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Selected topics of molten fluorides in the field of nuclear engineering

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A new reference electrode in fluoride melts and a new concept for a spent zircaloy wastes treatment using a mixture of fluoride and chloride melt are proposed. Electrochemical formation of Au_2Na on Au wire in a LiF–KF–NaF shows the equilibrium potential of the reaction: $2Au + Na^+ + e^- = Au_2Na$ at 0.535 V vs. K^+/K in LiF–NaF–KF eutectic melt at 773 K. The (Au_2Na + Au) electrode demonstrates excellent characteristics as a reference electrode in terms of reproducibility, stability and reversibility. LiF–LiCl–KCl melt enhances dissolution and deposition rate of zirconium, which enable us to develop a new decontamination process for a spent zircaloy. Electrochemical decontamination using LiF–LiCl–KCl melt is experimentally achieved a clearance level.

1. Introduction

Molten salts are widely applied to the nuclear engineering field, such as liquid fuel, coolant, electrolyte for producing and reprocessing of nuclear materials and so on. A vast range of support works and studies have thus been done for more than 60 years and most studies are related to molten fluorides because of their excellent physico-chemical properties [1]. The drawback of fluoride melts, however, still remains, roughly classifying into two categories: (1) reference electrodes for some fluoride melts have not been established and thereby data obtained by using uncertain electrode or quasi reference electrode are unacceptable from thermodynamic points of view and (2) solidified fluorides contaminating the object materials are difficult to be removal at room temperature due to low solubility of solid fluorides in aqueous solution. Thus, there are still some rooms for research and development on molten fluoride processing. In the following, the attractive possibilities on fluoride melt from both fundamental and practical aspects will be described to focus two topics recently done by the present authors.

2. Reference electrode for a LiF–KF–NaF melt [2]

2.1. Necessity of a reference electrode for a LiF–KF–NaF eutectic melt

Among many kinds of molten fluorides, a LiF–NaF–KF eutectic melt (LiF:NaF:KF = 46.5:11.5:42.0 mol%, m.p. = 732 K) is the most systematically studied melt in the field of electrochemistry [1]. However, precise and quantitative electrochemical study is rather difficult to conduct in this system due to lack of a good reference electrode. Although several reference electrode systems such as the Ni(II)/Ni in a boron nitride compartment have been tested [3], there is no reference electrode which has thermodynamical significance, excellent stability, durability, reversibility, reproducibility and simple structure. The long-range instability of the electrode was due to reaction of electrode materials with fluoride [3].

In this study, the electrochemical behavior of Au electrode and the electrochemical formation of Au–Na alloy in the melt are first studied. Since the Au–Na alloy shows a very stable potential, it is suggested to be used as a stable reference electrode in a LiF–NaF–KF eutectic melt. Therefore, the main characteristics of (Au_2Na + Au) reference electrode, such as reproducibility, stability and reversibility, are then investigated.

2.2. Cathodic limit of LiF–KF–NaF

According to the literature [4–8], the cathodic limit at Pt, Ni and Cu electrodes in the LiF–NaF–KF eutectic melt has been suggested to be the deposition of potassium. However, no experimental evidence has been shown so far. Therefore, the potentials of Li^+/Li, Na^+/Na and K^+/K are measured using each alkali metal electrode in the LiF–NaF–KF eutectic melt. In order to determine the cathodic limit of the melt at the nickel electrode, Li, Na, K metal electrodes were designed for measuring the potential of Li^+/Li, Na^+/Na and K^+/K, respectively. A nickel wire spot-welded to porous Ni at the bottom was inserted in an alumina tube. Alkaline metals (Li, K, Na)

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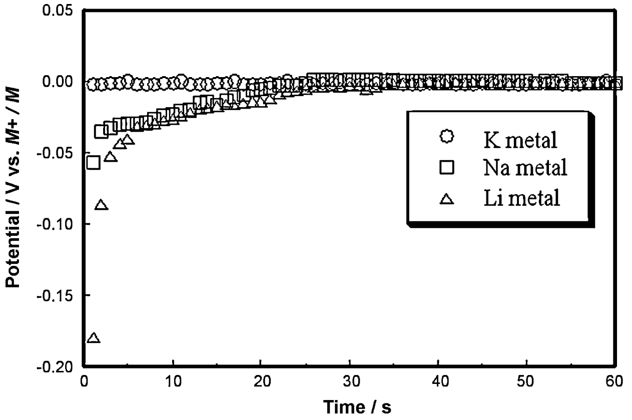

Fig. 1. Potential transient curves of Li, Na and K metal electrode in a LiF–NaF–KF eutectic melt at 773 K [2].

were directly into the tube and then the potentials were recorded, respectively. Fig. 1 shows the obtained potential transient curves for the alkali metal electrodes against the potential of the M^+/M (M = alkali metal electrodeposited on a Ni electrode) dynamic reference electrode. The potential of K^+/K coincides well with that of M^+/M. The potentials of Li^+/Li and Na^+/Na are more negative than the potential of M^+/M in the beginning. After 30 s, the potentials of Li^+/Li and Na^+/Na recover to the same potential as that of M^+/M. The observed potential shifts are explained by the displacement reaction occurring on the Li and Na electrodes. These results demonstrate the cathodic limit at Ni electrode in the LiF–NaF–KF eutectic melt corresponding to the deposition of potassium. Therefore, electrode potentials are hereafter expressed with reference to the K^+/K dynamic reference electrode prepared by electrodepositing potassium metal on a Ni electrode.

2.3. Electrode behavior of Au

The electrode behavior of Au is investigated by cyclic voltammetry at 773 K. The obtained voltammogram is shown in Fig. 2. Large cathodic current at 0 V and large anodic current at 3.8 V correspond to the deposition of alkali metals and the dissolution of Au, respectively. Besides these currents, a pair of redox peaks was observed at around 0.5 V. The peaks are considered to correspond to the formation of Au-alkali metal alloy and anodic dissolution of alkali metal from the alloy, respectively. Open-circuit potentiometry is conducted to further investigate the alloy formation. Open-circuit potential transient curve are recorded at a Au electrode after electrolysis at 0 V for 300 s in a LiF–KF–NaF eutectic melt at 773 K. Since the deposited alkali metal diffuses into the inside of the Au electrode, the electrode potential gradually shifts to more positive values. The observed stable potential plateau at 0.535 V is considered to be attributed to the existence of coexisting phase of Au-alkali metal alloy.

Based on these results, potentiostatic cathodic electrolysis is conducted at a Au electrode at 0.3 V for 2 h to obtain the alloy sample. The XRD pattern of this sample is ascribed to Au_2Na (cubic unit cell, a = 0.779 nm), indicating that the cathodic current peak at 0.45 V in Fig. 2 corresponds to the formation of Au_2Na phase. According to the phase diagram of Au–Na system [9], only Au_2Na alloy exists as a solid alloy at the experiment temperature below 1275 K. In order to examine the anodic reaction at 0.6 V, potentiostatic anodic electrolysis is conducted at 0.6 V for 1 h using the previously formed Au_2Na electrode. The obtained sample is also analyzed by XRD, which shows the existence of only Au. From these results, the pair of redox peaks in Fig. 2 and the potential plateau at 0.535 V of the open-circuit voltammogram are proved to correspond to the following reaction:

$$2\mathrm{Au} + \mathrm{Na}^+ + \mathrm{e}^- = \mathrm{Au_2Na} \qquad (1)$$

Deposited potassium metal at cathodic limit is chemically substituted with Au_2Na during the experiment, because Au_2Na is thermodynamically stable than potassium metal on a gold electrode. Therefore, reoxidation peak corresponding to the cathodic peak at 0 V is not visible in Fig. 2.

2.4. Durability of (Au_2Na + Au) electrode

Since the (Au_2Na + Au) electrode shows a very stable potential, it is suggested to be used as a stable reference electrode in a LiF–NaF–KF system. Potentiostatic electrolysis is conducted at a Au electrode at 0 V (vs. K^+/K). It suggests that two phases (Au_2Na + Au) coexist. Then, using the (Au_2Na + Au) electrode as a reference electrode, the electrolysis is repeated with another Au electrode under the same conditions. Fig. 3 shows the measured potential transient curve after the electrolysis. The potential difference is observed for about 3 h till coexisting (Au_2Na + Au) phase starts to appear on new Au electrode. After that, the potential difference remains within 1 mV and lasted more than 25 h. This result shows that (Au_2Na + Au) reference electrode has good stability and reproducibility. A reliability reference electrode must give a fixed

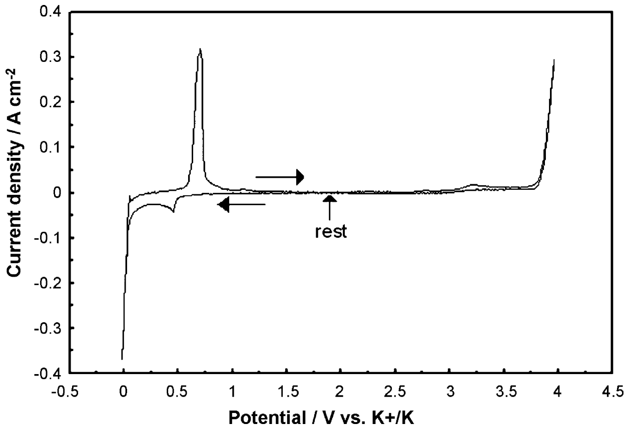

Fig. 2. Cyclic voltammogram at Au electrode in a LiF–NaF–KF eutectic melt at 773 K. Scan rate: 0.1 V s^{-1} [2].

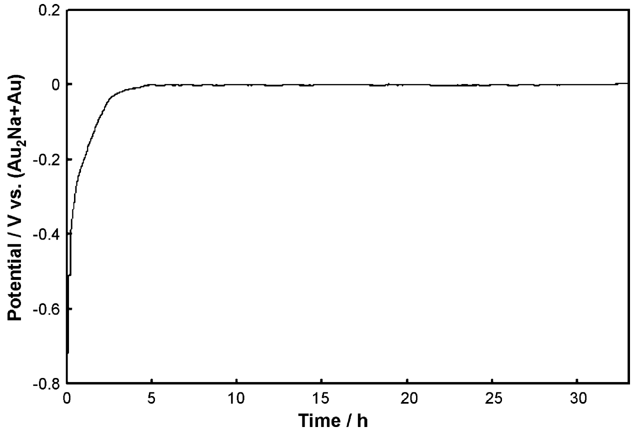

Fig. 3. Open-circuit potential transient curve of a Au electrode after electrolysis at 0 V for 600 s in a LiF–NaF–KF eutectic melt at 773 K [2].