

Examination on Electrochemical Behaviors of Niobium Chloride in Molten LiCl-KCl by Cyclic Voltammetry

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1. Introduction

Niobium (Nb) is one of the major alloying elements which has been widely utilized in nuclear industry to enhance corrosion resistance under high temperature and pressure (e.g., fuel cladding and CANDU pressure tube). In addition, it is also contained in various types of nuclear structural materials like stainless steel, Inconel. Niobium is monoisotopic elements with ^{93}Nb , but a long lived radioisotope, ^{94}Nb , is generated and accumulated in the materials during irradiation inside or near a nuclear reactor. This radioisotope is often the key element, elevating the radioactive waste hierarchy of the activated materials from the low level waste (LLW) to the intermediate level waste (ILW) because the ^{94}Nb concentration limit for the LLW in Korean radioactive waste classification system is low as 111 Bq/g.

Electrorefining in LiCl-KCl has been widely utilized not only in nuclear industry but also in rare earth and refractory elements industry to separate target elements from the ore and waste. The chloride-based separation technique would also be applied for the Nb contained metallic radioactive waste. Electrochemical behaviors of Nb has to be fully understood during electrorefining to monitor and manage the anode and cathode potential utilized to suppress dissolution and deposition of Nb on the anode and cathode respectively. In LiCl-KCl, it has been identified that Nb has various oxidation states (Nb^{5+} , Nb^{4+} , Nb^{3+} , Nb_xCl_y , Nb), but the number of reports regarding redox mechanism of the states in LiCl-KCl is limited [1][2].

In this study, the electrochemical redox behaviors of Nb in LiCl-KCl-NbCl₅ (1wt.%) at 450°C are examined by cyclic voltammetry (CV) which is the most widely used technique for qualitative and quantitative analysis for electrochemical redox mechanism and properties. Diverse scan rates, scan ranges at the fixed concentration and temperature are investigated, and the redox reactions of Nb for each redox peaks of cyclic voltammograms are suggested by the peak shapes with comparison to the reported papers. The identified Nb behavior will be utilized to design an electrochemical decontamination process for lowering the Nb contained waste hierarchy.

2. Experimental

The reagent of LiCl-KCl-1wt.% NbCl₅ for the CV experiments were prepared with LiCl-KCl eutectic and NbCl₅ of 99.9% purity from Alfa Aesar. All experimental procedures from the reagent preparation to the CV experiment were performed within the glovebox which is designed to limit oxygen and moisture concentrations to be < 0.1 ppm under Ar gas (99.99%) environment.

The electrochemical cell with the diameter of 13 mm for the CV experiments was placed in the electric resistance furnace installed by connecting to the bottom surface of the glovebox module as shown in Fig. 1. A temperature measuring quartz tube containing only eutectic LiCl-KCl molten salt with the identical size of the CV experiment tube was additionally placed right next to the CV cell to predict the temperature of the CV cell indirectly. The temperature of LiCl-KCl in the temperature cell was measured by a K-type thermocouple.

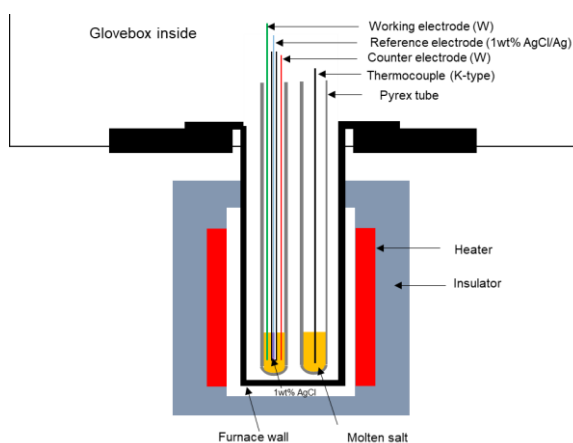


Fig. 1. A schematic showing an experimental setup for cyclic voltammetry.

Inert working and counter electrode made of tungsten wire with the diameter of 1 mm was inserted into the molten salt. The surface areas of the electrodes were determined by measuring the immersed depth of the electrode after the CV experiment, and the wetted depth was measured as about 13 mm. The reference electrode was the Ag/AgCl electrode, in which Ag metal wire with a diameter of 1 mm and purity of 99.99% was placed within the LiCl-KCl-AgCl (1wt. %) solution.

CV was performed with different scan rates (20 ~ 1500 mV/sec) and scan ranges (-1.1 ~ 1.0 V) to identify possible redox peaks.

3. Results

Fig. 2 shows cyclic voltammograms with different scan rates in the scan range from 1.0 to -1.1 V (vs. 1 wt.% Ag/AgCl). Due to the complexity from multiple oxidation states of Nb ion, multiple cathodic and anodic peaks were found. They were identified by referring to the literature data published by Lantelme *et al.* as summarized in Table 1 with major reactions which can contribute to each current peak [3].

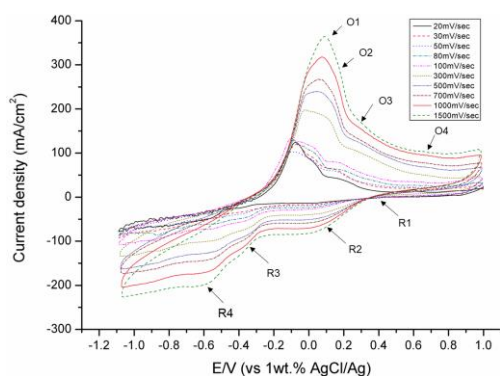


Fig. 2. Cyclic voltammograms showing the major redox reactions with different scan rates at 450°C.

Table 1. Comparison of possible reactions for CV peaks in LiCl-KCl-NbCl₅ system

Peak	This study (possible major reactions)	Lantelme (450°C, 5·10 ⁻² mol/L NbCl ₅ , molybdenum electrode) [3]
R1	Nb(V) + e ⁻ → Nb(IV)	Nb(V) + e ⁻ → Nb(IV)
R2	Nb(IV) + e ⁻ → Nb(III)	Nb(IV) + e ⁻ → Nb(III)
R3	Nb(III) + e ⁻ → Nb _x Cl _y (major)	Nb(III) + e ⁻ → Nb _x Cl _y
R4	Nb(III) + 3e ⁻ → Nb	Nb(III) + 3e ⁻ → Nb
O1	Nb → Nb(III) + 3e ⁻	Nb → Nb(III) + 3e ⁻
O2	Nb _x Cl _y → Nb(III) + e ⁻	
O3	Nb(III) + e ⁻ → Nb(IV)	Nb(III) + e ⁻ → Nb(IV)
O4	Nb(IV) + e ⁻ → Nb(V)	Nb(IV) + e ⁻ → Nb(V)

Peak potentials and corresponded redox reactions were consistent with CV results including peak shapes reported by Lantelme *et al.* [3]: Cathodic peaks for R3 and R4 were due to the formation of niobium subchloride (i.e., NbCl_x, x~2.33) and Nb metal deposition.

Fig. shows cyclic voltammograms with different scan ranges at the fixed scan rate of 100 mV/sec. It is noticed that the height for peak O1 increased as the negative potential limit became more negative since

the formation of metallic Nb is predominant by direct reduction of Nb(III) rather than the subchloride formation. The reaction for O2 peak is not clearly identified, but it is possibly due to the oxidation of niobium subchloride since the peak height for O2 increased as that for R3 increased as the negative potential limit became less negative with the preferential formation of the niobium subchloride.

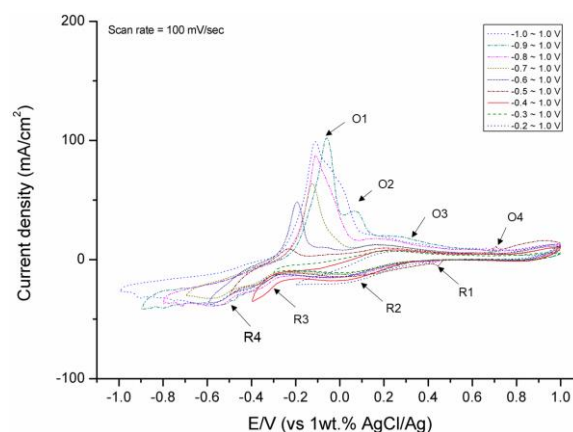


Fig. 3. Cyclic voltammograms with different scan ranges at the fixed scan rate of 100 mV/sec.

4. Summary

Electrochemical behaviors of Nb ion in the LiCl-KCl-NbCl₅ molten salt were examined. Cyclic voltammograms with different scan rates and scan range at 450°C showed possible electrochemical redox reactions which were identified by comparison to the literature data. Peak potentials for each redox reaction were consistent with the literature, but some redox reactions were not clearly defined due to the formation of subchloride compound in chloride salt. The electrochemical behaviors of Nb ion related to the subchloride formation as well as Nb metal deposition will be investigated for the future work.

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