ELECTROCHEMICAL BEHAVIOR OF LANTHANUM ION IN \( \text{LaCl}_3 \) SATURATED \( \text{AlCl}_3 \)-EMIC ROOM TEMPERATURE MOLTEN SALTS

Tetsuya Tsuda and Yasuhiko Ito
Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University
Sakyo-ku, Kyoto 606-8501, JAPAN

ABSTRACT

The solubility of lanthanum chloride (\( \text{LaCl}_3 \)) is dominated by the amount of \( \text{Al}_2\text{Cl}_7 \) anion in the aluminum chloride (\( \text{AlCl}_3 \)) - 1-ethyl-3-methylimidazolium chloride (EMIC) room temperature molten salt systems. Electrochemical experiments have been performed in \( \text{LaCl}_3 \) saturated \( \text{AlCl}_3 \)-EMIC (\( N = 0.667 \)) melts. Aluminum-lanthanum alloy which is thought to be in coexisting aluminum and \( \alpha \)-\( \text{Al}_{11}\text{La}_3 \) phase state or in the unidentified metastable / non-equilibrium state is formed at around \(-0.58 \) V vs. \( \text{Al(III)} / \text{Al} \) in the melt. From an analysis of the chronoamperometric transients it is suggested that the electrodeposition of this aluminum-lanthanum alloy on tungsten disk electrode involves instantaneous three-dimensional nucleation with mixed diffusion and kinetic controlled growth of the nuclei. In a \( \text{LaCl}_3 \) saturated melt (\( N = 0.667 \)) with excessive lithium chloride (\( \text{LiCl} \)) and small quantities of thionyl chloride (\( \text{SOCl}_2 \)) added, lanthanum metal is electrodeposited at around \(-1.95 \) V vs. \( \text{Al(III)} / \text{Al} \). The electrodeposited lanthanum metal does not undergo complete stripping from the electrode surface during anodic polarization.

INTRODUCTION

During the 1990s, a considerable number of studies have been made on ambient temperature melts. In particular, \( \text{AlCl}_3 \)-EMIC room temperature molten salt systems are studied by many researchers. This mainly comes from the fact that \( \text{AlCl}_3 \)-EMIC melts have superior properties, such as wide electrochemical window (~ 4.4 V), high conductivity (~ 0.02 S cm\(^{-1} \)), good thermal stability, and nonflammability. Taking these advantageous features into consideration, they have been studied in order to apply to energy conversion and material synthesis. For instance, in the field of lithium batteries, it
was reported that lithium metal can be electrodeposited in LiCl buffered molten salt systems containing SOCl₂ or HCl gas. The SOCl₂ added melt, which has low vapor pressure at room temperature, is stable in air and easier to handle than the HCl gas added melt. Concerning the surface processing, a large number of studies have been made on formation of aluminum-transition metal alloy layers, such as Al-Mn, Al-Cr, Al-Co and Al-Ni. However little attention has been paid to the electrodeposition of rare earth metals or their alloys. Although these metals and alloys have interesting properties, the electrochemical behavior of rare earth metal ions is not yet sufficiently clarified in AlCl₃-EMIC molten salt systems. There are only reports on the oxidation / reduction potential of Nd(III) / Nd(II) and Eu(III) / Eu (II). Based on this background, the purpose of the present study is to make clear of the electrochemical behavior of lanthanum ion and electrodeposited lanthanum metal and its alloys in AlCl₃-EMIC molten salt systems. We previously reported that the solubility of lanthanum chloride was very low in basic melts (N < 0.500) and LiCl buffered melts. Thus, in this study, we used only acidic melts to investigate the electrochemical behavior of lanthanum ion and the electrodeposition of lanthanum metal and aluminum-lanthanum alloys.

EXPERIMENTAL

The preparation and purification of EMIC and AlCl₃ were performed as described previously. AlCl₃-EMIC room temperature molten salts were prepared by mixing appropriate amounts of AlCl₃ and EMIC. Anhydrous LaCl₃ of 99.99 % purity (Aldrich, beads) was used as received and it was dissolved into AlCl₃-EMIC melts by stirring for five days at 343 K. Anhydrous lithium chloride is obtained by vacuum drying at 473 K in an electric furnace for three days. Thionyl chloride and benzen were dried over molecular sieves. Electrodeposits were rinsed in benzen for three times. All experiments were conducted in a three-electrode cell. Working electrodes were a tungsten disk (0.00785 cm²) or tungsten ribbon (0.14 cm²), counter electrode was a tungsten spiral. Reference electrode was an aluminum wire immersed in an acidic AlCl₃-EMIC (N = 0.667) melt separated by a glass frit (G-4). All experiments were carried out in an argon gas filled drybox at 298 K. Electrochemical measurements were performed with a Hokuto Denko HZ-3000 automatic polarization systems controlled with a Fujitsu FMV-C830L3 personal computer. Electrodeposits were analyzed by XPS and ICP. XPS spectra were recorded on a Shimazu ESCA-3200-01 X-ray photoelectron spectrometer. The XPS results were compared to the Ulvac-phai XPS spectra handbook. The composition of the electrodeposits was determined by ICP after being dissolved into hydrochloric acid (1 N). The solubility of lanthanum chloride in the melts was also measured by the same method. Ionic species in the melts were determined by Raman spectroscopy. Raman spectra of the samples were obtained by a BIO-RAD FTS-175C spectrometer using Nd:YAG laser (1200 mW).
RESULTS AND DISCUSSION

We previously investigated the electrochemical behavior of lanthanum ion in LiCl saturated and basic AlCl₃-EMIC room temperature melts. In the present study, we first examined the solubility of lanthanum chloride in acidic AlCl₃-EMIC room temperature melts. The solubility was approximately 2 and 50 mmol kg⁻¹ for the acidic melts with N = 0.524 and 0.667, respectively. From these and previous results, it was found that the solubility increased as the acidity of the melts increased. That is, the solubility of lanthanum chloride was dominated by the amount of Al₂Cl₇⁻ anion in the melts. To elucidate the dissolution mechanism of lanthanum chloride, the following mechanism of lithium chloride dissolution into acidic AlCl₃-EMIC melts was referred:

\[
\text{LiCl} + \text{Al}_2\text{Cl}_7^- \rightarrow 2 \text{AlCl}_4^- + \text{Li}^+ \quad (1)
\]

Similar to this lithium chloride dissolution mechanism, lanthanum chloride was assumed to dissolve into acidic AlCl₃-EMIC melts via the following reaction.

\[
\text{LaCl}_3 + 3 \text{Al}_2\text{Cl}_7^- \rightarrow 6 \text{AlCl}_4^- + \text{La(III)} \quad (2)
\]

In order to confirm reaction (2), Raman spectroscopy was conducted. Only Raman spectra of Al₂Cl₇⁻ anion was confirmed in an original AlCl₃-EMIC melt (N = 0.667). On the other hand, Raman spectra intensity of Al₂Cl₇⁻ anion decreased and that of AlCl₄⁻ anion increased in a LaCl₃ saturated AlCl₃-EMIC melt (N = 0.667). These results support our assumed mechanism. The results also indicate that it is difficult to experiment in low Al₂Cl₇⁻ anion concentration melts. Therefore we used an AlCl₃-EMIC (N = 0.667) melt, because it has a high concentration of Al₂Cl₇⁻ anions. The electrochemical behavior of lanthanum ion and the electrodeposition of lanthanum metal and their alloys in LaCl₃ saturated melts were investigated.

Figure 1 shows that the electrodeposition of aluminum metal on a tungsten disk electrode in a LaCl₃ saturated melt [Fig. 1(a)] requires a larger overpotential than that of pure aluminum metal in an AlCl₃-EMIC melt (N = 0.667) [Fig. 1(b)]. Figure 1(a) shows two stripping peaks, which indicate stripping waves of aluminum-lanthanum alloys. Therefore, further study was carried out by means of other electrochemical measurements and potentiostatic electrolysis.
Chronoamperometry was carried out in order to investigate the nucleation / growth process of the deposits. Potential steps were applied on the tungsten disk working electrode from an initial value of -0.2 V to the electrodepositing potential value. Typical current-time transients are shown in Fig. 2. These transients show the ordinary shape for a nucleation process. The current increases due to the nucleation and growth of nuclei after the decay of double layer charging current. A current maximum value, $i_m$, is reached when the diffusion zones of the growing nuclei begin to overlap. The time at which $i_m$ is observed, $t_m$, is dependent on the applied potential, becoming shorter as the potential is made more negative. This is explained by the shortenings of the time required for the diffusion layer to overlap due to the increase of nucleation density. Also it is found that each current-time transient does not correspond to the experimental diffusion-limited Cottrell currents at longer time, these results suggest that the growth process occur under mixed diffusion and kinetic control.

The electrodeposition of metals or alloys on substrates from AlCl$_3$-EMIC melts often involves a three-dimension nucleation / growth process. Basically, the three-dimension nucleation / growth is described as either instantaneous nucleation on a fixed number of active sites or progressive nucleation on an infinite number of active sites. The normalized dimensionless expression for these two models are given as follows:

For instantaneous nucleation,

$$\left( \frac{i}{i_m} \right)^2 = \frac{1.9542}{(t/t_m)} \left[ 1 - \exp \left[ -1.2564 \left( \frac{t}{t_m} \right) \right] \right]^2$$  \hspace{1cm} (3)

For progressive nucleation,

$$\left( \frac{i}{i_m} \right)^2 = \frac{1.2254}{(t/t_m)} \left[ 1 - \exp \left[ -2.3367 \left( \frac{t}{t_m} \right)^2 \right] \right]^2$$  \hspace{1cm} (4)

If the electrodeposition is involved with instantaneous or progressive nucleation / growth, the dimensionless experimental current-time transients should correspond to the theoretical curves given by eq. (3) or eq. (4). Figure 3 shows the plots of $(i/i_m)^2$ vs. $(t/t_m)$ from experimental data depicted in Fig. 2. Theoretical curves for eq. (3) and eq. (4) are also plotted in Fig. 3. The experimental result is in good agreement with the
In order to analyze the composition of the deposits, potentiostatic electrolysis was conducted at \(-0.58\) V in a LaCl\(_3\) saturated AlCl\(_3\)-EMIC (\(N = 0.667\)) melt. The obtained sample was analyzed by XPS and ICP. The result of XPS analysis was shown in Fig. 4. The peak binding energy of Al 2s spectra of the sample shifted to the high energy side compared to the aluminum metal spectrum. That suggests that the obtained samples were aluminum oxide. For the La 4d spectra, the observed spectra are similar to that of lanthanum oxide. Oxidation of sample seemed to occur in air when the samples were set on the XPS spectrometer. Moreover, the composition of the obtained samples was analyzed by ICP. The aluminum to lanthanum weight ratio was approximately 98 to 2. From these results and the phase diagram of aluminum-lanthanum alloy, it is suggested that the obtained sample is in the coexisting aluminum metal and \(\alpha\)-Al\(_{11}\)La\(_3\) phase state. However, since the alloy was formed at relatively low temperature, the obtained phase may consist of metastable or non-equilibrium state.

Cyclic voltammogram for a tungsten disk electrode in a LaCl\(_3\) saturated AlCl\(_3\)-EMIC (\(N = 0.667\)) melt after addition of excessive LiCl and small quantities of SOCl\(_2\) is given in Fig. 5. In this figure, three reduction waves and only one oxidation wave are shown. It was reported that the SOCl\(_2\) and lithium reduction / oxidation potentials in a LiCl saturated acidic AlCl\(_3\)-EMIC melt after addition of SOCl\(_2\) are around 0.6V and \(-2.25V\)\(^1\), respectively. Accordingly, wave A represents oxidation of SOCl\(_2\), and wave C and D indicates lithium deposition and stripping, respectively. Reduction of lanthanum ion is thought to occur at wave B. However there was no oxidation wave corresponding to this reduction wave B. Judging from the above, we assumed that the passive layer, such as La(OH)\(_3\), La\(_2\)O\(_3\), and LaCl\(_3\), was formed on a tungsten disk electrode from residual water or SOCl\(_2\) in the melt. In the case of lithium secondary battery, it is well known that the electrodeposited lithium metal reacts with water or SOCl\(_2\) to produce a solid electrolyte interphase (SEI) film, such as LiCl, Li\(_2\)O and LiOH, in water or SOCl\(_2\) containing electrolytes\(^{20,23}\). Also, in the case of electrodeposited lanthanum metal, a similar reaction is thought to occur: the electrodeposited lanthanum metal reacts with SOCl\(_2\) and changes to LaCl\(_3\). An Anodic wave corresponding to the cathodic wave B may not have been observed by this reaction. To obtain more information, potentiostatic electrolysis was conducted around \(-1.95V\). Figure 6 shows the XPS spectra of Al 2s and La 4d. No XPS spectra corresponding to Al 2s are observed. On the contrary, the La 4d spectra shows sharp spectra of lanthanum oxide. However, spectra of lanthanum chloride or lanthanum metal was not observed. Since lanthanum metal and lanthanum chloride are very reactive, they might have reacted with water and oxygen during the preparation for analysis. The existence of lanthanum was also confirmed by ICP. Current values decreased during the electrolysis and reached almost zero after 15 minutes and the current efficiency was very low. These results were thought to be caused by formed SEI film. The obtained sample did not have metallic luster but black luster. When they were placed
in air, they changed to white. The features of the deposits resembled electrodeposited lanthanum metal in a LiCl-KCl molten salt.

CONCLUSION

We investigated the electrochemical behavior of lanthanum ion in LaCl$_3$ saturated AlCl$_3$-EMIC melts. It turned out that the LaCl$_3$ solubility was dominated by the amount of Al$_2$Cl$_7$ anion in AlCl$_3$-EMIC melts. A LaCl$_3$ saturated AlCl$_3$-EMIC (N = 0.667) melt was used for electrochemical measurements and electrodeposition because it has high LaCl$_3$ solubility. It was suggested that aluminum-lanthanum alloy electrodeposits at -0.58 V in a LaCl$_3$ saturated AlCl$_3$-EMIC (N = 0.667) melt. From the results of XPS and ICP and phase diagram of aluminum-lanthanum alloys, the obtained alloy is thought to be in the coexisting aluminum and $\alpha$-Al$_{11}$La$_3$ phase or in the unidentified metastable / non-equilibrium state. Furthermore, it was also indicated that lanthanum metal electrodeposits at -1.95V in a LaCl$_3$ saturated AlCl$_3$-EMIC (N = 0.667) melt after addition of excessive LiCl and small quantities of SOCl$_2$. The electrodeposited lanthanum metal was thought to have changed to lanthanum oxide during preparation for analysis.

REFERENCES

1. J. Fuller, R. A. Osteryoung, and R. T. Carlin, J. Electrochem. Soc., 142, 3632 (1995).
2. J. Fuller, R. T. Carlin, and R. A. Osteryoung, J. Electrochem. Soc., 143, L145 (1996).
3. C. S-Kelley and R. T. Carlin, J. Electrochem. Soc., 140, 1606 (1993).
4. C. S-Kelley and R. T. Carlin, J. Electrochem, Soc., 141, 873 (1994).
5. B. J. Piersma, D. M. Ryan, E. R. Schumacher, and T. L. Riechel, J. Electrochem. Soc., 143, 908 (1996).
6. H. C. De Long, J. A. Mitchell, P. L. Hagans, R. T. Carlin, G. R. Stafford, and P. C. Trulove, in Molten Salts XI, P. C. Trulove, H. C. De Long, G. R. Stafford, S. Deki, Editors, PV 98-11, p.40, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).
7. T. P. Moffiat, J. Electrochem. Soc., 141, L115 (1994).
8. M. Matsunaga, T. Kitzazaki, K. Hosokawa, S.Hirano, and M. Yoshida, in Molten Salts IX, C. L. Hussey, D. S. Newman, G. Mamantov, and Y. Ito, Editors, PV 94-13, p.422, The Electrochemical Society, NJ (1994).
9. D. E. Clinton, P. C. Trulove, P. L. Hagans, and H. C. De long, Molten Salt Forum, 5-6, p.593 (1998).
10. M. Matsunaga, M. Morimitsu, M. Nagano, and T. Tsuda, Molten Salt Forum, 5-6, 601 (1998).
11. J. A. Mitchell, W. R. Pitner, C. L. Hussey, and G. R. Stafford, *J. Electrochem. Soc.*, 143, 3448 (1996).
12. W. R. Pitner, C. L. Hussey, and G. R. Stafford, *J. Electrochem. Soc.*, 143, 130 (1996).
13. M. Lipsztajn and R. A. Osteryoung, *Inorg. Chem.*, 24, 716 (1985).
14. W-J. Gau and I-W. Sun, *J. Electrochem. Soc.*, 143, 914 (1996).
15. T. Tsuda and Y. Ito, in *Abstracts of 1999 Asian Conference on Electrochemistry*, p.149 (1999).
16. T. J. Melton, J. Joyce, J. T. Maloy, J. A. Boon, and J. S. Wilkes, *J. Electrochem. Soc.*, 137, 3865 (1990).
17. C. S-Kelley, J. Fuller, R. T. Carlin, and J. S. Wilkes, *J. Electrochem. Soc.*, 139, 694 (1992).
18. B. Scharifker and G. Hills, *Electrochim. Acta*, 28, 879 (1983).
19. R. Greef, R. Peat, L. M. Peter, D. Pletcher, and J. Robinson, *Instrumental Methods in Electrochemistry*, Chapter 9, Ellis Horwood, Chichester (1985).
20. R. T. Carlin and J. Fuller, in *Molten Salts X*, R. T. Carlin, S. Deki, M. Matsunaga, D. S. Newman, J. R. Selman, and G. R. Stafford, Editors, PV 96-7, p.362, The Electrochemical Society Proceedings Series, Pennington, NJ (1996).
21. R. T. Carlin and J. Fuller, U.S. patent 5,552,238 (1996).
22. A. N. Dey, *Electrochim. Acta*, 21, 377 (1976).
23. Y. Zhang and C-S. CHA, *Electrochim. Acta*, 37, 1211 (1992).
Fig. 1 Cyclic voltammogram for a tungsten disk electrode in a LaCl$_3$ saturated AlCl$_3$-EMIC (N = 0.667) melt (a) and an original AlCl$_3$-EMIC (N = 0.667) melt (b).

Fig. 2 Chronoamperograms for a tungsten disk electrode in a LaCl$_3$ saturated AlCl$_3$-EMIC (N = 0.667) melt.
Fig. 3 Comparison of the dimensionless experimental current-time transients derived from chronoamperograms with the theoretical curves for three-dimensional (a) instantaneous and (b) progressive nucleation on a tungsten disk electrode.

Fig. 4 XPS spectra of deposits obtained by potentiostatic electrolysis at \(-0.58\) V for \(0.5 \text{ C cm}^{-2}\) in a \(\text{LaCl}_3\) saturated \(\text{AlCl}_3\)-EMIC (\(N = 0.667\)) melt.
Fig. 5 Cyclic voltammogram for a tungsten disk electrode in a LaCl₃ saturated AlCl₃-EMIC (N = 0.667) melt after addition of excessive LiCl and small quantities of SOCl₂.

Fig. 6 XPS spectra of deposits obtained by potentiostatic electrolysis at -1.95 V for 0.5 C cm⁻² in a LaCl₃ saturated AlCl₃-EMIC (N = 0.667) melt after addition of excessive LiCl and small quantities of SOCl₂.