the value of limiting current (i_l) gradually decreases as time goes on, so after potential step, the unsteady state limiting current (i_l) at any moment can be expressed [11] as

$$i_l = n F A k_{fc} (1 - 2 k_{ft}^{1/2} / D^{1/2} \pi^{1/2}) \quad (5)$$

The plot of i_l versus $t^{1/2}$ is also linear (as shown in Fig. 6) and $D = 1.90 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ can be calculated from the slope $m = (-2 n F A k_{fc}^2) / (D \pi)^{1/2}$ and the intercept $d = n F A k_{fc}$ of $i_l - t^{1/2}$. This value is close to the value obtained from the cyclic voltammogram. The Fig. 5(b) is the current—time curve of Cu electrode in the same system.

3.3 Potential—time curve of galvanostatic method

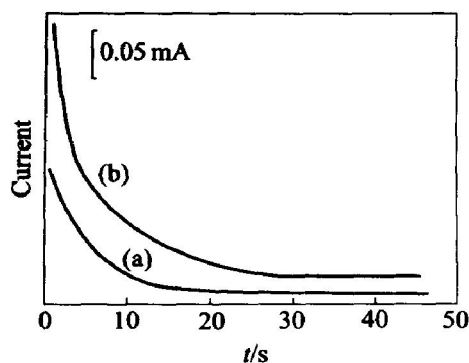


Fig. 5 Current-time curves on Pt (a) and Cu (b) electrodes in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3$ - $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4$ -DMF

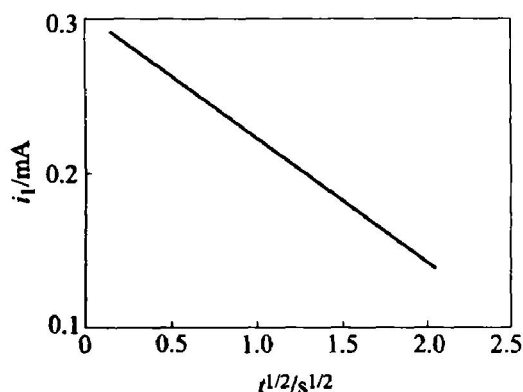


Fig. 6 i_1 - $t^{1/2}$ curve of potential step of $\text{Er}(\text{III})$ in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3$ - $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4$ -DMF

The potential-time (φ - t) curves at current step of Pt electrode in ErCl_3 - LiClO_4 -DMF at 303 K are shown in Fig. 7. From these measurements, it can be found that the values of transition time (τ) gradually decrease as i increases, according to Sand formula^[11]:

$$\tau = n^2 F^2 (\pi D c^2) / (4 i^2) \quad (6)$$

From the slope $m' = n^2 F^2 (\pi D c^2) / 4$ of the line of τ vs i^{-2} , it can be found $D = 1.86 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$.

3.4 Electrodeposition of Er on Cu electrode

Electrolytic experiment was carried out in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3$ - $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4$ -DMF system at 303 K and cathodic current density at $25 \text{ A} \cdot \text{m}^{-2} \sim 50 \text{ A} \cdot \text{m}^{-2}$ using Cu electrode. The time of electrolytic was 40 min and a delicate, lustrously yellow and strong adhering film was obtained. The deposits were analyzed by means of EDAX and the result indicates that the film contains Er 95% (mass fraction). Fig. 8 is the XRD pattern of a film deposited for 1.0 h, no other diffraction peak was found in the XRD pattern besides the peaks of Cu substrate, which suggested that the film should be amorphous. Fig. 9 is the SEM photograph, it shows that there exist a lot of grains in the film surface,

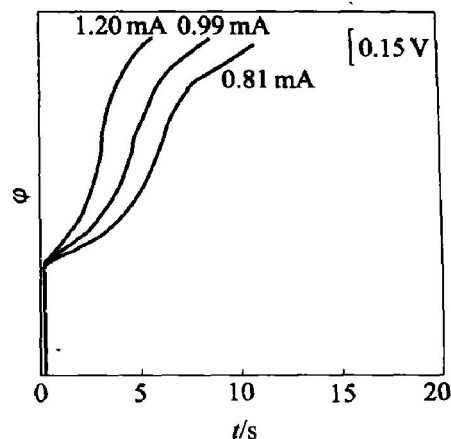


Fig. 7 φ - t curve of Pt electrode in $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ErCl}_3$ - $0.1 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4$ -DMF system

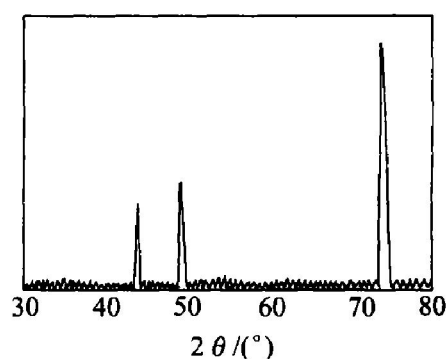


Fig. 8 X-ray diffraction pattern of alloy film

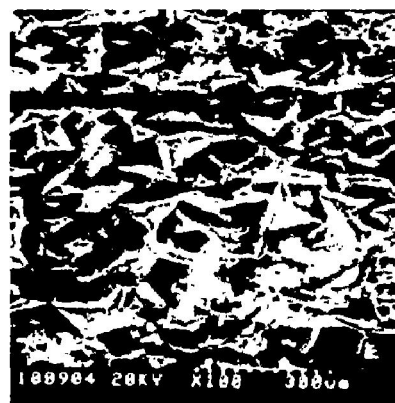


Fig. 9 Surface shape analyzed by SEM

and it is possible that the grain was caused by the Er of film which was oxidized when it was exposed to air.

4 CONCLUSIONS

1) The electroreduction of $\text{Er}(\text{III})$ to Er in DMF solution at 303 K on Pt electrode is irreversible.

2) The diffusion coefficient and transfer coefficient of $\text{Er}(\text{III})$ on Pt electrode in ErCl_3 - LiClO_4 -DMF system are $1.96 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ and 0.081 respectively at 303 K, which were determined by the methods of the cyclic

voltammetry, potential step, curve of electrode potential-time.

3) Er was prepared by galvanostatic electrolysis on Cu electrode in $\text{ErCl}_3\text{-LiClO}_4\text{-DMF}$ system, the deposit containing Er over 95% (mass fraction) was obtained.

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