



Real-time monitoring of metal ion concentration in LiCl–KCl melt using electrochemical techniques



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ABSTRACT

Cyclic voltammetry (CV) and chronoamperometry (CA) were employed to develop a real-time monitoring system for the pyrochemical process. These electrochemical techniques showed a good linearity of the current and the passed charges with the concentration of a solute even up to 9 wt.% in a LiCl–KCl melt, showing the potential for real application. To apply CA to the pyrochemical process, where the concentration of actinides and/or lanthanides is largely variable, the repeating chronoamperometry was designed and successfully tested at a wide range of Nd³⁺ ion concentration of up to 9 wt.%.

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1. Introduction

Spent nuclear fuel discharged in a nuclear power plant includes a significant amount of high-level wastes as well as a large amount of unreacted uranium [1–4]. Recently, the pyrochemical process has attracted much attention in that the electrochemical process recovers the unreacted uranium and reduces the volume of high-level wastes in spent nuclear fuel [2]. Since the uranium and transuranium (TRU) elements are recovered during the pyrochemical process, it is critical to accurately determine the material flow of actinides and fission products in an electrolyte of molten salt during the process operation [5,6]. Conventionally, destructive analysis techniques are performed for quantitative and qualitative analyses of uranium and transuranium elements, but they often require tedious chemical separation procedures and radiometric or spectrometric measurements [5,7,8]. In contrast, the direct determination of elements in the molten salt may present the real-time monitoring of nuclear materials and the meaningful information on the safeguards if the electrochemical process operates as declared.

Since a pyrochemical process system is mainly configured in an electrochemical environment, the electrochemical measurement method is one of the most potential tools to monitor the process, and thus several electrochemical techniques have been examined [7,9]. However, these approaches have been useful to measure the concentrations of solute ions in molten salt at up to ~4 wt.%. Therefore, the fact that the

concentration of uranium ions rises up to 9 wt.% during the pyrochemical process greatly demands the development of a new technique for the real-time monitoring of electrochemical reactions in molten salt [2]. In this work, we evaluated a few electrochemical techniques and optimized these techniques for the real-time monitoring during the pyrochemical process.

2. Experimental

Lithium chloride (LiCl)/potassium chloride (KCl) eutectic salts (anhydrous beads) and neodymium chloride (NdCl₃) were obtained from Aldrich Co. Ltd. (purity ≥ 99.99%). Silver chloride (AgCl) was purchased from Alfa Aesar (purity ≥ 99.998%). All chemicals were used as received.

The electrochemical reaction vessel was made from a quartz tube (350 mm in length, 20 mm in outer diameter, and 2 mm in wall thickness) using a glass blowing technique. A W wire electrode (0.1 mm diameter) was used as a working electrode. An Ag|Ag⁺ reference electrode was prepared by immersing the Ag wire into a LiCl–KCl eutectic melt containing 1.00 wt.% of AgCl. All potentials reported in this work will be with respect to the Ag|Ag⁺ reference electrode unless otherwise specified. Finally, the top of the reference electrode was sealed with Teflon tape to prevent evaporation of the molten salt at high temperatures.

The temperature of the molten salt was measured to 1 °C accuracy using a calibrated K type Chromel–Alumel thermocouple wire. Cyclic voltammograms were obtained using a Gamry Reference 3000 interfaced with a computer. All performance and sample preparations were carried

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out in a glove box with an argon atmosphere where both the oxygen and moisture levels were maintained at less than 1 ppm [10].

3. Results and discussion

Two electrochemical techniques, cyclic voltammetry and chronoamperometry, were employed to test the real-time electrochemical monitoring of a wide range of solute concentrations in LiCl–KCl melt. Fig. 1 shows cyclic voltammograms (CV) of NdCl₃ in LiCl–KCl melt. The reduction current associated with Nd electrodeposition begins to increase at -1.95 V vs. Ag|Ag⁺ and peaks at -2.1 V. On the returning sweep, the anodic current attributed to the Nd dissolution appears at -1.95 V and rises gradually as the potential is swept positively. The anodic peak

potential has a tendency to shift toward the positive direction as the NdCl₃ concentration increases in the melt, suggesting that the thicker deposit obtained in the high concentration needs more time to be dissolved. The CVs obtained with over 2 wt.% of NdCl₃ show a crossover feature ascribed to the acceleration of the electrodeposition on the Nd metal surface [11]. Fig. 1b shows the NdCl₃ concentration dependence on the anodic and cathodic peak currents of the CV in Fig. 1a. In an irreversible system, it is well known that the cathodic peak current is linearly dependent on the concentration of the reactants according to the Berzins–Delahay equation [12],

$$I_p = 0.61 \frac{(nF)^{3/2}}{\sqrt{RT}} CS\sqrt{vD}$$

where I_p is the peak current, v is the scan rate, n is the number of electron in the reaction, F is the Faraday constant, R is the gas constant, T is the temperature, C is the ion concentration, S is the electrode area, and D is the diffusion coefficient of the ions. The linear relationship between the peak current and the concentration in Fig. 1b allows for the determination of the diffusion coefficient of Nd³⁺ ions, which was estimated to be 2.05×10^{-5} cm²/s at 723 K. This value is comparable with the value in the literature of 1.1×10^{-5} cm²/s at 723 K [13]. However, it should be noted that the anodic peak current is not always reproducible because the dissolution reaction rate of the electrodeposit is greatly dependent on the structure of the electrodeposit, the condition of the interface between the electrode and the solution, etc.

It is also possible to compute the quantity of Nd³⁺ ions electrodeposited or oxidized by integrating the current in the CV. Fig. 1c shows the charges passed during the anodic (or cathodic) scan when varying the Nd³⁺ concentrations. Here, the cathodic and anodic charges are almost equal to each other, indicating that the cathodic scan reduced most of the Nd³⁺ onto the electrode, whereas the anodic scan then dissolved most of the Nd⁰ deposit in the melt. Notably, a good linearity between passed charges and Nd³⁺ concentration up to 9 wt.% of NdCl₃ in Fig. 1c emphasizes that this electrochemical approach has potential for the real-time monitoring of nuclear elements during the pyrochemical process.

Fig. 2a shows the chronoamperometry (CA) results obtained at various potentials in LiCl–KCl melt containing 2.0 wt.% of NdCl₃. Immediately after the potential was applied, the current abruptly increased owing to a very quick charging at the electrode, and then gradually decreased. Fig. 2b displays the variation in the steady state current with the applied potential. While the steady current was maintained constant at ~ 0 A until the potential approached -2 V, the current enhanced negatively at a potential more negative than -2.0 V and peaked at -2.1 V. Interestingly, the CVs in Fig. 1a showed very similar current maxima at -2.1 V during a negative scan.

Fig. 2c shows CA results obtained at -2.1 V in LiCl–KCl melt containing various concentrations of NdCl₃. The steady state current beyond the spike is attributed to the Faradaic electrodeposition reaction of Nd³⁺, where the current increased as the concentration of NdCl₃ increased. In addition, the melts containing more than 4 wt.% of NdCl₃ show a gradual current increase after a short period (1–5 s) that decreases with the concentration (Fig. 2c), suggesting that such current increase may result from the acceleration of Nd electrodeposition on electrodeposited Nd surface or the increment of the surface area by Nd electrodeposition. Therefore, the current obtained at 0.9 s linearly increases with the NdCl₃ concentration up to 9 wt.%, whereas the value at 10 s increases in a non-linear manner beyond a 4 wt.% concentration (Fig. 2d).

The results presented here indicate that the CV and CA are very suitable to apply to the real-time monitoring of actinide and lanthanide ions in the molten salt. However, in order to use these techniques for real-time monitoring in the pyrochemical process, the following are required. First, an electrochemical real-time monitoring system should give exact information on the concentration of elements in the process.

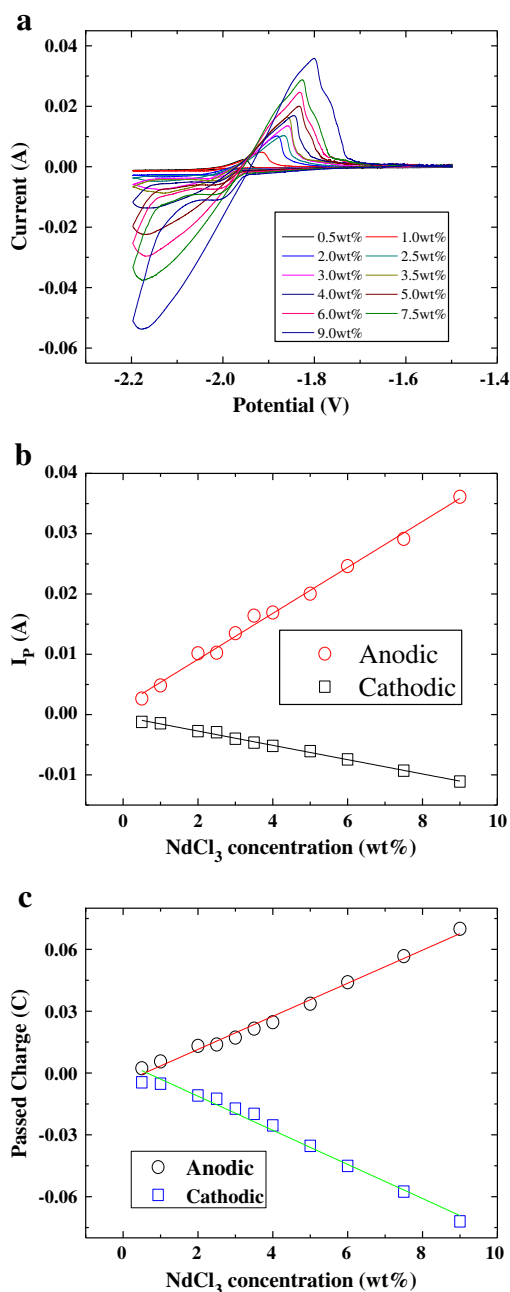


Fig. 1. Cyclic voltammograms (a) obtained in LiCl–KCl melt with various concentrations of NdCl₃ at 450 °C; working electrode: W wire, scan rate: 200 mV/s. (b) Concentration dependence of peak currents in Fig. 1a. (c) Concentration dependence of passed charges in Fig. 1a.

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