# Effect of Electrode Materials on the Exchange Current Density Using Tafel Measurement

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## 1. Introduction

For the optimization of pyroprocessing, the electrochemical data, especially the exchange current density of lanthanides and actinides are of importance. However, the knowledge of the exchange current density in high temperature eutectic is rare, and there are controversial opinions and estimates about the effect of various electrode materials on the exchange current density [1]. In this study, the effect of different electrode materials such as tungsten, glassy carbon, nickel, and platinum on the exchange current density was investigated using Tafel measurement.

## 2. Experimentals

*2.1 Chemicals*

For the Tafel measurements, $CeCl_3$ and $SmCl_3$ were melted in anhydrous LiCl-KCl eutectic salt at 500°C. The concentration of $CeCl_3$ varied in the range of 1.0wt%, and the concentration of $SmCl_3$ was prepared to be 5.0wt%. For each electrode, three samples were prepared to examine the reproducibility of exchange current densities.

*2.2 Apparatus*

$CeCl_3$ and $SmCl_3$ were contained in the LiCl-KCl eutectic salt in a 40 mm diameter quartz cell. A cap with 6 holes was closed at the top of cell for stable positioning of electrodes.

Tungsten rod (Nilaco, 1.0 mm in diameter, 99.95% purity) was used as a counter electrode and an Ag/AgCl electrode (Alfa Aesar 99.99%, 1.0 mm diameter Ag wire in 1wt% AgCl-LiCl-KCl) was used as a reference electrode encased in a thin-end pyrex glass tube. For the measurements of exchange current densities using different electrode materials, tungsten ($\emptyset = 1.0$ mm), glassy carbon ($\emptyset = 2.0$ mm), nickel ($\emptyset = 1.0$ mm), and platinum ($\emptyset = 1.0$ mm, molded onto the tungsten rod) were used as the target working electrodes.

Experiments were performed in a glove box under high-purity argon gas condition (99.999% Ar, $H_2O$ and $O_2 < 10$ ppm). The temperature was maintained at 500 ± 10°C in the furnace placed at the bottom of glove box.

## 3. Results and Discussion

*3.1 Tafel measurement*

The exchange current density of $CeCl_3$ was determined using Tafel equation (Eq. 1), a simplified Butler-Volmer equation. Fig. 1 shows the Tafel plot of $CeCl_3$ in LiCl-KCl molten salt at 500°C measured in the potential range of –2.10 V to -1.95 V, including the equilibrium potential of -2.00 V. The Tafel measurement was first initiated after the deposition of Ce metals on the electrode by applying the overpotential of -0.15 V for 5 sec with a scan rate of 20 mV/s. By fitting the linear Tafel slope to the zero-overpotential, as presented in Fig. 1, the exchange current densities were obtained.

$$\ln(-j) = \ln(j_0) - \frac{\alpha_c n F \eta}{RT} \qquad (1)$$

where j is the exchange current, $j_0$ is the exchange current density, $\alpha_c$ is the cathodic charge transfer coefficient, η is the overpotential, F is the Faraday constant, R is the gas constant, and T is the absolute temperature.

Using the tungsten working electrode, the exchange current density of Ce was determined to be 17.61±0.20 $mA/cm^2$, which is in good agreement with other literature data studied by K.C. Marsden and B. Pesic [2] by considering the concentration dependency of the exchange current density.

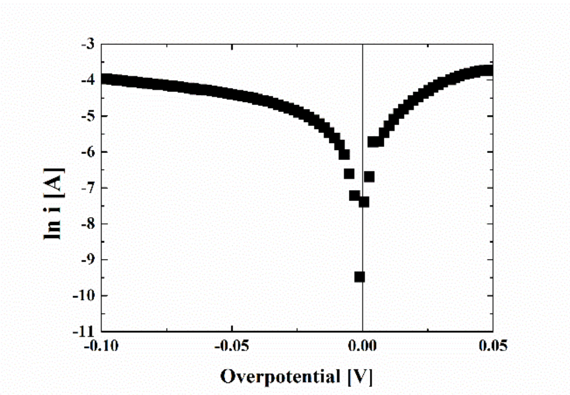


Fig. 1. Tafel plot of $CeCl_3$ with tungsten electrode in LiCl-KCl eutectic salt at 500°C.

*3.2 Effect of different working electrodes on the exchange current density*

As shown in Fig. 2, the exchange current densities of Ce(III)/Ce(0) and Sm(III)/Sm(II) were obtained with different electrode materials of tungsten, glassy carbon, nickel, and platinum. The difference in the exchange current density of $CeCl_3$ was marginal within the uncertainty level, whereas $SmCl_3$ showed a remarkable difference in the exchange current density, depending on the electrode materials. The possible reason was that the working electrode is coated by deposition on its surface with Ce metals. Therefore, it was concluded that there are only interactions between the Ce(0) coated working electrode (W, GC, Ni, and Pt) and the Ce(III) ions. This was confirmed by the soluble/soluble reaction of Sm(III)/Sm(II), which is not subject to the deposition process.

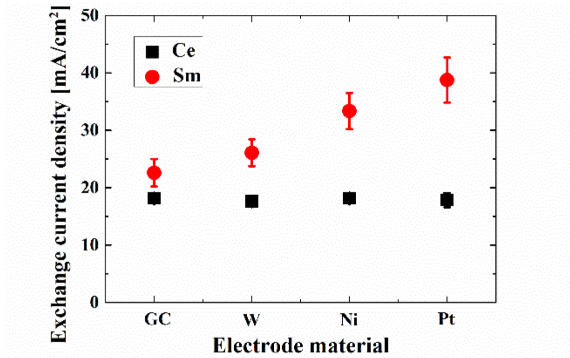


Fig. 2. The exchange current density of $CeCl_3$ and $SmCl_3$ with various electrode materials.

## 4. Conclusion

We investigated the effect of different electrode materials on the exchange current density by the soluble/insoluble reaction of Ce(III)/Ce(0) and the soluble/soluble reaction of Sm(III)/Sm(II). The former is probably associated with the deposition of target elements on the electrode surface by applying negative overpotential before the Tafel measurement for the Ln(III)/Ln(0) reactions.

## REFERENCES


[1] I. Choi, B.E. Serrano, S.X. Li, S. Herrmann, S. Phongikaroon, “Determination of exchange current density of $U^{3+}$/U couple in LiCl-KCl eutectic mixture”, Proceedings of Global 2009, Paris, France (2009).

[2] K.C. Marsden, B. Pesic, “Evaluation of the electrochemical behavior of $CeCl_3$ in molten LiCl-KCl eutectic utilizing metallic Ce as an anode”, J. Electrochem. Soc. 158, F111 (2011).