

Electrochemical Processing of Rare-Earth and Rare Metals by Using Molten Salts*

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Abstract

The electrochemical processing of rare-earth chlorides such as LaCl_3 , CeCl_3 , NdCl_3 , SmCl_3 and DyCl_3 in alkali chloride baths has been investigated in NaCl , KCl and eutectic LiCl-KCl by means of electrochemical transient methods. The thermodynamic behaviour of Ce-O-Cl and Fe-O-Cl systems is discussed in terms of electrode potential – pO^{2-} diagram. Low current efficiency found in the case of Nd electrowinning has been attributed to the dissolution of Nd in the bath. The analyses of electrochemical measurement required the elucidation of the effects of the factors such as under-potential deposition, metal dissolution, moisture and oxygen partial pressure.

INTRODUCTION

Recently, there has been a wide interest in the development of a process for producing and recycling rare earths, because rare earths are utilized as important elements for high-performance magnets [1], and are bringing difficulties in dry processes of spent nuclear fuel which are recently drawing attention. Electrowinning of rare earths can be done by the use of molten alkali halide bath. However, it is known that the current efficiency of the electrowinning of some rare earths such as neodymium or samarium is very low [2–6] for the electrolysis in alkali or alkaline-earth chloride melts. For the development of a process to produce pure rare earth metals with high current efficiency, it is important to understand the electrochemical behaviour of rare-earth metal ions when electrowinning was put in practice in molten salts. The reaction process on the surface of electrode can be characterized by electrochemical analysis such as cyclic voltammetry (CV) and chronopotentiometry. The electron number of the electrode reaction, the kind

of electrode reaction, diffusion coefficient and rate constant of comparatively slow reaction can be obtained by these techniques. In the current study, the mechanism of the electrolytic reduction and other phenomena affecting the electrolytic reduction process have been studied by means of cyclic voltammetry and chronopotentiometry. Molten KCl and $58.5\text{LiCl}-41.5\text{KCl}$ were chosen as the electrolytic baths at the temperature ranges of 1070 and 1260 K, and 620–900 K, respectively. As the rare-earth sources to be studied, LaCl_3 , SmCl_3 , CeCl_3 , NdCl_3 and DyCl_3 have been chosen.

EXPERIMENTAL

All of the chemicals used were dehydrated by heating in argon up to the melting temperatures of the salts. After the salts being melted, dried HCl was bubbled into the melts, and argon was bubbled into the melts to remove the residual HCl from the melts.

The experimental equipment of the cyclic voltammetry consists of a potentiostat, a function generator, an X–Y recorder, an intelligent recorder and a personal computer. Flag type electrodes made of platinum and gold with 1 cm^2 surface were used as the working

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electrode. A graphite rod with about 15 cm² surface area was used as the counter electrode, and a silver wire immersed in LiCl – KCl – 5 mol. % AgCl was used as the reference electrode. The concentrations of rare earths chlorides were changed from about 3 × 10⁻⁵ to 8 × 10⁻⁵ mol cm⁻³. The sweep rates were varied from 50 to 1000 mV s⁻¹.

RESULTS AND DISCUSSION

Mechanism of electroreduction in molten KCl

To clarify the electrochemical window range of the electrode materials, CV was done in molten KCl without doping. Platinum and gold worked as electrochemically stable electrodes at the window ranges of 0.4 and 1.2 V, and 0 and 1.2 V, respectively. At the potential within the window range no peak due to impurities in the bath was observed. As will be discussed later, platinum easily forms compound with deposited rare earths, and the compounds formed on the electrode surface seemed to stay, but, contrary to this case, the gold elec-

trode absorbs and transfers the deposits deep inside it.

The mechanism of electrochemical reduction of LaCl₃ has been investigated by the CV at 1067 K. Figure 1, *a* shows the cyclic voltammogram observed with a flag type electrode. As shown in Fig. 1, *a*, at the cathodic sweep, there are three peaks at -0.95, -1.18 and -1.4 V, and anodic peaks are at -1.21, -1.1, -0.55 and -0.2 V. The reverse potentials were changed to confirm the correspondence between cathodic and anodic peaks. It was found that the anodic peaks at -0.2, -0.55, -1.1, and -1.21 V correspond to cathodic peaks at -1.18, -0.95 and -1.4 V, respectively. Thus, the cyclic voltammogram observed with platinum electrode indicates rather complex reduction-oxidation mechanism. On the contrary, the cyclic voltammograms observed with gold electrode had rather simple shape. As shown in Fig. 1, *b*, only one cathodic peak at -1.2 V and one anodic peak at -1.0 V were observed. The number of the electrons involved in the cathodic peaks was calculated from the difference of the potential giving peak current E_p and the potential giving half of the peak current $E_{p/2}$ according to equation

$$E_p - E_{p/2} = \Delta RT / (nF) \quad (1)$$

where Δ represents the extent of the irreversibility and was found to be about 2. Therefore, the electrode reaction for the reduction of LaCl₃ can be expressed by equation



The peak at -1.4 V observed in the cathodic branch in Fig. 1, *a* corresponds to the deposition of La from La³⁺. The -0.95 and -1.18 V cathodic peaks were considered to correspond to the under-potential deposition forming intermetallic compounds between La and Pt.

The CV was done using the Au and Pt electrodes for CeCl₃ in KCl at 1298 K. The cyclic voltammogram observed with Pt electrode is shown in Fig. 2. The voltammogram for Au electrode was similar to that of platinum electrode. The voltammogram contains two cathodic peaks at -0.6 and -0.95 V, and two anodic peaks at -0.47 and -0.83 V.

When the potential was reversed at -0.76 V, an anodic peak was found at -0.47 V. The re-

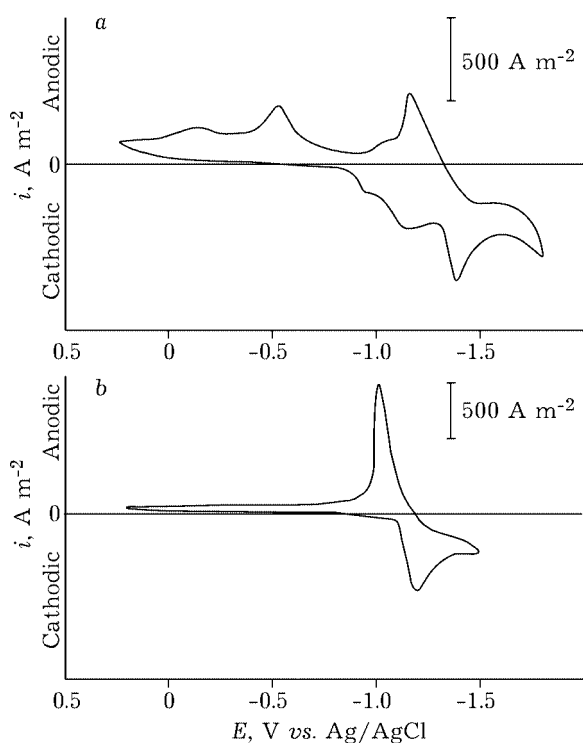


Fig. 1. Cyclic voltammograms of LaCl₃ in molten KCl at 1087 K with Pt (*a*) and Au (*b*) working electrodes. Sweep rate: 0.2 V s⁻¹.

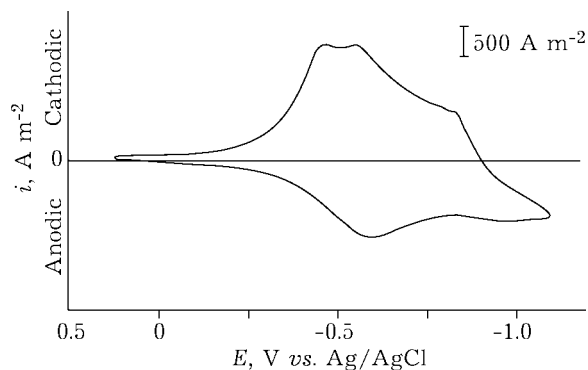


Fig. 2. Cyclic voltammogram of Ce^{3+} in molten KCl at 1298 K with Pt working electrode. Sweep rate: 0.2 V s^{-1} .

verse potential -1.1 V yielded five anode peaks at -0.47 , -0.54 , -0.56 , -0.79 and -0.83 V . These facts indicate that the broad peak observed at 0.95 V consists of more than 3 peaks. Figure 2 which is the case for reverse potential -1.3 V contains only two anode peaks. The chronopotentiogram for Ce^{3+} at 1068 K as shown in Fig. 3 has a potential hesitating region at about 0.52 V , but the potential does not rise sharply after this hesitating region. The electron number could not be determined precisely from voltammogram, because the peaks of voltammogram could not be resolved. The potential-time plots for the chronopotentiogram fitted best for the case where deposit is soluble, and yielded electron number from 1 to 2. Based on the

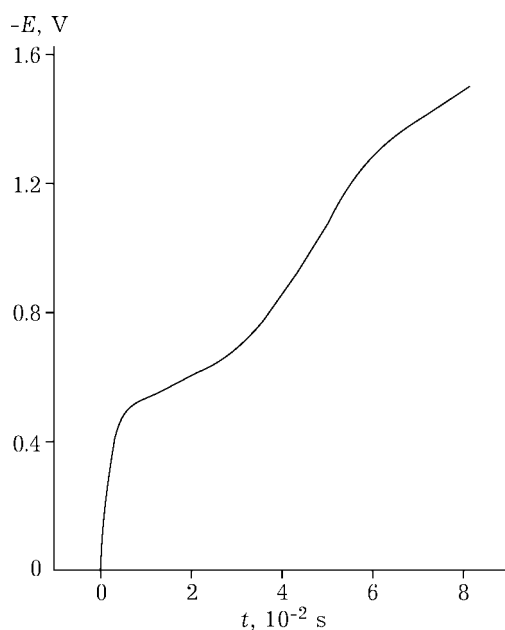


Fig. 3. Chronopotentiogram of Ce^{3+} in molten KCl at 1174 K and 0.92 kA m^{-2} with Pt working electrode.

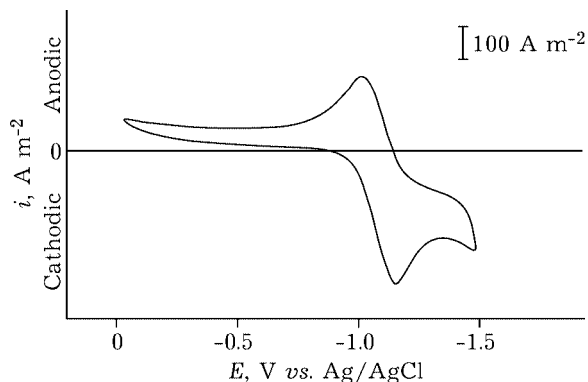


Fig. 4. Cyclic voltammogram of DyCl_3 in molten KCl at 1146 K with Au working electrode. Sweep rate: 0.2 V s^{-1} .

results obtained, it can be concluded that the reduction process of Ce^{3+} consists of more than two steps.

The cyclic voltammogram of DyCl_3 in molten KCl at 1146 K with the Au working electrode shown in Fig. 4 has one cathode peak at -1.16 V and one anode peak at -1.03 V . The reversibility of the voltammogram was confirmed. The electron number of the electrode reaction was 2.2. The electrode reaction can be expressed by equation



The cyclic voltammogram of SmCl_3 at 1090 K with Au working electrode is shown in Fig. 5. At the cathode branch the current starts to rise at -0.7 V and reaches maximum limit current at -0.95 V . The second cathode peak occurs at -1.32 V . The first cathodic voltammogram yields electron number one, and the second peak, two. The chronopotentiogram indicates that the first cathode reaction fits well

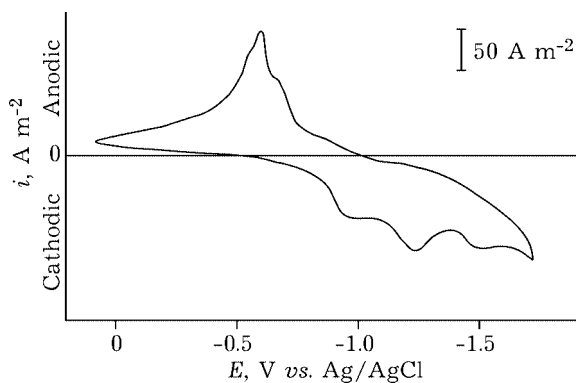


Fig. 5. Cyclic voltammogram of SmCl_3 in molten KCl at 1039 K with Au working electrode. Sweep rate: 0.1 V s^{-1} .

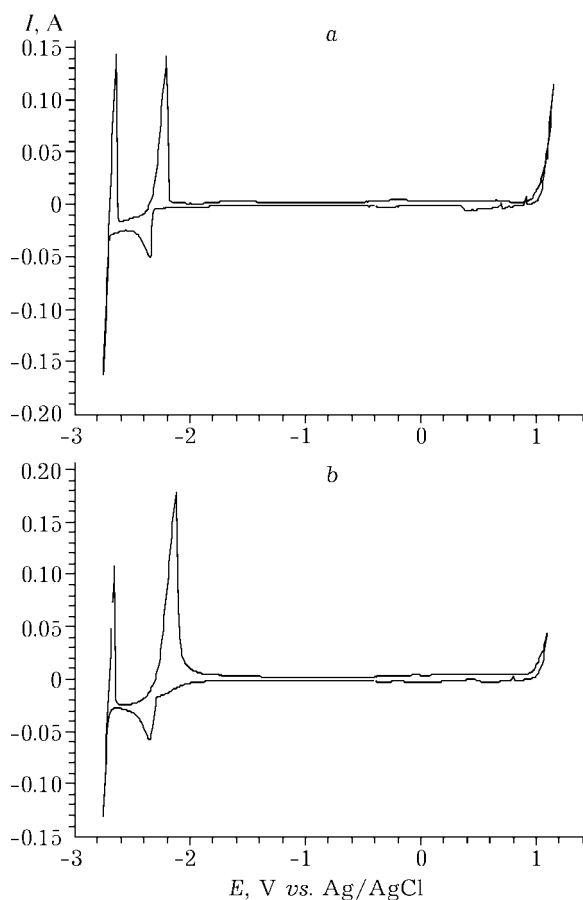


Fig. 6. Cyclic voltammograms of LaCl_3 (a) and NdCl_3 (b) in LiCl-KCl with W working electrode at 723 K. Sweep rate: 0.1 V s^{-1} .

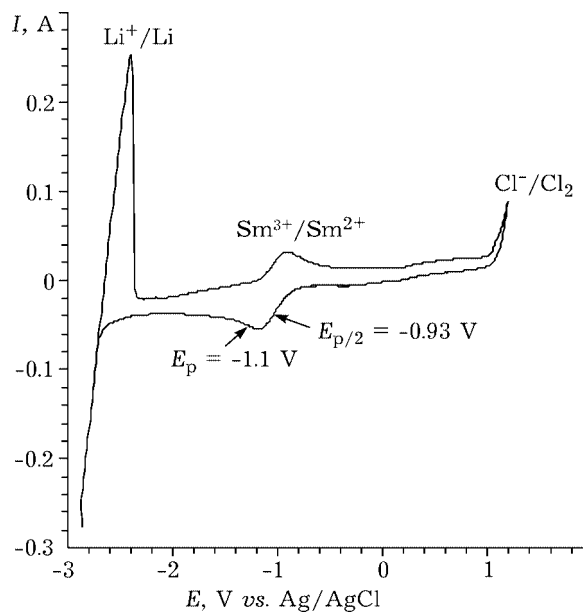


Fig. 7. Cyclic voltammogram of SmCl_3 in LiCl-KCl containing KF with W electrode at 723 K. Sweep rate: 0.25 V s^{-1} .

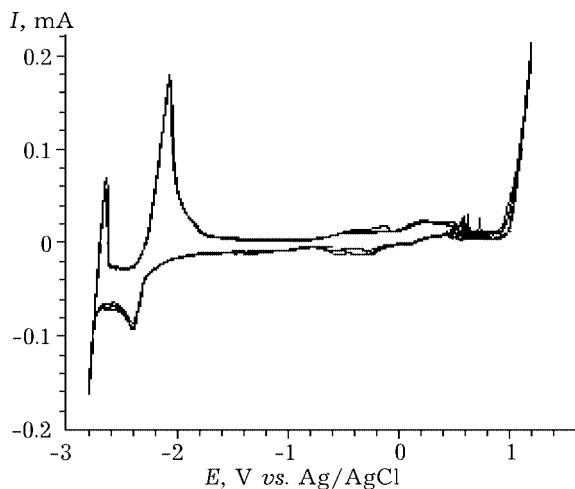


Fig. 8. Cyclic voltammogram of DyCl_3 in LiCl-KCl with W electrode at 723 K. Sweep rate: 0.1 V s^{-1} .

with the curve derived on the basis of soluble product. Therefore, it is concluded that Sm^{3+} is reduced to Sm according to eqs. (4) and (5) for the case of Au working electrode:



However, Tang *et al.* [7] reported that SmCl_3 could be reduced to SmCl_2 in KCl . This difference may be attributed to the underpotential deposition on Au electrode used in the current study.

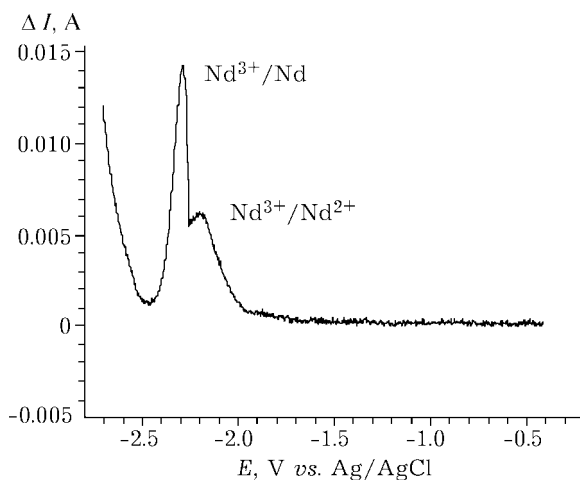
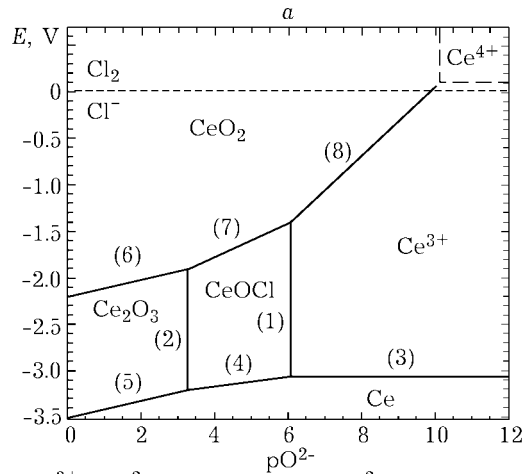
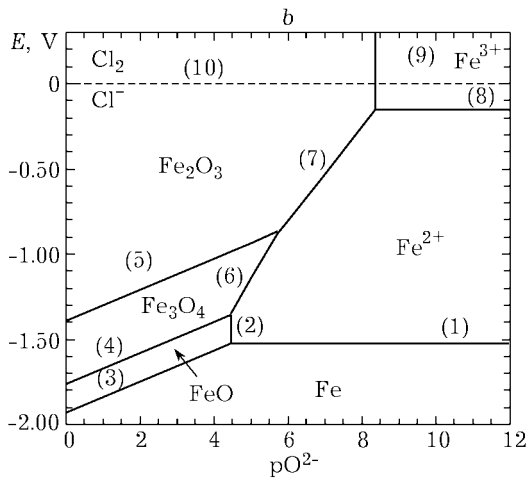


Fig. 9. Differential pulse voltammogram of NdCl_3 in LiCl-KCl at 723 K with W electrode. Pulse height: 20 mV; pulse width: 50 ms; pulse period: 0.5 s.



- (1) $\text{CeOCl (s)} = \text{Ce}^{3+} + \text{O}^{2-} + \text{Cl}^-$ $p\text{O}^{2-} = 6.035 + \log [\text{Ce}^{3+}]$
- (2) $\text{Ce}_2\text{O}_3 \text{ (s)} + 2\text{Cl}^- = 2\text{CeOCl (s)} + \text{O}^{2-}$ $p\text{O}^{2-} = 3.3$
- (3) $\text{Ce}^{3+} + 3e^- = \text{Ce}$ $E_3 = -3.056 + 0.061 \log [\text{Ce}^{3+}]$
- (4) $\text{CeOCl (s)} + 3e^- = \text{Ce} + \text{O}^{2-} + \text{Cl}^-$ $E_4 = -3.424 + 0.061 p\text{O}^{2-}$
- (5) $\text{Ce}_2\text{O}_3 + 6e^- = 2\text{Ce} + 3\text{O}^{2-}$ $E_5 = -3.425 + 0.0916 p\text{O}^{2-}$
- (6) $2\text{CeO}_2 + 2e^- = \text{Ce}_2\text{O}_3 + \text{O}^{2-}$ $E_6 = -2.219 + 0.0916 p\text{O}^{2-}$
- (7) $\text{CeO}_2 + \text{Cl}^- + e^- = \text{CeOCl} + \text{O}^{2-}$ $E_7 = -2.521 + 0.183 p\text{O}^{2-}$
- (8) $\text{CeO}_2 + e^- = \text{Ce}^{3+} + 2\text{O}^{2-}$ $E_8 = -3.627 - 0.1831 \log [\text{Ce}^{3+}] + 0.366 p\text{O}^{2-}$



- (1) $\text{Fe}^{2+} + 2e^- = \text{Fe}$ $E_1 = -1.522 + 0.0916 \log [\text{Fe}^{2+}]$
- (2) $\text{FeO} = \text{Fe}^{2+} + \text{O}^{2-}$ $p\text{O}^{2-} = 4.44 + \log [\text{Fe}^{2+}]$
- (3) $\text{FeO} + 2e^- = \text{Fe} + \text{O}^{2-}$ $E_3 = -1.929 + 0.0916 p\text{O}^{2-}$
- (4) $\text{Fe}_3\text{O}_4 + 2e^- = 3\text{FeO} + \text{O}^{2-}$ $E_4 = -1.762 + 0.0916 p\text{O}^{2-}$
- (5) $3\text{Fe}_2\text{O}_3 + 2e^- = 2\text{Fe}_3\text{O}_4 + \text{O}^{2-}$ $E_5 = -1.394 + 0.0916 p\text{O}^{2-}$
- (6) $\text{Fe}_3\text{O}_4 + 2e^- = 3\text{Fe}^{2+} + 4\text{O}^{2-}$ $E_6 = -2.973 - 0.275 \log [\text{Fe}^{2+}] + 0.366 p\text{O}^{2-}$
- (7) $\text{Fe}_2\text{O}_3 + 2e^- = 2\text{Fe}^{2+} + 3\text{O}^{2-}$ $E_7 = -2.447 - 0.183 \log [\text{Fe}^{2+}] + 0.274 p\text{O}^{2-}$
- (8) $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$ $E_8 = -0.156 + 0.183 \log ([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$
- (7) $\text{Fe}_2\text{O}_3 + 2e^- = 2\text{Fe}^{2+} + 3\text{O}^{2-}$ $p\text{O}^{2-} = 8.36 + 0.667 \log [\text{Fe}^{3+}]$
- (10) $\text{Cl}_2 + 2e^- = 2\text{Cl}^-$ $E_{10} = 0 + 0.0916 \log P_{\text{Cl}_2}$

Fig. 10. Pourbaix diagrams for Ce-O-Cl (a) and Fe-O-Cl (b) systems.

Mechanism of the reduction of LaCl_3 , NdCl_3 , SmCl_3 and DyCl_3 in molten LiCl-KCl

To clarify the reduction mechanism of the rare earths chlorides in 58.5 LiCl-41.5 KCl eutectic melts, CV has been carried out over the temperature range of 630–900 K. In case that the overlapping of the CV peaks was significant, a differential pulse voltammetry which has higher resolution in the spectrum, was examined to extract electrochemical parameters which would be indispensable for the determination of the mechanism of the electroreduction.

The cyclic voltammograms obtained for LaCl_3 , NdCl_3 , SmCl_3 and DyCl_3 in molten LiCl-KCl are shown in Figs. 6–8. As shown in Figs. 6, *a* and 8, two partially overlapped peaks are observed for NdCl_3 and DyCl_3 . Therefore, DPV method was applied to gain higher resolution in the spectra, and shown in Fig. 9 for the case of NdCl_3 . As clearly shown in Fig. 9, two peaks are resolved enough for the electrochemical analyses. The electrode reactions for the reduction of each chloride are summarized as follows. It was found that SmCl_3 could not be reduced to Sm as far as LiCl-KCl was used as the bath:



The current efficiency of the electrodeposition of Nd from LiCl-KCl bath was low according to the previous study (8). This fact can be attributed to the coexistence of Nd^{2+} and Nd^{3+} ions which would cause the shuttle reaction, and decrease the current efficiency. The same behaviour can be expected for the case of electroreduction of DyCl_3 based on the mechanism determined in the current study.

Electrochemical behaviour of the Ce-O-Cl and Fe-O-Cl systems

Electrochemical behaviour of Ce-O-Cl and Fe-O-Cl systems in the NaCl-2CsCl has been

examined. For this purpose, redox potentials were determined from the results of the e.m.f. measurements of the electrochemical cells and CV. On the other hand, the pO^{2-} was changed by adding Na_2CO_3 into the solvent. The e.m.f. was measured with changing the amount of Na_2CO_3 added. The potential - pO^{2-} diagrams were constructed for Ce-O-Cl and Fe-O-Cl systems based on these results, and shown in Fig. 10. In the measurement of the CV for the Ce-O-Cl system, even if the electrode was polarized anodically until the Cl_2 was evolved, Ce^{3+} was not oxidized to Ce^{4+} . In Fig. 10, *a* the dotted line represents the guessed line bordering the Ce^{3+} and Ce^{4+} . Based on these results, it was concluded that the cerium ion would not cause a shuttle reaction in NaCl-2CsCl solvents and would not result in the decrease in the current efficiency. But iron ion produces both Fe^{3+} and Fe^{2+} ions within the electrochemical window of the solvent, and might cause the shuttle reaction at both electrodes.

CONCLUSION

Electrochemical behaviours of LaCl_3 , CeCl_3 , DyCl_3 and SmCl_3 have been studied in molten KCl bath by means of the cyclic voltammetry and chronopotentiometry. The cyclic voltammograms depend on the material used for the working electrodes. This is because the deposits of the electrochemical reduction reacted easily with platinum and gold at high temperatures. The former metal forms rather stable intermetallic compounds on the surface, and the compounds are stripped anodically at the characteristic potentials. Gold often absorbs the deposit and gives simple voltammogram.

The mechanism of the electrochemical reduction has been discussed. Lanthanum chloride and dysprosium chloride can be reduced to metallic state in molten KCl. Samarium chloride was also reduced to metallic state with two step electrode reactions on the gold working electrode. However, dissolution of deposited metal must be taken into consideration for the case of massive deposition.

For the case of 58.5LiCl-41.5KCl bath, mechanisms of the electroreduction of the LaCl_3 ,

Nd, Sm and Dy chlorides have been investigated. In case of NdCl_3 , the reason for the low current efficiency described in the previous report was attributed to the shuttle reaction between Nd^{2+} and Nd^{3+} ions. Similar behaviour could be expected for the case of the reduction of the DyCl_3 because Dy^{3+} and Dy^{2+} coexist in the LiCl-KCl bath.

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