Journal of Nuclear Materials 476 (2016) 179–187

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Effects of temperature, concentration, and uranium chloride mixture on zirconium electrochemical studies in LiCl–KCl eutectic salt

Robert O. Hoover [a], Dalsung Yoon [b], Supathorn Phongikaroon [b, *]

[a] Department of Chemical and Materials Engineering and Nuclear Engineering Program, University of Idaho, Center for Advanced Energy Studies, 995 University Blvd, Idaho Falls, ID 8340, USA
[b] Department of Mechanical & Nuclear Engineering, Virginia Commonwealth University, 401 West Main St., Richmond, VA 23284, USA

ARTICLE INFO

Article history:
Received 26 January 2016
Received in revised form
19 April 2016
Accepted 20 April 2016
Available online 22 April 2016

ABSTRACT

Experimental studies were performed to provide measurement and analysis of zirconium (Zr) electrochemistry in LiCl–KCl eutectic salt at different temperatures and concentrations using cyclic voltammetry (CV). An additional experimental set with uranium chloride added into the system forming UCl_3–$ZrCl_4$–LiCl–KCl was performed to explore the general behavior of these two species together. Results of CV experiments with $ZrCl_4$ show complicated cathodic and anodic peaks, which were identified along with the Zr reactions. The CV results reveal that diffusion coefficients (D) of $ZrCl_4$ and $ZrCl_2$ as the function of temperature can be expressed as $D_{Zr(IV)} = 0.00046\exp(-3716/T)$ and $D_{Zr(II)} = 0.027\exp(-5617/T)$, respectively. The standard rate constants and apparent standard potentials of $ZrCl_4$ at different temperatures were calculated. Furthermore, the results from the mixture of UCl_3 and $ZrCl_4$ indicate that high concentrations of UCl_3 hide the features of the smaller concentration of $ZrCl_4$ while Zr peaks become prominent as the concentration of $ZrCl_4$ increases.

1. Introduction

Electrochemical processing (also known as pyroprocessing, electrometallurgical, or pyrochemical technology) was first developed by Argonne National Laboratory to treat used metallic sodium-bonded fuel from the Experimental Breeder Reactor-II (EBR-II) [1–3]. This technique is still being used at Idaho National Laboratory (INL) and widely studied by many researchers because it has some advantages when compared with the conventional aqueous processes, including compact space requirement, production of the mixed fuel, and treatment of fast reactor fuel [4]. During irradiation, the metallic sodium bond material is incorporated into the fuel [3], which limits the disposal options due to the highly exothermic reaction with water [5]. In general, the driver fuel, post-irradiation, contains approximately 80.6 wt% uranium (U) and 10.8 wt% zirconium (Zr), with the remainder fission products (FPs) [6]. The used EBR-II driver fuel rods are chopped and loaded into stainless steel fuel dissolution baskets as an anode, which are then lowered into a molten LiCl–KCl eutectic (58 mol%: 42 mol%) salt containing nominally 5–10 wt% UCl_3 at 773 K for an electrorefining process [6]. Generally, it is operated in a galvanostatic mode, so a current is applied with a cutoff voltage to electrochemically oxidize and dissolve U into the electrolyte salt while Zr and FPs remain in the anode baskets. Overall, the goal of the electrochemical process is to anodically dissolve U at the anode basket and collect pure U at the solid steel cathode.

Ideally, as mentioned above, the Zr should remain unoxidized in the anode basket due to the difference in the standard potentials between U and Zr. The reported apparent standard potentials of U and Zr are −1.3 V and −1.22 V vs. Ag/AgCl at 723 K, respectively [7–9]. However, the small difference in the standard potentials causes unavoidable Zr oxidation along with U. Additionally, in the electrorefining process, the potential applied at the anode basket needs to be sufficiently higher than the standard potential of U/U^{3+} to maintain a high dissolution rate of U at the anode basket [10], resulting in Zr dissolution into the salt. In the early years of electrorefining operation at INL, Zr retention was the primary goal under the U.S. Department of Energy (DOE) demonstration program, while during the Advanced Fuel Cycle Initiative (AFCI), more emphasis had been put on achieving complete actinide dissolution [6]. Zr buildup in the electrorefiner (ER), primarily in the cadmium pool, is illustrated and reported by Li and Simpson [6].

---

* Corresponding author.
E-mail address: sphongikaroon@vcu.edu (S. Phongikaroon).

http://dx.doi.org/10.1016/j.jnucmat.2016.04.037
0022-3115/© 2016 Elsevier B.V. All rights reserved.

Due to this behavior, it is clear that Zr has been building up in the ER at INL and must be periodically collected. To develop a method of collecting Zr in a pure (free from U contamination) state, the electrochemical behaviors of U and Zr, both separately and together, in the LiCl–KCl eutectic molten salt must be understood. These actions provide an important motivation to focus on the zirconium electrochemistry as little attention has been paid to it in the past. Early work in 1965 by Baboian et al. [9] provided a specific study on the potentials and stabilities of zirconium chlorides ($ZrCl_4$ and $ZrCl_2$) in molten LiCl–KCl at 723 K for low concentrations of Zr (less than 0.05 mol%). Since then, there have been several other experiments and computational models focusing on understanding Zr behaviors in molten salt systems complicated by the low sublimation point (604 K) and hygroscopic properties of $ZrCl_4$, along with complex behaviors in the stepwise process [9–17]. However, electrochemical properties of $ZrCl_4$ including the diffusion coefficient, the apparent standard potential, and the standard rate constant have been poorly accumulated and understood because of the complexity of the Zr ion formations and difficulty of Zr handling as previously mentioned.

In the present study, series of experimental runs were conducted by systematically varying the concentration of $ZrCl_4$ up to 5 wt% in the molten LiCl–KCl salt at three different temperatures (723, 773, and 823 K) using two electrochemical methods—cyclic voltammetry (CV) and chronopotentiometry (CP). Furthermore, to better reflect the conditions in an operating used nuclear fuel ER, an additional set of experiments with quaternary salt UCl_3–$ZrCl_4$–⊖ LiCl–KCl was also performed to explore the behavior of U and Zr together. It is expected that this research study will offer an enhancement in the electrorefining process for current operation and future process design.

2. Experimental

Experiments were conducted in a sealed glove box with an inert argon atmosphere with O_2 and H_2O concentrations less than 3.0 ppm. A Kerrlab melting furnace for melting and maintaining the salt at desired temperatures was placed inside the glove box as shown in Fig. 1(a). There were two experimental schemes: (1) zirconium tetrachloride ($ZrCl_4$) experiments under different temperatures and concentrations and (2) variations with additional uranium trichloride (UCl_3).

In the first scheme, the salt mixtures were composed of LiCl–KCl eutectic from AAPL (99.99%) and zirconium tetrachloride ($ZrCl_4$, 99.5+%) from Alfa Aesar. The salt was loaded into a 16.8 cm tall tapered glassy carbon crucible (Sigradur®, HTW-Germany) with outside diameters of 4.1 cm and 4.5 cm at the bottom and top, respectively, and a wall thickness of 0.3 cm. This glassy carbon crucible was then placed into a magnesium oxide (MgO) secondary crucible to contain any molten salt upon possible breakage of the crucible before loading it into the furnace. The working electrode was a tungsten rod (diameter of 2.0 mm and length of 30 cm, Alfa Aesar, 99.95%) and the counter electrode was a glassy carbon rod (diameter of 3.0 mm and length of 30 cm, Sigradur®, HTW-Germany). The glassy carbon rod was in contact with the glassy carbon crucible making the entire crucible and rod in contact with the electrolyte the counter electrode. A silver wire in LiCl–KCl-5.0 mol% AgCl (Alfa Aesar, ultra dry, 99.997%) in a Pyrex® body was used as a reference electrode. A view of the electrodes and connections can be seen in Fig. 1(b), while the schematic design of the cell is shown in Fig. 2.

While $ZrCl_4$ is soluble and stable in the molten eutectic, pure $ZrCl_4$ sublimes at 604 K [18], which is lower than the melting point of the LiCl–KCl eutectic, from 621 K to 634 K [19]. To overcome this issue, a modified process was developed to trap $ZrCl_4$ underneath the LiCl–KCl until the salt melts and all $ZrCl_4$ can be all dissolved into the eutectic by working with a tapered glassy carbon crucible (see Fig. 3). The pure LiCl–KCl eutectic was first melted and consolidated into a single ingot in the tapered glassy carbon crucible. When cooled overnight, the LiCl–KCl ingot was removed from the crucible and approximately 1 cm was cut off the bottom of the salt ingot (see Fig. 3(a)). The powdered $ZrCl_4$ was added to the crucible and the ingot with the bottom cut off was placed over the top of the $ZrCl_4$ powder in the crucible (Fig. 3(b)). Due to the taper, the salt ingot sits tightly against the walls of the crucible and above this powder. With this method, there was no evidence of $ZrCl_4$ vaporization and inductively coupled plasma mass spectrometry (ICP-MS) analysis of the salt mixtures following each experiment showed that all the $ZrCl_4$ that was added to the mixture remained in the crucible.

In the second scheme, the behavior of $ZrCl_4$ together with UCl_3 in the LiCl–KCl eutectic was studied as there is nominally 10 wt%

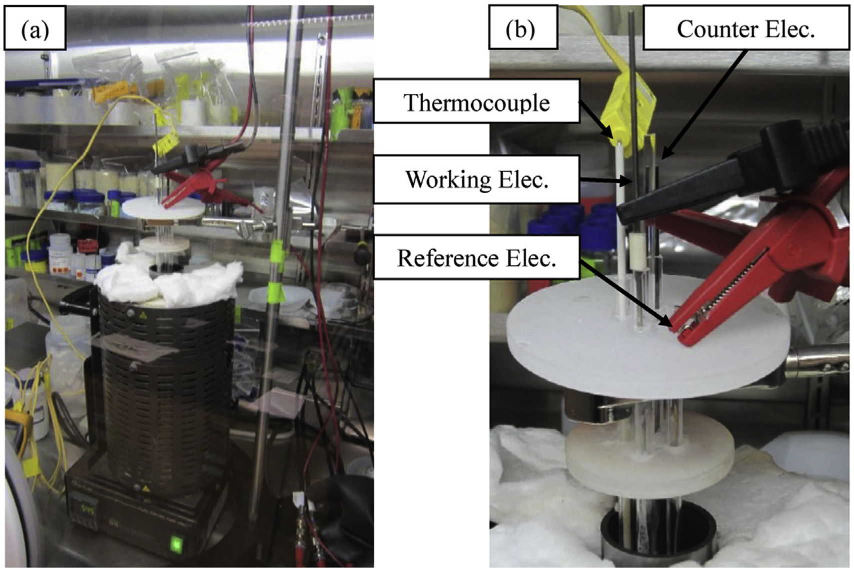

Fig. 1. (a) Experimental setup in the glove box with (b) close-up view of the electrodes and connections.