

Cyclic Voltammograms for LiCl-KCl Solution Containing CeCl₃

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1. Introduction

Liquid cadmium in a pyrochemical process has been known as an electrode to form intermetallic compounds by the reaction with transuranium (TRU) or rare earth (RE) elements [1, 2]. Because of this reaction, the redox potentials of TRU or RE elements could be changed between a solid electrode and a liquid Cd electrode [3]. The redox potentials of the above elements on the solid cathode were relatively easily obtained but little information on the redox potentials was available on the Cd electrode. Cyclic voltammogram help identify how many kinds of reaction compounds could be formed between some elements and liquid electrodes such as Cd and Bi. In this study, the electrode reactions of Ce in LiCl-KCl-CeCl₃ solution were investigated and compared on the solid W and the liquid Cd electrode. From these results, the difference between the reduction potentials of Ce was obtained between these two electrodes.

2. Methods and Results

2.1 Experimental procedures

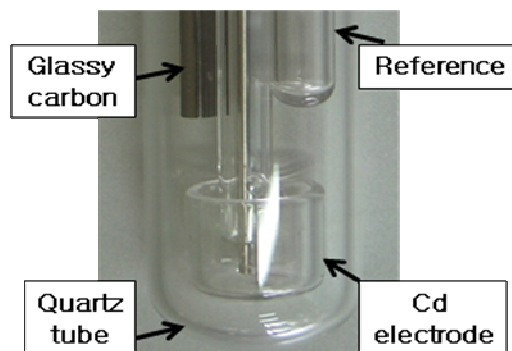


Fig. 1 Electrochemical cell

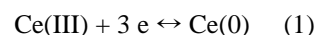
All the experiments were conducted at 773 K under a purified Ar atmosphere less than 10 ppm of oxygen and 10 ppm of water. The electrochemical cell used for the voltammetric studies is shown in Fig. 1. Two kinds of cathodes were used, that is, one is solid W wire of 1 mm in diameter and the other is a liquid Cd cathode, where W wire of 1 mm in diameter was used as a lead wire of Cd cathode. A glassy carbon of 3 mm in diameter was used as a counter electrode. A silver-silver chloride (1wt%AgCl in LiCl-KCl) electrode contained in a thin Pyrex glass tube was used as a reference. A Pyrex

crucible containing 2 ~ 3 g of Cd was dipped into the quartz tube which contained 9 g of LiCl-KCl and 0.1g of CeCl₃.

The cyclic voltammetric measurements were performed using an Autolab equipped with a PGSTAT 302N potentiostat and GPES 4.9 software package. The scanning rate for the cyclic voltammetry was fixed at 100 mV/s in this study.

2.2 Cyclic voltammetry

Fig. 2 shows a cyclic voltammogram in the LiCl-KCl-CeCl₃ solutions on a W electrode. Because Ce³⁺ were major ions in the solution and the W electrode did not react with the solution, the reaction proceeded sharply at -2.0V as a deposition and at -1.9V as a dissolution such as



The reduction peak potential and anodic peak potential were -2.01 V and -1.91V on the W electrode, respectively.

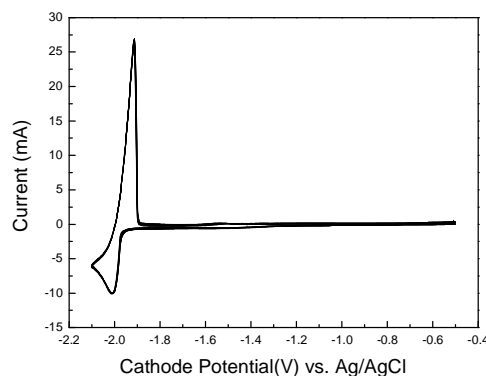


Fig. 2 Cyclic voltammogram of a LiCl-KCl-1wt%CeCl₃ solution at 773K on the W electrode.

Fig. 3 shows cyclic voltammograms in the LiCl-KCl-CeCl₃ solutions on the liquid Cd electrode. Following procedures were conducted in order to obtain a Ce cyclic voltammogram on the Cd electrode. First, cyclic voltammograms were obtained on the LiCl-KCl solution and then the LiCl-KCl-1%CeCl₃ solution in the same potential range of -0.5 ~ -1.8V. Second, the two cyclic voltammogram profiles were subtracted each other.

Curve (a) and Curve (b) show the cyclic

voltammograms in the pure LiCl-KCl solution and in the LiCl-KCl-CeCl₃ solution on the liquid Cd, respectively. The subtraction of the currents between Curve (a) and Curve (b) makes it to avoid the Li deposition effect.

The reduction peak potential and the anodic peak potential were, respectively, -1.5 V and -1.4 V on the liquid Cd cathode as shown in Fig. 3. It is shown that the Ce peak potential on the liquid Cd cathode is about 500mV positive than that on the solid W electrode. This is because Ce elements were stabilized in the liquid Cd due to its very low activity coefficient in the Cd.

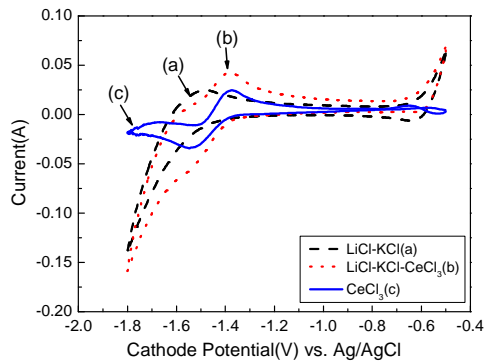


Fig. 3 Cyclic voltammograms of a LiCl-KCl-1wt%CeCl₃ solution at 773K on the liquid Cd electrode.

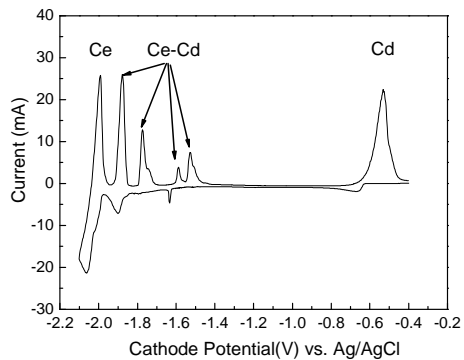


Fig. 4 Cyclic voltammograms of a LiCl-KCl-CeCl₃-CdCl₂ solution at 773K on the solid W electrode.

Fig. 4 shows the cyclic voltammogram of LiCl-KCl-CeCl₃-CdCl₂ solution on the W electrode. CdCl₂ begin to reduce to Cd at the potential range of -0.4 ~ -0.5V and therefore the surface of W electrode would be slightly deposited by the Cd element. As the potential increases in the negative direction, Ce also would be deposited with the Cd element. Small amount of Cd coated on the surface of W electrode make it to form almost all the intermetallic compounds in the Cd-Ce alloys. In the Cd pool, it will be difficult to form the many kinds of intermetallic compounds. Because of that, peaks

were not separated on the Cd pool electrode as shown in Fig. 3.

3. Conclusions

The reduction peak potential and anodic peak potential were -2.01 V and -1.91V on the W electrode, respectively. The reduction peak potential and the anodic peak potential were, respectively, -1.5 V and -1.4 V on the liquid Cd cathode. It is shown that the Ce peak potential on the liquid Cd cathode is about 500mV positive than that on the solid W electrode. These cyclic voltammogram showed that many kinds of reaction compounds could be formed between Ce elements and liquid Cd electrodes.

Acknowledgements

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