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ELECTRODEPOSITION OF NEODYMIUM IN NEODYMIUM *p*-TOLUENESULFONATE-DMF①

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ABSTRACT The highly soluble neodymium *p*-toluenesulfonate in organic solvent was prepared for the first time and was used as electrolyte in DMF for the electrodeposition of neodymium. The electrode process of the reduction of Nd(Ⅲ) was studied by cyclic voltammetry, chronoamperometry and chronopotentiometry. Experimental results indicate that the electroreduction of Nd(Ⅲ) to Nd is irreversible one-step reaction, the diffusion coefficient of Nd(Ⅲ) was determined to be $4.3\times10^{-7}\mathrm{cm^2\cdot s^{-1}}$ at 25 ℃. The effect of transition metal ions such as Co(Ⅱ), Ni(Ⅱ) and Cu(Ⅱ) on the electrodeposition of neodymium was discussed. Neodymium with purplish red luster and Nd-Co, Nd-Ni films were obtained in homogeneous, dense and amorphous form by potentiostatic electrolyzing.

Key words neodymium *p*-toluenesulfonate dimethylformamide electroreduction of Nd(Ⅲ) electrodeposition of neodymium Nd-Co, Nd-Ni film

1 INTRODUCTION

Rare earth metals and their alloys, especially rare earth-iron group alloys, have many special properties and can be used to prepare functional materials. Their films are now produced by sputtering or vacuum plating. But the cost is high, the productivity is low and the composition of the alloy is difficult to control. To solve these problems electrodeposition may be a good way. Because rare earths are very active, the electrodeposition of rare earth and their alloys are often carried out in nonaqueous solution including molten salt and organic electrolyte. We had prepared some alloys of active metals, for example, RE-iron group and Ti-Ni in low temperature melt[1-3]. To prepare rare earth metals by electrolyzing, Moeller *et al* electrodeposited Y, Nd and La using $(CH_3COO)_3Y$, $NdBr_3$ and $La(NO_3)_3$ as electrolyte in ethylenediamine at a applied voltage of 110 V[4]. Recently this field was attended increasingly on the purpose to prepare rare earth alloys by electrodeposition. The electrodeposition of Y, Dy, Sm-Co, Gd-Co, Nd-Fe, Dy-Fe in organic solvent has been reported[5-10], however, the low solubility of the electrolytes such as $RE(CH_3COO)_3$, $RECl_3$ $RE(NO_3)_3$, in organic solvent causes the low electric conductivity, the heavy concentration polarization. Therefore, increasing the solubility of electrolytes is the key to the success of electrodeposition of rare earth alloys.

In recent works, we prepared neodymium *p*-toluenesulfonate which was soluble in organic solvent and was used as electrolyte. The anhydrous salts, $CoCl_2$ and $NiCl_2$, were used as electrolyte, these salts were also soluble in DMF[11]. The electroreduction of Nd(Ⅲ) and the electrodeposition of neodymium and Nd-Co, Nd-Ni were studied in DMF as part of the basic research for electrodeposition of rare earth alloy films.

2 EXPERIMENTAL

DMF(AR) was distilled under vacuum and molecular sieve was added to remove water. The supporting electrolyte, $(n\text{-Bu})_4NBF_4$, was pre-

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pared following the literature[12]. Neodymium *p*-toluenesulfonate was prepared by the reaction of Nd_2O_3(99.95%) and p-$CH_3C_6H_4SO_3H \cdot H_2O$ (AR). After recrystallization the salt was analyzed by TG (Thermogravimetry), DSC(Differential Scanning Calorimetry) and EDAX(X-ray Energy Dispersive Analysis). The hydrous salts, $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$, were dehydrated at 120 ℃ under vacuum and preserved in the desiccator contained P_2O_5.

The electrochemical measurements were carried out with HD-1A functional generator, HDV-7C potentiostat and 3086 X-Y recorder. Pt(99.9%), glassy carbon and Cu(99.95%) were used as working electrodes, spectrally pure graphite or Pt was used as counter electrode, the reference electrode was SCE(Saturated Calomel Electrode) which was connected to the cell through a salt bridge. All the potential values in this paper are vs SCE. The cell was H shape whose cathode and anode chamber were isolated by sintered glass. Argon was blown into the electrolytic solution to remove oxygen. The electrochemical test was carried out in argon atmosphere. The deposit was analyzed by EDAX and XRD(X-ray Diffraction).

3 RESULTS AND DISCUSSION

3.1 Fundamental characteristics of neodymium *p*-toluenesulfonate as electrolyte in DMF

EDAX was used to analyze the content of the elements Nd and S in the prepared salt, the result shows that the ratio of Nd∶S equals 1∶3, thus it can be infered that the composition of the salt is as follows: $(p\text{-}CH_3C_6H_4SO_3)_3Nd \cdot xH_2O$. The data of DSC and TG are listed in Table 1.

From the DSC curve, it can be seen that two phase changes happened in the temperature range of 30 to 603 ℃, the first one with weak endotherm from 106.8 to 184.5 ℃, the second with strong exotherm from 347.5 to 625.2 ℃. On the TG curve two mass loss processes can be found in the corresponding temperature range mentioned above. The change with weak endotherm and small loss of mass from 106.8 to 184.5 ℃ is due to water loss, according to the values of mass loss on TG curve, the number of lost water is calculated to be 2. Hence, the number of crystal water of neodymium *p*-toluenesulfonate crystalline hydrate is 2. The change with strong exotherm and large loss of mass from 347.5 to 625.2 ℃ should be the decomposition or oxygenolysis reaction of the salt before its melting.

Table 1 Data from DSC and TG experiments of neodymium *p*-toluenesulfonate crystal

Peak	DSC			TG	
	t/ ℃	Onset / ℃	ΔH / (J·g^{-1})	t / ℃	Mass loss/ %
First peak	106~ 184	113	109	230	5.20
Second peak	347.5~ 625.2	442.3	− 7384	626	64.64

DSC and TG experiments indicate that neodymium *p*-toluenesulfonate hydrate can lose all the crystal water before 184.5 ℃, and is stable to heat, not easy to be oxidized or hydrolyzed before 347.5 ℃. Experiment also shows that neodymium *p*-toluenesulfonate crystal will be destroyed and lose crystal water after being immersed in ethanol. Moreover, it does not deliquesce in the air, on the contrary, it is easy to effloresce.

The solubility test shows neodymium *p*-toluenesulfonate is easy to dissolve in organic solvents such as DMF, DMSO, ethylenediamine, formamide. For example, 100 mL DMF can dissolve neodymium *p*-toluenesulfonate about 116 g at 25 ℃. Compared with $RECl_3$, $RE(NO_3)_3$, the solubility is very high. The electrochemical window of p-$CH_3C_6H_4SO_3Na$ − (n-Bu)$_4$$NBF_4$ − DMF is 3.4 V(from − 1.9 V to 1.5 V) determined by cyclic voltammetry.

3.2 Electroreduction of Nd(Ⅲ)

3.2.1 Cyclic voltammogram of reduction of Nd (Ⅲ)

Fig. 1 shows the cyclic voltammogram of Pt electrode (0.51 cm^2) in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ − (n-Bu)$_4$ NBF_4 − DMF at different sweep rates (v). A cathodic wave started at − 0.45 V with an anodic peak on reversed scan. The peak potential of the cathodic wave shifted negatively with the increasing of sweep rate. The differences between the cathodic peak potentials and the anodic peak potentials are large. The cathodic peak current increases with $v^{1/2}$ linearly (Fig. 2). All these characteristcs indicate that the electrode reaction is irreversible. A deposit with purplish red luster was obtained by potentiostatic electrolyzing on copper electrode and it can be dissolved in 0.1 mol/L HCl quickly with large amounts of gas released. EDAX analysis proves that the deposit is neodymium. Therefore, the cathodic wave is due to the reduction of Nd(III) to Nd and the anodic peak corresponds to the stripping of Nd.

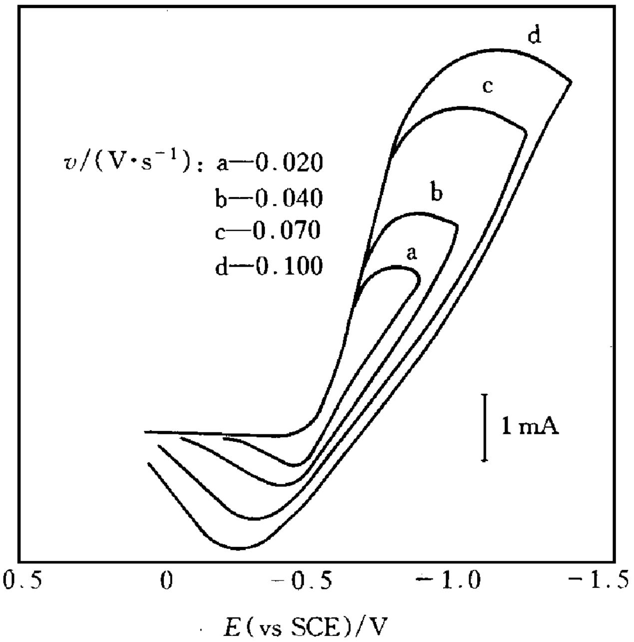

Fig. 1 Cyclic voltammograms of Pt electrode (0.51 cm^2) in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ (0.04 mol/L) − $(n\text{-}Bu)_4NBF_4$ (0.03 mol/L) − DMF at 25 ℃

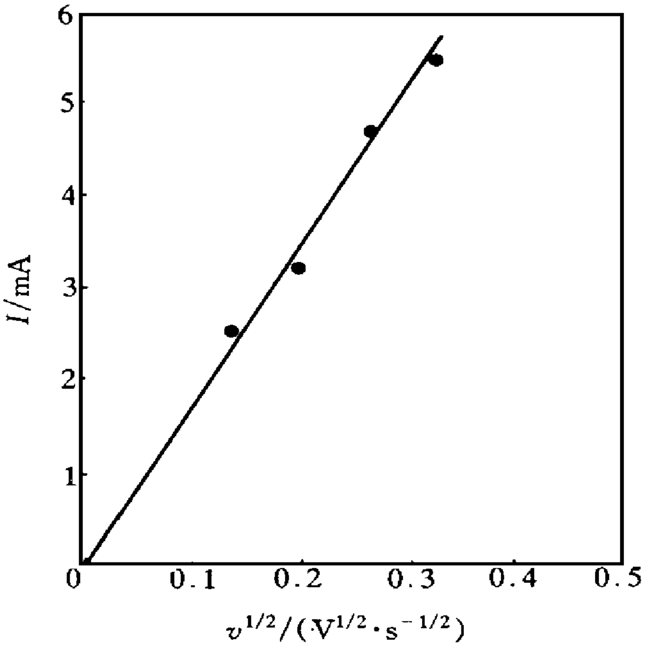

Fig. 2 Plot of I_p vs $v^{1/2}$ for Fig. 1

For the irreversible charge transfer, the peak current equation can be described as follows[13]:

$$I_p = 0.4958\, nF(\alpha n_\alpha FDv/RT)^{1/2}Ac \quad (1)$$

According Eq. (1) with α equal 0.4 (calculated from $E-t$ curve at current step, see 3.2.3) and the slope of the line in Fig. 2, the diffusion coefficient of Nd(III) in the solution was calculated to be $4.34\times10^{-7} cm^2\cdot s^{-1}$ at 25 ℃.

3.2.2 Current-time curve at potential step

Fig. 3 shows $I-t$ (current-time) curves of glassy carbon electrode in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ − $(n\text{-}Bu)_4NBF_4$ − DMF at different potential steps. The current is near zero before the potential of − 0.5 V. After the potential of − 0.6 V the electroreduction of Nd(III) could be observed as shown in Fig. 3(b), (c) and (d). For an irreversible reaction, at a short time the relation between current and time can be treated as fol-

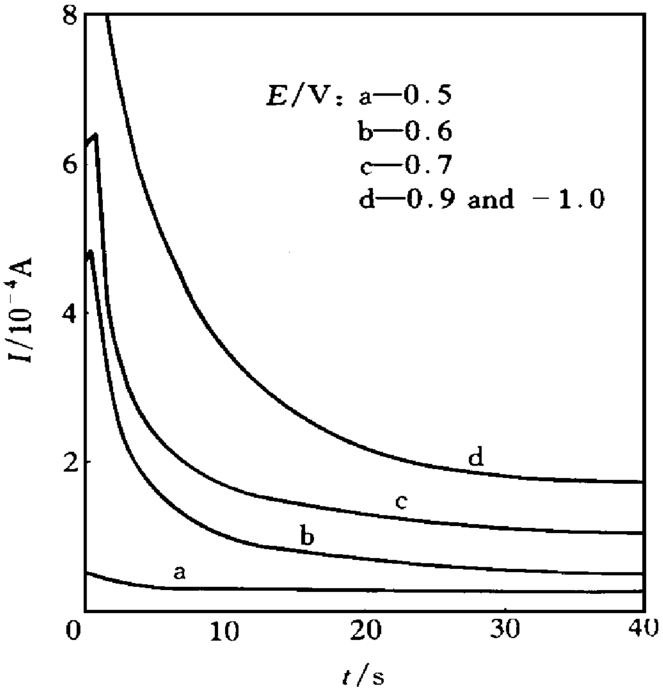

Fig. 3 $I-t$ curve of glassy carbon electrode (0.28 cm^2) in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ (0.04 mol/L) − $(n\text{-}Bu)_4NBF_4$ (0.03 mol/L) − DMF at 25 ℃

lows[14]:

$$I = nFAk_f c(1 - 2k_f t^{1/2}/\pi^{1/2}D^{1/2}) \qquad (2)$$

The plot of I—$t^{1/2}$ is a straight line (see Fig. 4).

From the Eq. (2) and the slope and the intercept of the line in Fig. 4, the diffusion coefficient of Nd(Ⅲ) in the solution was obtained to be $2.3 \times 10^{-7} cm^2 \cdot s^{-1}$ at 25 ℃, which agreed to the value of D calculated from cyclic voltammogram. The low value in a solvent with low viscosity suggests that the reacting species must be large. In fact the solvate exists between Nd(Ⅲ) and DMF[15], the order of affinity is as: DMF> TBP> NO_3^- > H_2O[16].

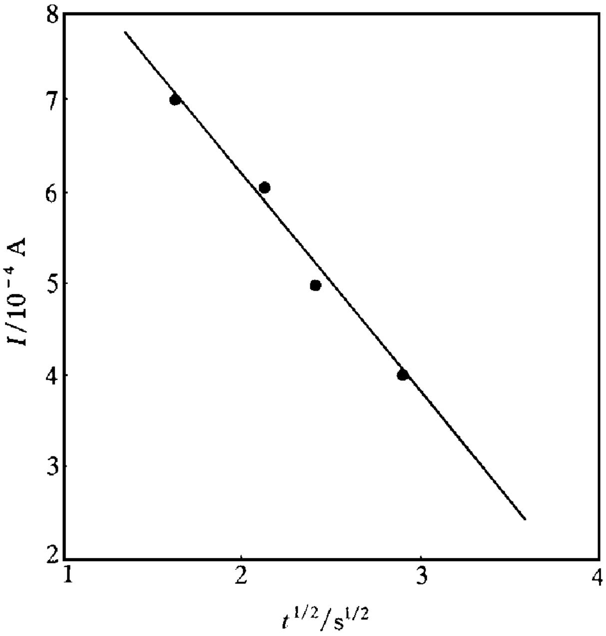

Fig. 4 Plot of I—$t^{1/2}$ for Fig. 3(d)

3.2.3 Potential-time curve at current step

The E—t (potential-time) curve following a current step (4.0 mA) on the Pt electrode in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ – $(n\text{-}Bu)_4NBF_4$ – DMF is shown in Fig. 5, in which only one potential plateau is found. The electrochemical reaction: Nd(Ⅲ) + 3e →Nd happened after the potential of – 0.52 V. Experiment at different current steps expressed that the whole E—t curve shifted to negative potential with increasing the current, suggesting that the electroreduction of Nd(Ⅲ) is irreversible. For irreversible electrode process the relation between potential and time is as follows[13]:

$$E = E^{0'} + (RT/\alpha n_a F)\ln(nFk_f c/i) + (RT/\alpha n_a F)\ln[1 - (t/\tau)^{1/2}] \qquad (3)$$

The plot of E—$\ln[1-(t/\tau)^{1/2}]$ is a straight line as illustrated in Fig. 6. According to Eq. (3) and the slope of the line in Fig. 6, α was calculated as 0.4 approximately.

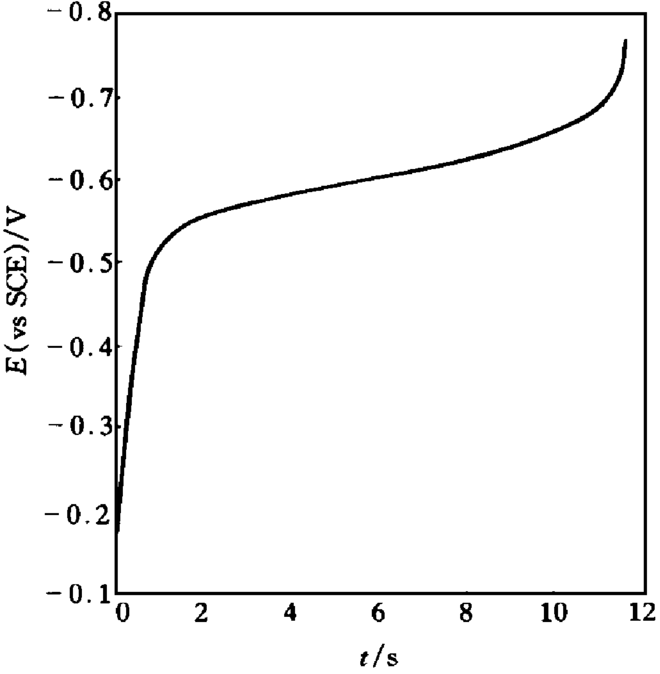

Fig. 5 E—t curve at current a step(4.0 mA) of Pt (0.51 cm^2) in $(p\text{-}CH_3C_6H_4SO_3)_3Nd$ (0.04 mol/L) – $(n\text{-}Bu)_4NBF_4$ (0.03 mol/L) – DMF at 25 ℃

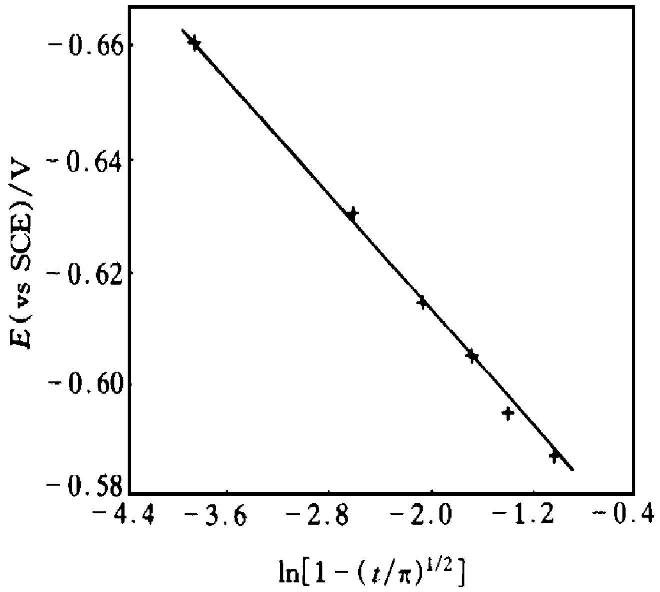

Fig. 6 Plot of E—$\ln[1-(t/\tau)^{1/2}]$ for Fig. 5

3.3 Effect of transition metal ions on the electroreduction of Nd(Ⅲ)

Fig. 7 shows the cyclic voltammogram of Pt electrode in (p-$CH_3C_6H_4SO_3)_3Nd$ – $CoCl_2$ – (n-Bu$)_4NBF_4$ – DMF. Two cathodic waves, starting at 0.48 V and – 0.32 V, correspond to the electroreduction of Co(Ⅱ) and Nd(Ⅲ) respectively. Compared with the electroreduction of Nd(Ⅲ) shown in Fig. 1, the starting potential shifted positively. On sweeping back, two anodic peaks appeared in turn, the one at negative potential was due to the stripping of Nd and another was due to the stripping of Co. The anodic peak of the Nd stripping is higher than that in Fig. 1 and is very sharp.

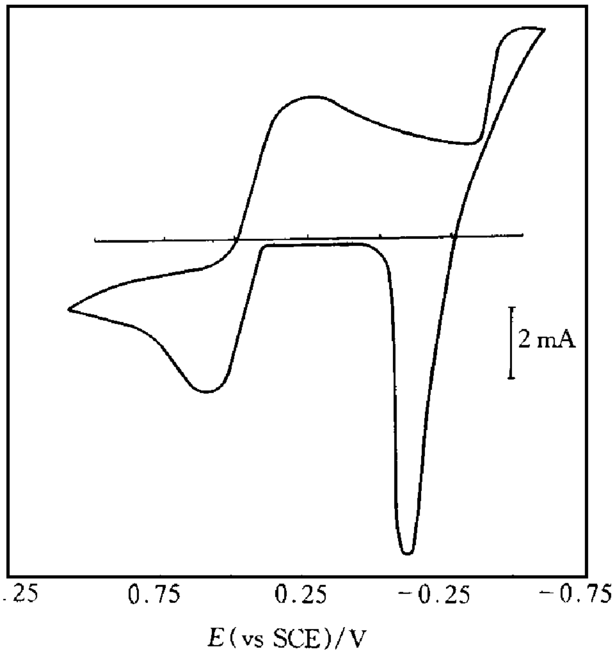

Fig. 7 Cyclic voltammogram of Pt electrode (0.51 cm^2) in (p-$CH_3C_6H_4SO_3)_3Nd$ (0.04 mol/L) – $CoCl_2$(0.03 mol/L) – (n-Bu$)_4NBF_4$(0.03 mol/L) – DMF at 25 ℃, 20 mV•s^{-1}

Neodymium film can be obtained on copper electrode by potentiostatic electrolyzing, but the film was thin and the cathodic current decreased with time elapsing. However, the above result expresses that the electroreduction of Nd(Ⅲ) was enhanced when the solution contains Co(Ⅱ). Maybe this is because the form of the complex ion of Nd(Ⅲ) with DMF is changed after Co(Ⅱ) is added into the solution. DMF contains two coordination atoms, nitrogen and oxygen, the coordination between Nd(Ⅲ) and oxygen is strong, while the coordination between Co(Ⅱ) and nitrogen is strong. Experiment shows that other transition metal ions such as Ni(Ⅱ), Cu(Ⅱ), etc, which coordinate with nitrogen strongly, have the same action to the electroreduction of Nd(Ⅲ). The study on the complex form of Nd(Ⅲ) and Co(Ⅱ) or other transition metal ions with DMF remains to be a subject for further study.

3.4 Electrodeposition of Nd-Co and Nd-Ni

The films of Nd-Co and Nd-Ni were obtained by potentiostatic electrolyzing in (p-$CH_3C_6H_4SO_3)_3Nd$ – $CoCl_2$ – (n-Bu$)_4NBF_4$ – DMF and (p-$CH_3C_6H_4SO_3)_3Nd$ – $NiCl_2$ – (n-Bu$)_4NBF_4$ – DMF on Cu electrodes. SEM observation shows that they are dense, homogenous and cohered with the copper substrate firmly. The composition of these films was obtained by EDAX as 21.45% Nd, 78.55% Ni in Nd-Ni and 6.1% Nd, 93.9% Co in Nd-Co. No diffraction peak was found in XRD patterns, so the films were in amorphous state.

4 CONCLUSIONS

(1) Neodymium p-toluenesulfonate was prepared and used as electrolyte in DMF for the electrodeposition of Nd. Its composition is determined as (p-$CH_3C_6H_4SO_3)_3Nd \cdot 2H_2O$. The solubility of the dehydrated salt in DMF is very high, compared with $RECl_3$, $RE(NO_3)_3$.

(2) The electroreduction of Nd(Ⅲ) to Nd in DMF is irreversible in one step. The diffusion coefficient of Nd(Ⅲ) is determined to be $4.3 \times 10^{-7} cm^2 \cdot s^{-1}$ at 25 ℃.

(3) The electroreduction of Nd(Ⅲ) can be enhanced when Co(Ⅱ) is reduced at the same time.

(4) The films of neodymium with purplish red luster and Nd-Co, Nd-Ni were obtained by potentiostatic electrolyzing on copper substrate. These films were in amorphous state and cohered with copper substrate firmly.

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