

**ELECTROCHEMICAL BEHAVIOURS OF LANTHANIDE FLUORIDES IN THE
ELECTROLYSIS SYSTEM WITH LiF-NaF-KF SALT**

**Joon-Bo Shim, Sung-Chan Hwang, Eung-Ho Kim, Young-Ho Kang, Byung-Jik Lee
and Jae-Hyung Yoo**

Korea Atomic Energy Research Institute
P.O. Box 105, Yusong, Daejeon, 305-600, Korea

Abstract

As a part of partitioning studies, the experiments of cyclic voltammetry and electrolytic reduction with the liquid bismuth cathode were conducted to investigate electrochemical behaviours of lanthanide elements in the electrorefining system employing LiF-NaF-KF eutectic salt as the electrolyte. The cyclic voltammograms for NdF_3 and GdF_3 were obtained at various potential scan rates, respectively. The cathodic and anodic peak currents of the elements increased in proportion to the square root of the potential scan rate. According to changes of the potential difference between the coupled cathodic and anodic peaks, reversibilities of the reduction-oxidation reactions in this system were evaluated. In addition, further behaviours of electrochemical reaction of the elements were examined through electrolytic tests of the system using liquid bismuth as the cathode at fixed current densities.

Introduction

The R&D activities for the partitioning and transmutation of long-lived radionuclides are actively in progress in advanced nuclear countries. [1,2] Long-lived radionuclides contained in the spent nuclear fuel can be recovered by the pyrochemical separation processes using high temperature molten-salts [3-7] and recycled to the reactor for transmutation, which results in the waste containing short-lived or stable nuclides. The resulting waste, therefore, will show a remarkable reduction in the radiological toxicities and can be disposed of under milder conditions. At present, various concepts for the transmutation of long-lived radionuclides are being studied in several countries. One of the concepts for the transmutation which uses an Accelerator Driven System (ADS) is a hybrid system composed of a proton accelerator and a sub-critical reactor. [8,9]

KAERI is performing research on the concept of a hybrid system focusing on the sub-critical reactor for transmutation of long-lived radionuclides. [10] The pyroprocessing option might be preferable from the viewpoint of process simplicity, nuclear proliferation resistance, and economy. [1-3] A conceptual and basic study of the relevant fuel cycle based on the pyroprocess is also being carried out for the future feasible advanced process. [10-12] Many of these studies have been carried out in the form of international collaboration. In the pyroprocess many studies are extensively focused on the separation of minor actinides from lanthanides by means of electrolysis. [13-15]

Previously, we have investigated some electrochemical behaviours of lanthanides (Gd and Nd) and/or transuranic elements in the LiF-NaF-KF (FLINAK) eutectic salt at 773K using the cyclic voltammetry and potentiostatic electrolysis techniques in collaboration with the AEA Technology (the U.K.). The LiF-NaF-KF salt mixture containing lanthanides and transuranic elements showed a little complex cyclic voltammogram. [16] However, the electrochemical properties of lanthanides, *i.e.* Nd and Gd, in the LiF-NaF-KF salt have not been examined in detail.

In this study, in order to examine fundamental electrochemical behaviours upon the system consisting of only lanthanide elements such as Gd and/or Nd in the LiF-NaF-KF eutectic salt at 773K electrochemical experiments such as the cyclic voltammetry and galvanostatic reduction on the liquid bismuth cathode were carried out.

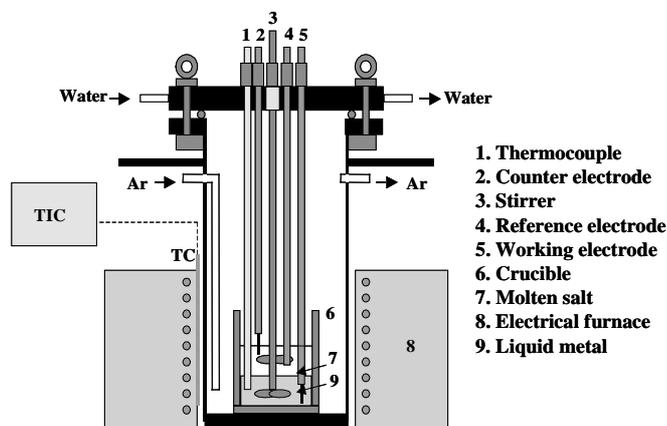
Experimental

Electrochemical experiments such as cyclic voltammetry and galvanostatic reduction were carried out at 773K using the electrochemical cell as shown in Figure 1. In this electrochemical study a three-electrode system was utilised. A quasi reference electrode (Q.R.E.) consisting of a molybdenum metal rod of 3.0mm diameter (product of the Rare Metallic Co.) and electrical insulating tube was used. [17] The working electrode using tungsten wire (OD 1.0mm) was straight pin with a short length (10mm) for the cyclic voltammetry. The working electrode made with liquid bismuth for galvanostatic reduction experiments was prepared as a pool type on the bottom of crucible. The counter electrode was a molybdenum metal rod of 3.0mm diameter.

Chemicals used in this study, such as LiF (99.98%), NaF (99.99%), KF (99.99%), NdF₃ (99.99%) and GdF₃ (99.99%) were purchased from the Alfa Aesar Co. or Aldrich Co. The FLINAK eutectic salt (m.p. 727K) was made up of the following composition, LiF-NaF-KF (46.5-11.5-42 mol%) and used as the electrolyte. The mixture of salt reagents was heated at 673K (>12 hours) under Ar gas flow in order to dry it.

The potentiostat was a model WAT-100 (Wonatech Co.) connected to a personal computer. The cathodic potentials were monitored continuously during the galvanostatic reduction experiment. All experiments were carried out in a glove box filled with high purity (99.999+%) Ar gas.

Figure 1. Schematic diagram of the electrochemical cell

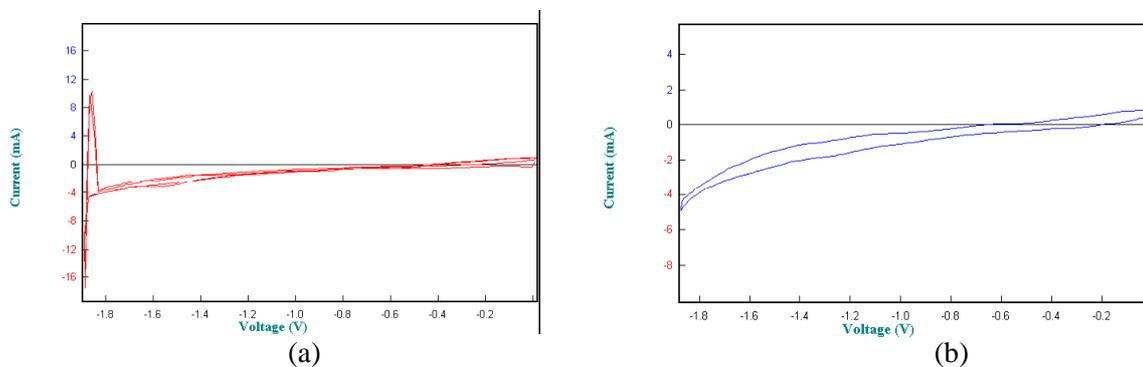


Results and discussion

Cyclic voltammogram of the pure FLINAK salt

In order to prepare a FLINAK melt without impurities a mixture of salt reagents in high density graphite crucible was dried at 673K more than 12 hours under Ar gas flow then heated to 773K. A cyclic voltammogram for this pure FLINAK electrolyte with a salt decomposition potential of -1.88V is shown in Figure 2(a). There is no reduction peak of impure ions in the potential window from zero to -1.89V showing that the clear FLINAK melt was prepared. Also, we could confirm that pure tungsten wire (99.99+%) can be used as the working electrode material on the basis of the CV result obtained in the potential range prior to the salt decomposition potential (Figure 2(a)).

Figure 2. Cyclic voltammograms of the LiF-NaF-KF melt without impurities at 773K Scan rates ($v=0.10\text{ V/s}$). Initial scan direction: Cathodic



Voltammetric results of lanthanide fluorides in the FLINAK salt [13-15]

Neodymium fluoride in the FLINAK salt

The cyclic voltammograms of the FLINAK mixture prepared by dissolving NdF_3 (0.5 mol%) in the LiF-NaF-KF eutectic salt were measured in the range of 0 to -1.89 V at the scan rate (ν) of 0.1 V/s and at different scan rates ($\nu=0.02\sim 0.30$ V/s). The results are shown in Figure 3. Two cathodic peaks (P_{c1} and P_{c2}) are observed at near -1.15 and -1.35 V with the coupled anodic peaks (P_{a1} and P_{a2}) at around -0.55 and -0.20 V, and one uncoupled anodic peak (P_{a3}) is detected at around -0.10 V.

It is considered that according to cyclic voltammogram (Figure 3(a)) of Nd the first reduction peak (P_{c1}) at near -1.15 V corresponds to one electron transfer process as following equation (1) and the second reduction peak (P_{c2}) at around -1.35 V is resulting from the deposition of Nd(II) ions on the Mo cathode (equation (2)).

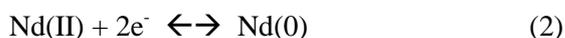
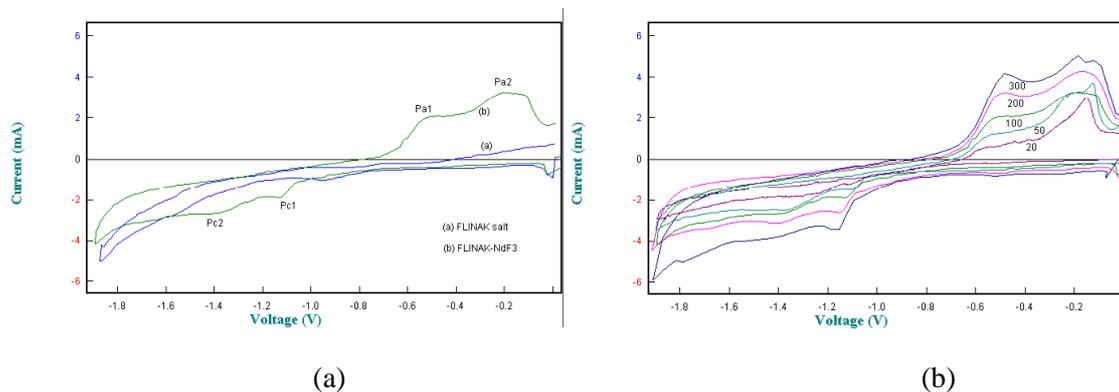


Figure 3. Cyclic voltammograms of the LiF-NaF-KF eutectic salt containing NdF_3 (0.5 mol%) measured in the potential range from 0 to -1.89 V (a) at $\nu=0.10$ V/s, (b) at different scan rates ($\nu=0.02\sim 0.30$ V/s). Initial scan direction: Cathodic

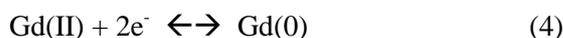


In order to examine the reversibility of the reaction (1), the CV measurements were performed in the range of 0 to -1.89 V at various potential scan rates ($\nu=0.02\sim 0.3$ V/s). The results are shown in Figure 3(b). As seen from Figure 3(b), the values of the peak potential differences ΔE_{c1} ($=E_{a1} - E_{c1}$) increase with an increase in the scan rate. Moreover, the cathodic peak currents (i_{c1}) vary linearly with $\nu^{1/2}$. These results suggest that the reaction (1) is diffusion controlled and not reversible.

Gadolinium fluoride in the FLINAK salt

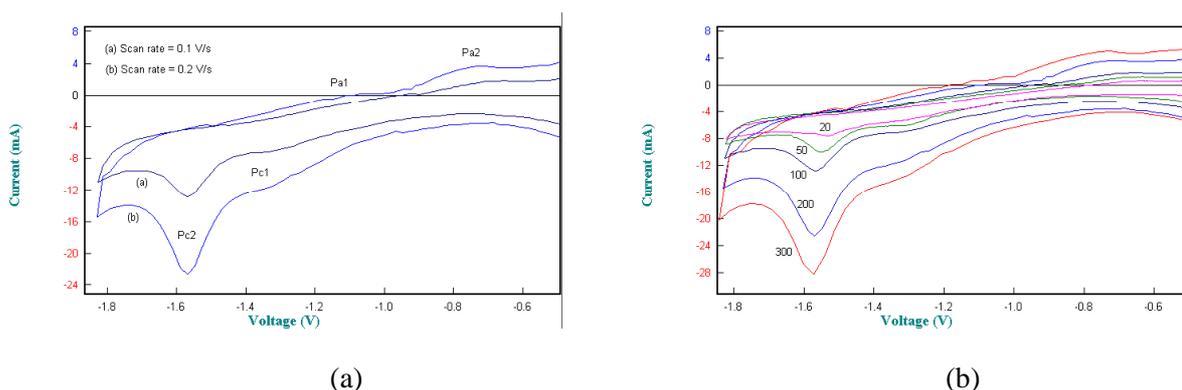
The cyclic voltammograms of the FLINAK mixture made by dissolving GdF_3 (0.5 mol%) in the LiF-NaF-KF eutectic salt were measured in the range of -0.5 to -1.82 V at the scan rate (ν) of 0.1 and 0.2 V/s and at different scan rates ($\nu=0.02\sim 0.30$ V/s). The results are shown in Figure 4. Two cathodic peaks (P_{c1} and P_{c2}) are observed at around -1.30 and -1.57 V with the coupled anodic peaks (P_{a1} and P_{a2}) at near -1.20 and -0.77 V.

Based on cyclic voltammograms (Figure 4(a)) of Gd it seems likely that the first reduction peak (P_{c1}) at near -1.30 V might be attributed to one electron transfer process as following equation (3) and the second distinct reduction peak (P_{c2}) at around -1.57 V corresponds to the deposition of Gd(II) ions on the Mo cathode (equation (4)).



In order to examine the reversibility of the reactions (3) and (4), the CV measurements were performed in the range from -0.5 to -1.82 V at various potential scan rates ($v=0.02\sim 0.3$ V/s). The results are shown in Figure 4(b). As seen from Figure 4(b), the electrochemical reduction-oxidation reactions of gadolinium ions in the FLINAK salt take place reversibly according to the fixed position of peak potentials (E_{c1} , E_{c2} , E_{a1} , E_{a2}) in spite of the variations of the potential scan rate. Plots of peak current vs. the square root of the scan rate were linear for the peaks. This means that the electrochemical reactions of gadolinium ions are diffusion-controlled processes.

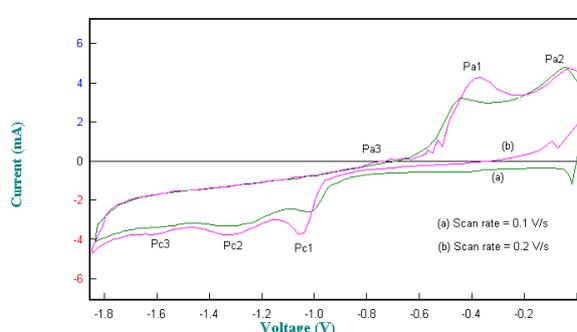
Figure 4. **Cyclic voltammograms of the LiF-NaF-KF eutectic salt containing GdF_3 (0.5 mol%) measured in the potential range from -0.5 to -1.82 V (a) at $v=0.10$ and 0.20 V/s, (b) at different scan rates ($v=0.02\sim 0.30$ V/s). Initial scan direction: Cathodic**



Neodymium and Gadolinium fluorides mixture in the FLINAK salt

The cyclic voltammograms of the FLINAK mixture by dissolving NdF_3 (0.5 mol%) and GdF_3 (0.5 mol%) in the LiF-NaF-KF eutectic salt were measured in the range of 0 to -1.83 V at the scan rate (v) of 0.1 and 0.2 V/s. As shown in Figure 5, three cathodic peaks (P_{c1} , P_{c2} and P_{c3}) are observed at around -1.02 , -1.30 and -1.60 V with the coupled anodic peaks (P_{a1} , P_{a2} and P_{a3}) at around -0.40 , -0.05 and -0.77 V. These cathodic and anodic peak couples were determined on the basis of above cyclic voltammetric behaviours obtained for the LiF-NaF-KF salt containing only NdF_3 and GdF_3 , respectively. It is considered that the cathodic peak (P_{c2}) and its coupled anodic peak (P_{a2}) might be formed due to the overlapped reduction-oxidation reactions of Nd and Gd ions. From these results (Figure 5) we could elucidate the redox behaviours of Nd and Gd mixture in the LiF-NaF-KF melt.

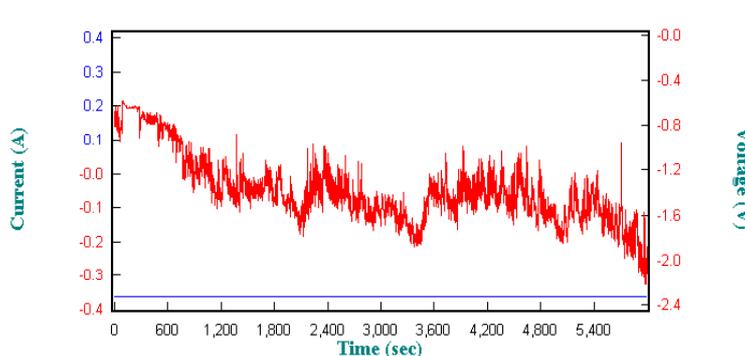
Figure 5. Cyclic voltammograms of the LiF-NaF-KF eutectic salt containing NdF₃ (0.5 mol%) and GdF₃ (0.5 mol%) measured in the potential range from 0 to -1.83 V (a) at v=0.10 and 0.20 V/s. Initial scan direction: Cathodic



Galvanostatic reductions of Gd and Nd ions using liquid Bi cathode

The electrolytic reduction tests of Gd and Nd ions were carried out using the liquid bismuth cathode at a fixed current density of 30mA/cm². Changes of potential and current vs. time were monitored during the galvanostatic electrolysis experiments. Also, cyclic voltammetric measurements were performed before and after each electrolytic reduction test in order to examine the changes of salt phase. A plot of potential and current vs. time for the electrochemical reduction of Gd ions is shown in Figure 6. From this plot of the potential change we can find a FLINAK salt decomposition potential value (-1.88 V) at the finishing time, which is agreed with the estimated from Figure 2 and the amounts of Nd and Gd ions added in the FLINAK salt phase.

Figure 6. Potential monitoring result during galvanostatic electrolysis of the LiF-NaF-KF eutectic salt containing GdF₃ (0.5 mol%) on the bismuth liquid cathode. Current density=30 mA/cm²



As the results of the galvanostatic electrolysis of the FLINAK mixture containing lanthanide (Nd and/or Gd) metal fluorides with the liquid bismuth cathode, it was confirmed that the salt phase could be prepared with the aid of cyclic voltammetric measurements before and after each galvanostatic reduction test. It is proposed that the cyclic voltammetry measurement can be used conveniently for in-situ detection of salt phase situation.

Conclusions

As a part of partitioning studies, the experiments of cyclic voltammetry and electrolytic reduction with the liquid Bi cathode were carried out to investigate fundamental electrochemical behaviours of lanthanide elements in the LiF-NaF-KF eutectic salt.

The cyclic voltammograms for the LiF-NaF-KF eutectic salt containing NdF₃, GdF₃ and their mixture were obtained at various potential scan rates, respectively. The electrochemical reductions of Nd and Gd show two-steps process, *i.e.* the reduction of trivalent ions (Nd(III) and Gd(III)) following to Nd(II) and Gd(II) ions which are reduced at further negative potentials to form metallic deposits.

The cyclic voltammograms for reduction-oxidation reactions of Nd ions in this system show that the values of the peak potential differences increase with an increase in the scan rate. These results suggest that the reaction of Nd is diffusion controlled and not reversible. However, it indicates that the reduction-oxidation reactions of Gd ions are reversible since the potential difference between the two peaks is approximately constant.

In addition, the galvanostatic reduction experiments of Nd and Gd ions were carried out on the liquid Bi cathode. It is proposed that the cyclic voltammetry technique can be conveniently applied to the in-situ detection of salt phase changes. The results obtained in this study would be useful for future studies and the separations of minor actinides from lanthanides by electrolysis in the LiF-NaF-KF eutectic salt system.

Acknowledgements

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REFERENCES

- [1] OECD/NEA (2000), *Pyrochemical Separations*, Proc. Workshop, Avignon, France, 14-16 March.
- [2] CEA (2000), *Assessment of Pyrochemical Processes for Separation/Transmutation Strategies-Proposed Areas of Research*, PG-DRRV/Dir/00-92. Edited by Reprocessing and Vitrification Research Department (DRRV), Fuel Cycle Division (DCC), CEA.
- [3] Y. Sakamura *et al.* (1998), *J. Nuclear Science Tech.*, 35, 49.
- [4] O. Shirai *et al.* (1998), *J. Alloys and Compounds*, 271-273, 685.
- [5] C. Pernel *et al.* (2001), *GLOBAL-2001*, Paris, France, 9-13 September.
- [6] F.R. Clayton, G. Mamantov and D.L. Manning (1974), *J. Electrochem. Soc.*, 121, 86.
- [7] M. Matsumiya, R. Takagi and R. Fujita (1998), *J. Nuclear Science Tech.*, 35, 137.
- [8] US DOE (1999), *A Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology*, A Report to Congress, DOE/RW-0519.
- [9] LANL (1996), *Accelerator-driven Transmutation of Waste (ATW)*, Proc. ATW meeting, 7-8 November.

- [10] H.S. Park and Y.S. Hwang (2001), *GLOBAL-2001*, Paris, France, 9-13 September.
- [11] M.V. Kormilitsyn *et al.* (2001), *GLOBAL-2001*, Paris, France, 9-13 September.
- [12] J.H. Yoo *et al.* (2001), *Development of High-level Radioactive Waste Treatment and Conversion Technologies*, Final Report, KAERI/RR-2127/2000.
- [13] M. Matsumiya *et al.* (1998), *J. Nuclear Science Tech.*, 35, 137.
- [14] Y. Sakamura *et al.* (1998), *J. Alloys and Compounds*, 271-273, 592.
- [15] R. Bermejo *et al.* (2001), *GLOBAL-2001*, Paris, France, 9-13 September.
- [16] J.B. Shim *et al.* (2001), *Actinides-2001*, Hayama, Japan, 4-9 November.
- [17] R.J. Gale and D.G. Lovering (1984), *Molten-salt Techniques*, Vol. 2, Plenum Press, New York, p.152.