

Electrochemical Investigation of Exchange Current Density of Uranium and Rare-earths Couples (M^{3+}/M^0) in LiCl-KCl Eutectic Electrolyte

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The objective of this work is to use electrochemical techniques to quantify the electrode reaction rate of some rare-earth elements and uranium in a LiCl-KCl eutectic electrolyte at 500°C. The exchange current densities of the oxidation-reduction couples of M^{3+}/M^0 (La^{3+}/La^0 , Ce^{3+}/Ce^0 , Pr^{3+}/Pr^0 , Nd^{3+}/Nd^0 , Gd^{3+}/Gd^0 , Y^{3+}/Y^0 , U^{3+}/U^0) on a tungsten electrode were measured by applying a linear polarization resistance technique. A region of linear dependence of potential on applied current could be found to describe the reaction rate of oxidation-reduction system. From these measurements, the estimated exchange current density was 0.38 mA/cm² for uranium, and was within the range of 0.27 to 0.38 mA/cm² for rare-earth elements.

Keywords: Linear polarization resistance technique, Exchange current density, Uranium, Rare-earths, LiCl-KCl.

1. INTRODUCTION

A pyrometallurgical process based on molten-salt electrochemical separation is now considered as one of the most promising options in an innovative nuclear fuel cycle [1, 2, 3, 4]. Electrorefining and electrowinning steps are configured as the key processes in which the actinides are separated from the bulk of the fission products in a molten-salt electrolyte by electrotransport [5, 6]. Despite extensive electrochemical researches conducted in this area, the basic electrochemical kinetic properties of the redox couple have not been thoroughly investigated. For this reason, the assessment of electrochemical kinetic data of actinides as well as those of rare-earths is of high importance.

The properties of the electrode reaction rate of uranium and fission products in molten-salt media are essential to be understood to optimize the separation process. This information may be necessary to model and design the future electrorefining or electrowinning systems [7, 8].

Polarization measurements are an important research tool in investigations of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and kinetics of electrode reaction in an oxidation-reduction system [9, 10].

A few attempts to relate electrochemical properties of an electrode reaction rate have been described in the literature [11, 12]. They showed that the slope of the linear portion of the polarization curve of U^{3+}/U^0 and Ce^{3+}/Ce^0 can be related to its electrode reaction rate. This approach has some foundation in theory and may have a rather wide applicability to many systems. Measurements of current-potential relations under carefully controlled conditions can yield information on the electrode reaction rates.

We report here the exchange current densities for the M^{3+}/M^0 (La^{3+}/La^0 , Ce^{3+}/Ce^0 , Pr^{3+}/Pr^0 , Nd^{3+}/Nd^0 , Gd^{3+}/Gd^0 , Y^{3+}/Y^0 and U^{3+}/U^0) on a tungsten electrode in a LiCl-KCl eutectic electrolyte at 500°C.

2. DERIVATION OF THE POLARIZATION RESISTANCE

The following Butler-Volmer equation is a generalized relationship between the applied electrochemical current density (i) and potential (η) for electrode reactions [9, 10]. The applicability of this simple relationship relies on the presence of a single charge-transfer-controlled electrode reaction.

$$i = -i_0 \left[\exp \left\{ -\frac{nF\alpha}{RT} \eta \right\} - \exp \left\{ \frac{nF(1-\alpha)}{RT} \eta \right\} \right] \quad (1)$$

Here, the exchange current density (i_0) may be calculated from the polarization resistance (R_{CT}), as derived below, where R is the ideal gas constant, T is the temperature, F is the Faraday constant, and α is the cathodic multi-step electron transfer coefficients, for the reduction-oxidation process. An extreme condition in the above equation can be obtained at $\Delta\eta < 10$ mV for a very small overpotential. The following relationship is clear at the low current region using the linear term of the Taylor expansion approximation (for small x , $\exp(x) \approx 1 + x + x^2/2! + x^3/3! + \dots$).

$$i = i_0 \left[1 - \frac{nF\alpha}{RT} \eta + \dots - 1 + \frac{nF(1-\alpha)}{RT} \eta + \dots \right] \quad (2)$$

$$\approx i_0 \frac{nF}{RT} \eta = \frac{1}{R_{CT}} \eta$$

In this region, the curve of $\Delta\eta/\Delta i$ is almost linear. This relationship is clear at the low current regions of the relationship between the applied potential and the current density for electrode reactions. Accordingly at low values of polarization, the dependence of the current on the polarization is usually linear (not logarithmic). This linear region is called polarization resistance due to its formal similarity to Ohm's law:

$$R_{CT} = \frac{RT}{i_0 nF} = \frac{\Delta\eta}{\Delta i} \quad (3)$$

The polarization resistance is an effective resistance imposed at the electrode surface by the finite rate of the electron-transfer process.

3. EXPERIMENTAL

LiCl-KCl mixed salts of eutectic composition (>99.99% certified purity, anhydrous beads) and rare-earth (RE) chlorides (RECl_3 , >99.99 %) were used as purchased from Sigma-Aldrich chemical Co. LLC. In addition, a stock solution of UCl_3 was prepared by the stoichiometric addition of CdCl_2 to the LiCl-KCl eutectic salts containing depleted uranium.

Electrolytic cells were made from quartz glass tubes which have 12.5 mm inner diameter (15 mm OD) as shown in Figure 1.

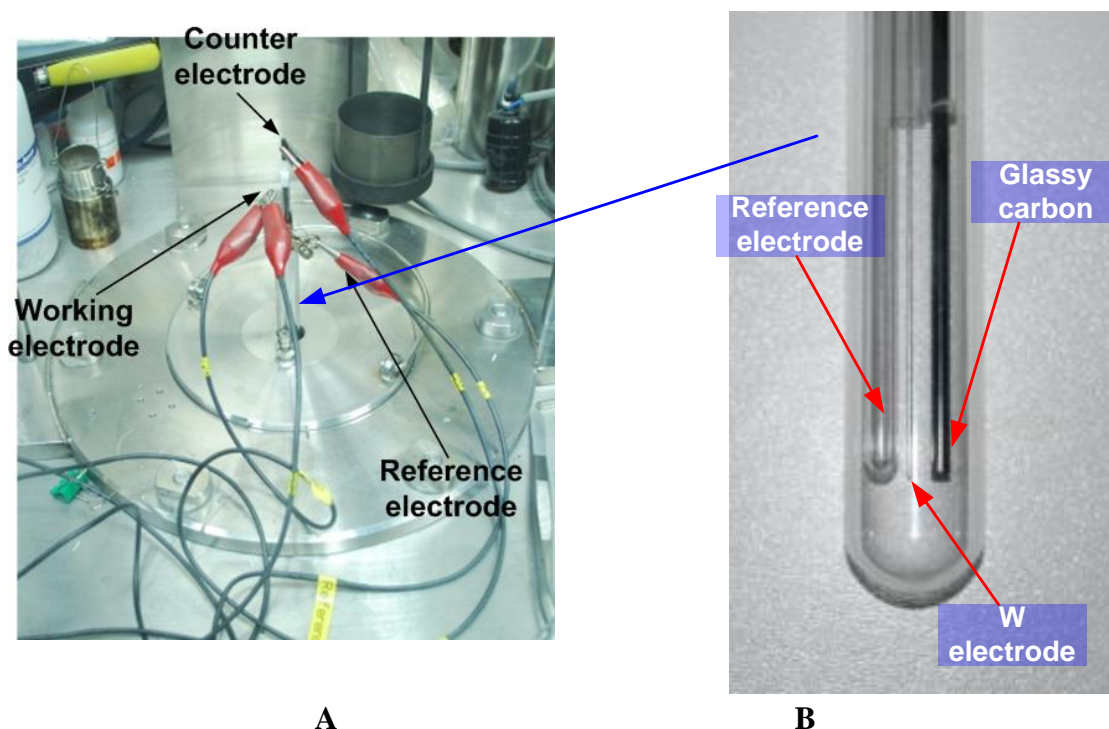


Figure 1. Experimental setup (A) and electrochemical quartz cell (B) in the glove box.

The cells were charged with about 7 g of LiCl-KCl eutectic salt containing 2 wt% RECl_3 or UCl_3 in each experiment. A 3 mm diameter glassy carbon rod (Alfa Aesar, USA) served as a counter electrode and an Ag/AgCl couple was used as a reference electrode. The Ag/AgCl electrode consisted of a Pyrex tube with a very thin bottom in which the LiCl-KCl eutectic mixture containing 1 mol% AgCl was placed and an Ag wire (dia. = 1 mm, Nilaco Co., Japan) was immersed in the salt. The working electrode was a tungsten wire (dia. = 0.8 mm, dipping height = 2.7 cm, apparent surface area = 0.68 cm^2 , Nilaco Co., Japan).

All electrochemical experiments were carried out in an argon atmosphere glove box with $\text{H}_2\text{O} < 1 \text{ ppm}$ and $\text{O}_2 < 3 \text{ ppm}$ as shown in Figure 2. The temperature of the molten salt was measured with $\pm 1.0 \text{ }^\circ\text{C}$ accuracy using a calibrated Type K (chromel–alumel) thermocouple.

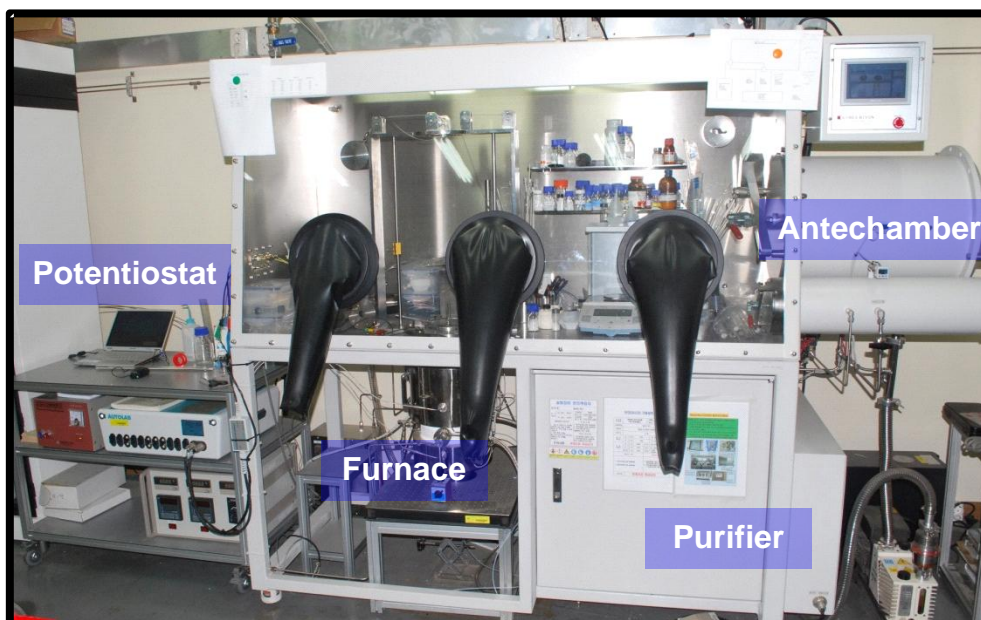


Figure 2. Argon atmosphere glove box for experimental setup.

Electrochemical polarization measurements were conducted potentiodynamically using a potentiostat/galvanostat (Autolab PGSTAT-302N) driven by the operation and application software program (NOVA 1.8).

4. RESULTS AND DISCUSSION

The linear polarization resistance technique, or simply polarization resistance, is a well-established method for determining the corrosion rate by using electrolytic test cells, described in ASTM G59 [13]. This technique involves measuring the change in the open circuit potential of the electrolytic cell when an external current is applied to it. For a small perturbation about the open-circuit potential, there is a linear relationship between the change in applied current per unit area of electrode (Δi) and the change in the measured voltage (ΔE). The ratio $\Delta E/\Delta i$ gives the polarization resistance term. The electrode reaction rate, expressed as the current density, is inversely related to the polarization resistance.

The polarization resistance can be determined from the ratio of the overpotential (η) to the applied current density (i_{App}) and the exchange current density i_0 is obtained from the following formula:

$$i_0 = \frac{RT}{F\eta} i_{App} \quad (4)$$

In this study, the working electrode was placed in the electrochemical cell and allowed to be formed with electroactive metal on the electrode surface using a linear sweep voltammetry 0 to -1.5 V (vs. 1 mol% Ag/AgCl) several times at a scan rate of 50 mV/s. This step is to make a coating of the electroactive metal on the surface of working electrode. Then, the working electrode is exposed to the

LiCl-KCl electrolyte solution containing an electroactive species for 1 hour before beginning a polarization resistance experiment. The open circuit potential (OCP) was measured and a potential variation of -15mV to $+15\text{mV}$ over OCP applied at a scan rate of 0.125mV/sec , while the corresponding changes in current were recorded. This condition is to make an OCP approximately corresponding to the formal potential of a redox couple of M^{3+}/M^0 and their concentration ratio. Consider the one-step reaction $M^3 + 3n e^- = M^0$, where M^3 is reduced to M^0 in a 3-electron reaction with formal potential E^0 :

$$E(\text{OCP}) = E^0 + \frac{RT}{3F} \ln \left(\frac{[M^{3+}]}{[M^0]} \right) \quad (5)$$

Figure 3 shows the linear polarization curves for M^{3+}/M^0 ($\text{La}^{3+}/\text{La}^0$, $\text{Ce}^{3+}/\text{Ce}^0$, $\text{Pr}^{3+}/\text{Pr}^0$, $\text{Nd}^{3+}/\text{Nd}^0$, $\text{Gd}^{3+}/\text{Gd}^0$, Y^{3+}/Y^0 and U^{3+}/U^0) on a tungsten electrode in a LiCl-KCl eutectic electrolyte at 500°C . Among them, the OCP of uranium couple (U^{3+}/U^0) is much nobler than those of rare-earth couples. It can be seen that the OCP of rare-earth couples are close to each other and ranged from -2.1 to -2.0 V(vs. 1 mol% Ag/AgCl).

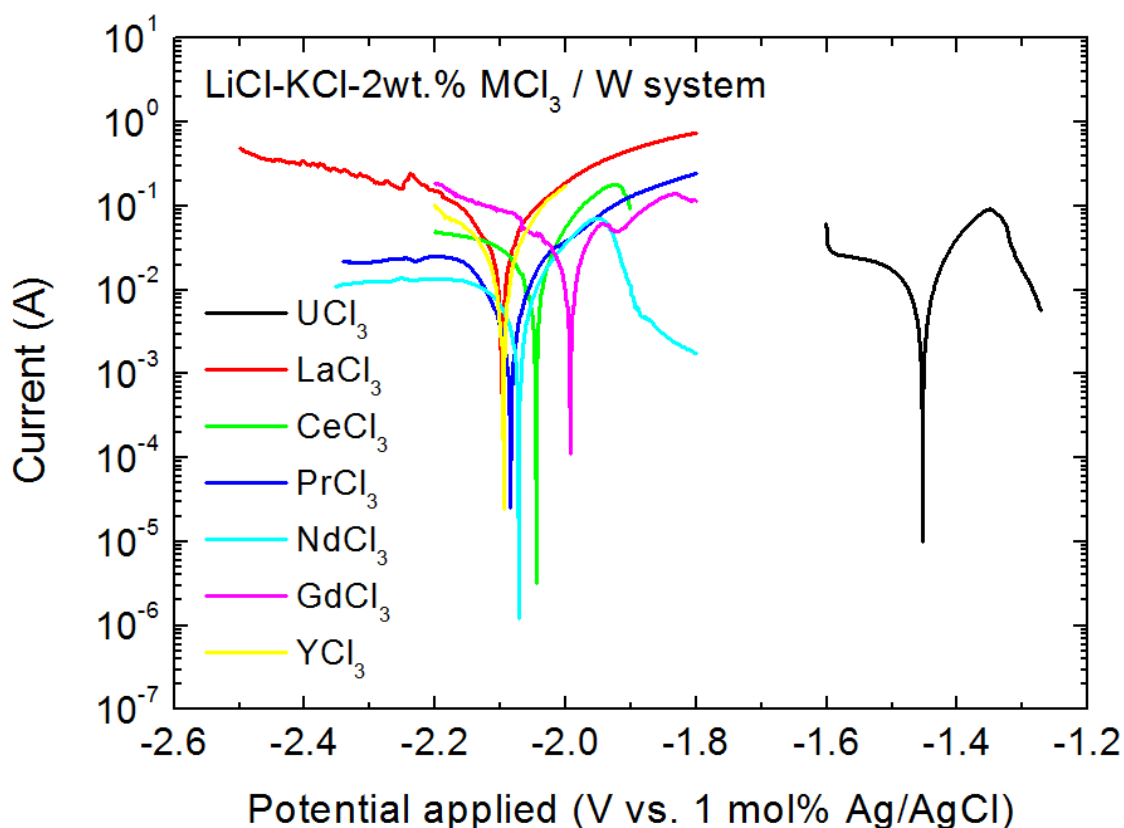


Figure 3. Linear polarization scans for couples of U^{3+}/U^0 , $\text{La}^{3+}/\text{La}^0$, $\text{Ce}^{3+}/\text{Ce}^0$, $\text{Pr}^{3+}/\text{Pr}^0$, $\text{Nd}^{3+}/\text{Nd}^0$, $\text{Gd}^{3+}/\text{Gd}^0$ and Y^{3+}/Y^0 in LiCl-KCl eutectic at 500°C (scan rate: 2 mV/s , concentration: $2\text{ wt.}\%$ MCl_3).

The linear polarization measurement of the U^{3+}/U^0 couple was conducted by applying a potential range over OCP at the electrode. The potentials were scanned from -1.6 to -1.3 V(vs. 1 mol%

Ag/AgCl) as shown in Figure 4. A 2.5 mV potential step and a slow rate of 2 mV/s were used. From this graph, we can see the both changes of cathodic and anodic current with potential are similar.

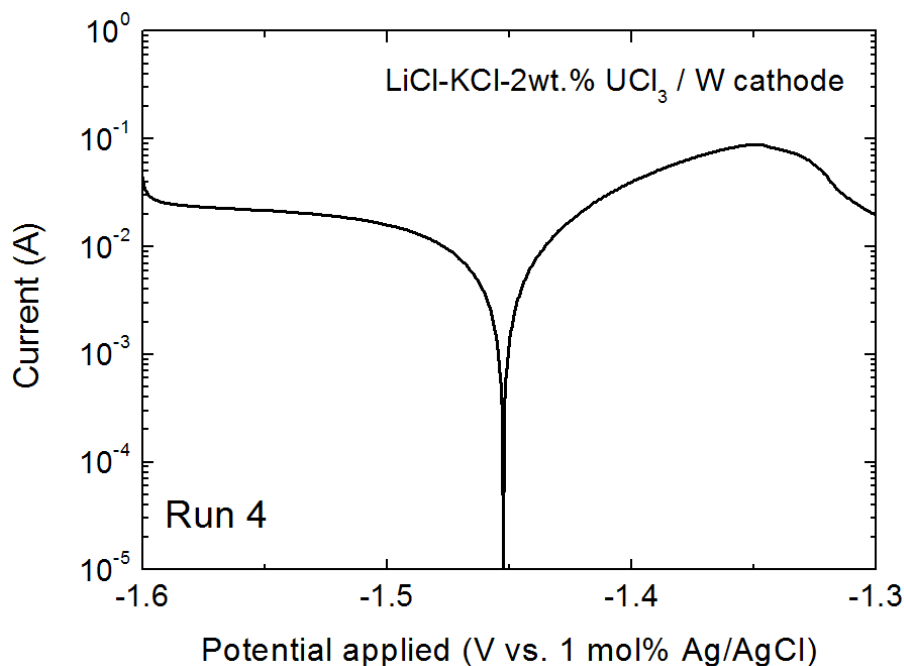


Figure 4. Linear polarization scan for U^{3+}/U^0 couple in LiCl-KCl eutectic at 500°C (scan rate: 2 mV/s, concentration: 2 wt.% UCl_3).

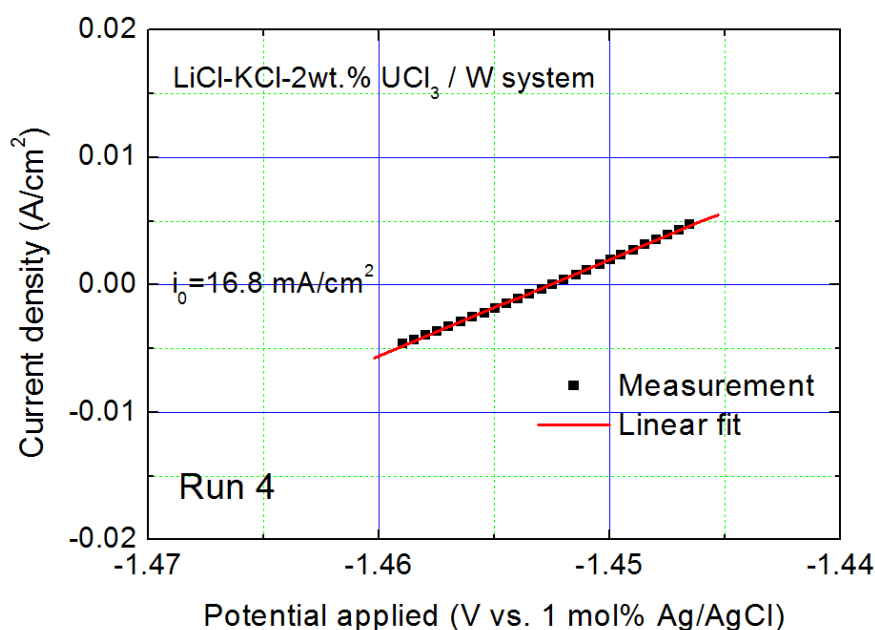


Figure 5. Linear regression plot of current density versus potential in the region near zero current for U^{3+}/U^0 couple in LiCl-KCl eutectic.

Figure 5 shows a typical estimation of exchange current density of the U^{3+}/U^0 couple at a tungsten electrode with a linear regression fit. The slope of the curves over OCP can be calculated by

performing a linear regression on data from -1.457 to -1.447 V (i.e., 5 mV cathodic and 5 mV anodic relative to OCP). In this measurement run, a calculated value of exchange current density was estimated to be 16.8 mA/cm². To estimate the exchange current density, the surface area of the working electrode was assumed from the diameter and immersion depth of the bare tungsten wire in the electrolyte region.

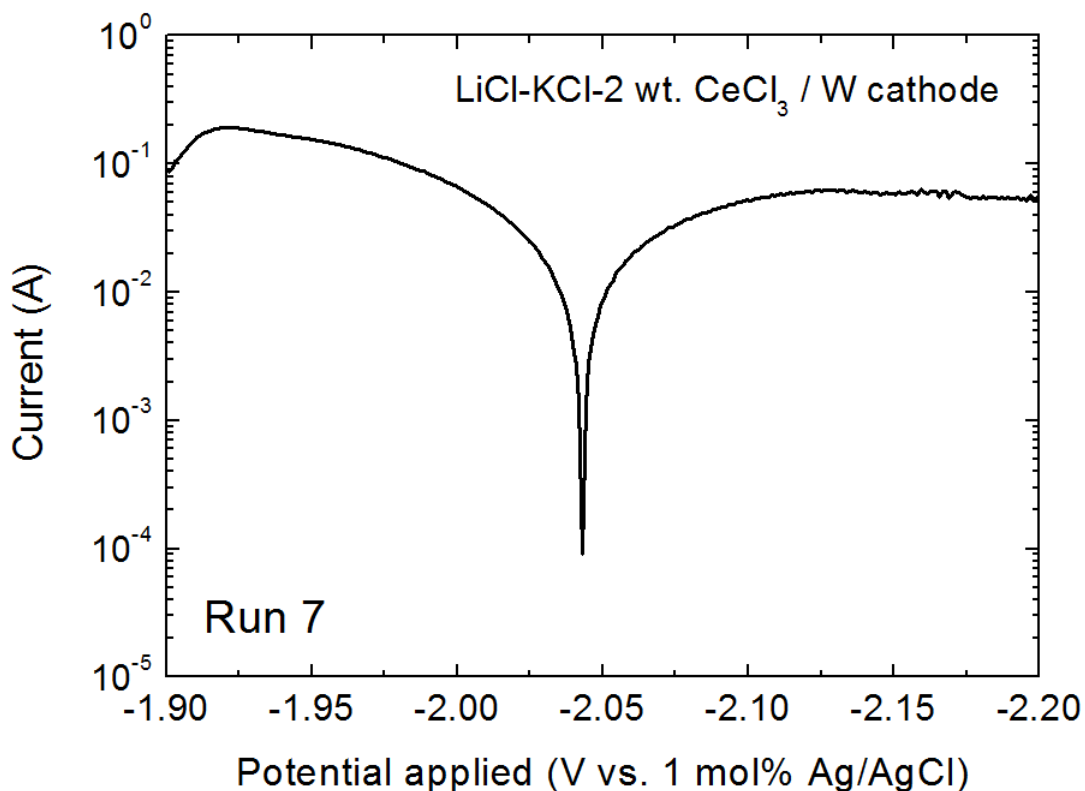


Figure 6. Linear polarization scan for Ce³⁺/Ce⁰ couple in LiCl-KCl eutectic at 500°C (scan rate: 2 mV/s, concentration: 2 wt.% CeCl₃).

The linear polarization measurement of the Ce³⁺/Ce⁰ couple was also performed by applying a potential over range of the OCP region as scanned from -1.9 to -2.2 V(vs. 1 mol% Ag/AgCl) (Figure 6). The slope of the curves over the linear range near the OCP can be calculated by performing a linear regression on data from -2.054 to -2.034 V. This regression slope gives a value of 41 mA/cm² as the exchange current density as fitted in Figure 7.

Each potentiodynamic scan was repeated 10 times for each M³⁺/M⁰ couple at a scan rate of 0.05 V/s. The results of the linear regression and their standard deviations are shown in Table 1. While the exchange current densities should be constant for each measurement run, it changed with the electrode surface conditions, possibly due to the surface area variation during the polarization measurement. The polarization resistance and exchange current density are estimated from the slope and found to be in this table.

The exchange current density of uranium in LiCl-KCl has been estimated by Choi [12] and found to be in the region of 20 to 60 mA/cm² for a melt of 3.27 wt % UCl₃ at 773 K. The estimates of the present study with uranium show slightly lower than that in the literature. On the other hand,

Marsden's estimates for cerium [13] showed these values to be in the region of 40 to 100 mA/cm² for 2.88×10⁻⁴ mol/cm³ CeCl₃ at 500°C.

Table 1. Estimated exchange current densities of M³⁺/M⁰ couples from the linear polarization curves.

U ³⁺ /U ⁰ (average exchange current density: 17.8 mA/cm ²)										
Run no.	1	2	3	4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	15.4	16.4	16.4	16.8	16.8	17.6	18.3	20.7	19.4	19.8
Standard deviation of the linear regression	7.42E-05	8.35E-05	7.26E-05	7.88E-05	7.90E-05	7.40E-05	1.07E-04	4.66E-05	5.43E-05	5.74E-05
Ce ³⁺ /Ce ⁰ (average exchange current density: 37.1 mA/cm ²)										
Run no.	1	2	3	4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	36	34	33	34	34	41	41	39	39	40
Standard deviation of the linear regression	4.23E-04	5.07E-04	5.21E-04	4.45E-04	4.58E-04	5.05E-04	4.07E-04	4.61E-04	4.97E-04	4.17E-04
La ³⁺ /La ⁰ (average exchange current density: 52.4 mA/cm ²)										
Run no.	1	2	3	4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	101	34	60	68	76	49	32	27	38	39
Standard deviation	9.27E-04	3.84E-03	5.71E-04	9.88E-04	8.80E-04	2.66E-04	4.36E-04	4.26E-04	4.09E-04	5.66E-04
Pr ³⁺ /Pr ⁰ (average exchange current density: 7.8 mA/cm ²)										
Run no.	1	2	3	4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	7.7	7.7	7.6	7.7	8.7	7.7	7.3	8.5	7.4	7.3
Standard deviation	1.48E-04	6.27E-05	1.35E-04	3.87E-05	8.66E-05	8.67E-05	5.98E-05	6.35E-05	3.43E-05	5.87E-05

The estimates of the present study with cerium also appear to be slightly lower than those in this literature. Compared to the Rockwell International's report for the experiments with Cd cathode

[14], these estimates show that the results were slightly in excess for La and Y.

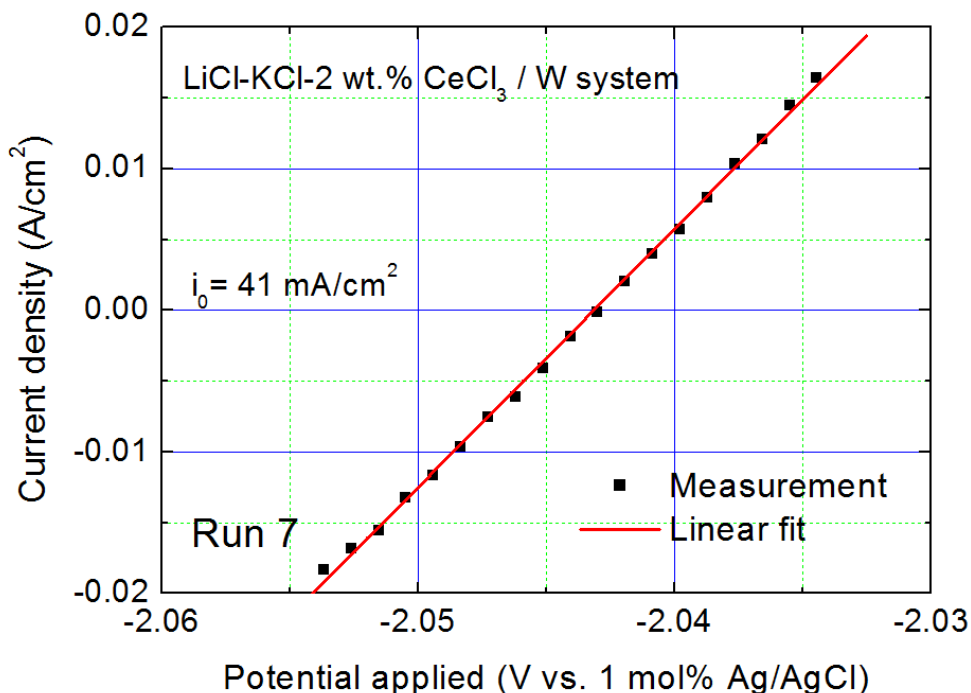


Figure 7. Linear regression plot of current density versus potential in the region near zero current for Ce³⁺/Ce⁰ couple in LiCl-KCl eutectic.

Table 1. Estimated exchange current densities of M³⁺/M⁰ couples from the linear polarization curves (continued).

Nd ³⁺ /Nd ⁰ (average exchange current density: 111.1 mA/cm ²)										
Run no.	1	2	3	4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	110	114	114	112	112	112	110	107	111	109
Standard deviation	6.65E-04	1.46E-03	1.59E-03	1.11E-03	1.27E-03	9.27E-04	8.35E-04	4.94E-04	1.35E-03	1.56E-03
Gd ³⁺ /Gd ⁰ (average exchange current density: 42.8 mA/cm ²)										
Run no.	1	2		4	5	6	7	8	9	10
Exchange current density (mA/cm ²)	45.1	46.3	39.3	40.4	43.2	36.9	41.8	41.6	41.6	51.7
Standard deviation	6.09E-04	3.25E-04	4.76E-04	4.92E-04	4.29E-04	2.97E-04	5.38E-04	6.07E-04	6.07E-04	3.72E-03
Y ³⁺ /Y ⁰ (average exchange current density: 45.2 mA/cm ²)										
Run no.	1	2		4	5	6	7	8	9	10

Exchange current density (mA/cm ²)	55.3	46.2	47.2	47.8	46.7	32.6	42.7	43.2	43.9	45.9
Standard deviation	2.65E-04	5.36E-04	5.39E-04	4.55E-04	3.33E-04	1.16E-03	4.56E-04	7.01E-04	5.40E-04	8.61E-04

However these results are much lower than the values of exchange current densities published for some transition elements [15-17]. These differences are interpreted as due to the different measurement approaches and techniques applied in the literature.

4. CONCLUSIONS

The kinetic constant, the exchange current density, is a fundamental electrochemical property that can be obtained from the linear slope of the current-overpotential polarization plots. Through the potentiodynamic polarization technique, it provided a reasonable, rapid method for quantitatively predicting the electrode reaction kinetics in the molten-salt system.

The exchange current density of some rare-earth elements and uranium were quantified by applying a linear polarization resistance technique in a LiCl-KCl eutectic mixture at 500°C. In all cases, the current-overpotential plots for assuming one-step reaction couples (M^{3+}/M^0) were found to be linear behaviors over a near OCP range, indicating a simple electron transfer reaction. From these measurements, the estimated exchange current density was about 0.38 mA/cm² for uranium and ranged within 0.27 to 0.38 mA/cm² for rare-earth elements.

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