

Reduction behaviors of Zr for LiCl-KCl-ZrCl₄ and LiCl-KCl-ZrCl₄-CdCl₂

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1. Introduction

Because zirconium is one of the elements of a metallic fuel fast breeder reactor, it is necessary to study its electrochemical behavior during the electrorefining process. According to several researchers [1-3], zirconium exists in many oxidation states in LiCl-KCl electrolyte [1-3]. The reduction potentials of most of the zirconium ions on the solid cathode are smaller (about 0.4V) than that of uranium, and thus zirconium can be recovered prior to uranium during the reduction stage. In the case of a liquid cadmium cathode, which is one of the major cathodes, the reduction potential can be changed because zirconium reacts with the liquid cadmium. Up to now, it has not been well known what the reduction potential of Zr was on the liquid Cd cathode. According to the Cd-Zr phase diagram, there are four intermetallic compounds between cadmium and zirconium. It is easier to use the solid cathode than the liquid cadmium cathode in LiCl-KCl-ZrCl₄ containing CdCl₂ to identify the formation of the Cd-Zr phase. In this study, the reduction behaviors of zirconium were compared in the LiCl-KCl-ZrCl₄ and LiCl-KCl-ZrCl₄-CdCl₂ solutions when using a solid cathode.

2. Methods and Results

2.1 Experimental Procedures

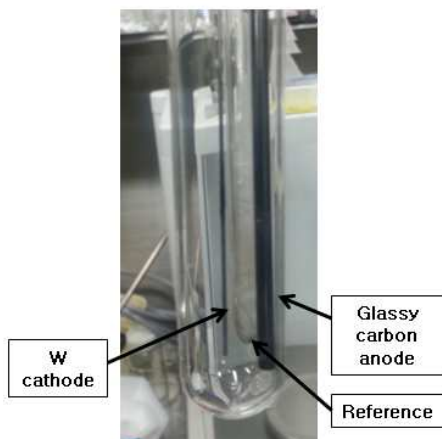


Fig. 1. Electrochemical cell used for this study.

All electrochemical experiments were conducted at 500°C in a glove box under a purified argon atmosphere of less than 1 ppm oxygen and 1 ppm water. The eutectic LiCl-KCl salt (58.8:41.2 mol%) was used as an electrolyte, where 1wt%ZrCl₄ and 0.15wt%CdCl₂ was added to the salt to observe the reduction behavior of Zr

and Zr-Cd intermetallics. The electrochemical cell used for the voltammetric studies is shown in Fig. 1. A solid W wire of 1 mm in diameter and a glassy carbon of 3 mm in diameter were used as a working and counter electrode, respectively. A silver-silver chloride (1wt%AgCl in LiCl-KCl) electrode contained in a thin Pyrex glass tube was used as a reference. The cyclic voltammetric measurements were performed using an Autolab equipped with a PGSTAT 302N potentiostat and GPES 4.9 software package.

2.2 Reduction behavior of Zr at a solid W cathode

Fig. 2 shows the reduction/oxidation behavior of Zr in a LiCl-KCl-1wt%ZrCl₄ solution, where the figure has two reduction peaks and three oxidation peaks. The reactions cited in Fig. 2 were mainly based on Sakamura's analysis [2]. However, Sakamura measured the CV from -0.4V, and thus the oxidation reaction of Zr²⁺ to Zr⁴⁺ around -0.2V was not mentioned in his paper. Chen et al. analyzed the unknown peak in Fig. 2 as the oxidation reaction of Zr²⁺ to Zr⁴⁺ [3]. Normally, the potential difference between the oxidation peak and reduction peak is smaller than 60mV even in one electron reaction. However, the unknown peak is located apart from 700mV if we consider it as the reaction of Zr²⁺ to Zr⁴⁺ or vice versa. From this result, it is thought that the unknown peak may not be the oxidation reaction peak of Zr²⁺ to Zr⁴⁺.

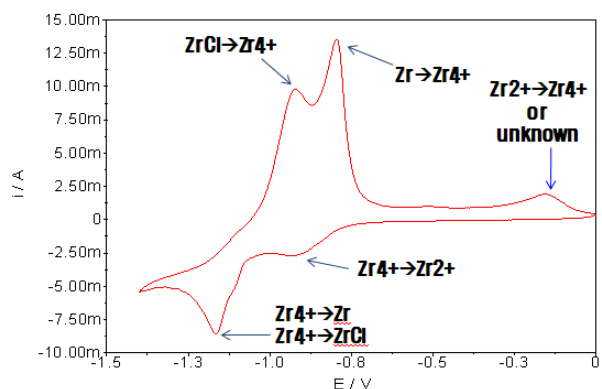


Fig. 2. Cyclic voltammogram of LiCl-KCl-1wt%ZrCl₄ at a scan rate 100mV/s at 500°C.

2.3 Reduction behavior of Zr at a Cd-coated W cathode

According to the phase diagram, four kinds of intermetallic compounds such as Cd₃Zr, Cd₂Zr, CdZr, and CdZr₂ can be formed between the Cd and Zr mixtures. The melting points of the intermetallic

compounds were unclear but seemed to be lower than 520°C. Fig. 3 shows the cyclic voltammogram of LiCl-KCl-1wt%ZrCl₄ containing about 0.1wt%CdCl₂. A Cd-Zr intermetallic peak around -1.0V was observed in the reduction sweep, but its oxidation peak was not seen in the oxidation sweep. The Cd-Zr oxidation peak may be accumulated in the oxidation peak at around -0.9V. It can be seen from Fig. 2 that the oxidation peak is the accumulated oxidation peak of Zr to Zr⁴⁺ and ZrCl to Zr⁴⁺. Murakami et al. showed that the reduction peak around -1.0V at Fig. 3 corresponded to the Cd₂Zr formation.

An unknown peak was also observed in Fig. 3 at the same potential as in Fig. 2. In the reduction sweep, Cd ions were first reduced to Cd, and Zr⁴⁺ ions were then reduced to Zr²⁺, meaning the first reduction reaction product was Cd. During the oxidation reaction, the reverse reaction should be proceeded, that is, the final oxidation reaction should be the oxidation reaction of Cd to Cd²⁺. However, as can be seen in Fig. 3, the unknown peak is the final peak in the oxidation sweep. It is therefore judged that the unknown peak is not the reaction of Zr²⁺ to Zr⁴⁺. The unknown peak is expected to be identified through additional study.

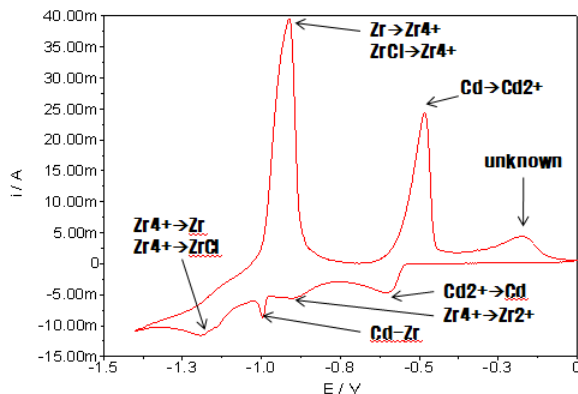


Fig. 3. Cyclic voltammogram of LiCl-KCl-1wt%ZrCl₄ containing about 0.1wt%CdCl₂ at a scan rate of 100 mV/s.

3. Conclusions

The reduction behavior of Zr at a solid W cathode and a Cd-coated W cathode was compared in a LiCl-KCl-ZrCl₄ solution at 500°C. It was observed from the results using a solid W cathode that Zr⁴⁺ ions were gradually oxidized to Zr²⁺, Zr, and ZrCl during the reduction sweep, but the final oxidation peak of Zr²⁺ to Zr⁴⁺ seemed to be unclear during the oxidation sweep. In the case of the Cd-coated W electrode, only a Cd₂Zr phase was formed at 500°C, which seemed to be related to the melting point of Cd-Zr intermetallics. Through additional studies at different temperatures, the formation behavior will be studied.

Acknowledgement

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