Identification of Redox Reactions of Nb in Molten LiCl-KCl Eutectic for Pyrochemical Decontamination

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1. Introduction

Niobium (Nb) is one of the refractory metals, which is widely used as a minor alloying element in the nuclear materials including fuel cladding and reactor structure components. $^{93}\text{Nb}$ is the single stable isotope, but the small amount of $^{94}\text{Nb}$ forms by the neutron-induced activation during the irradiation period. $^{94}\text{Nb}$ has the long half-life of 20,000 years, and its decay generates two high-energy gamma rays with 700 and 870 keV, indicating that $^{94}\text{Nb}$ becomes the major source of radioactivity of hardware wastes from nuclear power plants after the disintegration of short-lived radionuclides, and it can affect their classification for the hierarchy of the radioactive waste into low-level or intermediate level waste [1].

Pyrochemical decontamination processes with a molten salt system for radioactive wastes have been developed to reduce and manage their radioactivity by separating long-lived radioisotopes and recycling valuable elements such as Zr, Fe, or Ni. Their electrochemical behaviors in the molten salt are actively investigated [2], particularly in LiCl-KCl eutectic thanks to its low practicable temperature and low corrosivity. However, few data are available for the electrochemical redox reactions involving Nb in molten LiCl-KCl. Hence, it is necessary to investigate the electrochemical behaviors of Nb in LiCl-KCl to confirm the applicability of pyrochemical process for the decontamination of Nb-containing wastes.

In this study, cyclic voltammetry (CV) was performed to identify all possible redox reactions of Nb in LiCl-KCl-NbCl$_5$. In addition, pyrochemical decontamination processes for each different type of Nb-containing waste are suggested with the consideration of reduction potentials of elements of concern.

2. Experiment

Fig. 1 shows the configuration of setup for the electrochemical experiment. Two Pyrex tubes were placed at the same axial position inside of a furnace; one containing LiCl-KCl-1.0wt.% NbCl$_5$ (99.99%, Alfa Aesar) for CV, and the other for temperature measurement by a type-K thermocouple. A tungsten (W) wire with a diameter of 1.0 mm (99.99%, Alfa Aesar) was used as a working and counter electrode. All potentials were recorded with referenced to Ag/AgCl in which Ag wire (99.99%, Alfa Aesar) is immersed in LiCl-KCl-1.0wt%. AgCl.

CV was performed with a scan range from -1.0 to -1.1V at different scan rates (30 ~ 1500 mV/sec) at 450°C by using VersaSTAT3 potentiometer.

3. Results

Fig. 2 shows the voltammogram by CV with identified redox reactions. Peak current density and peak potentials were analyzed to confirm the reversibility of each reaction with the literature data available in [3][4][5].
Formal potentials of each redox couple were obtained by using cathodic peak potentials as a function of the scan rate, as summarized in Table 1.

Table 1. Comparison of formal potentials for identified redox reaction

<table>
<thead>
<tr>
<th>Formal potential (E°) for redox reactions (E/V vs Cl-/Cl₂) at 450°C</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(II) /Nb</td>
<td>-1.54</td>
</tr>
<tr>
<td>Nb(III)/NbCl₄</td>
<td>-1.44</td>
</tr>
<tr>
<td>Nb(IV)/Nb(III)</td>
<td>-1.48</td>
</tr>
<tr>
<td>Nb(V)/Nb(IV)</td>
<td>-1.61</td>
</tr>
</tbody>
</table>

* Present study

It can be noticed that the deposition of metallic Nb (peak R4) competed to that of insoluble nonstoichiometric Nb chloride compounds (peak R3). Thus, it is necessary to apply the potential more negative than -0.6 V (vs. Ag/AgCl) to obtain the metallic Nb deposit during potentiostatic separation of Nb during pyrochemical decontamination processes.

4. Pyrochemical Decontamination Process for Nb-Containing Wastes

Fig. 3 shows schematics of pyrochemical decontamination processes for the different type of Nb-containing waste. Depending on the reduction potentials of elements involved in the process, Nb can be extracted from the residual at the anode or molten electrolytes after the first stage of electrorefining (ER) process; for Zr-Nb waste, Nb remains at the anode and can be separated in the sequential ER process; for Fe-Cr-Nb and Ni-Cr-Nb wastes, Nb can be separated from the residual molten salt by the electrodiposition to purify the salt containing dissolved Cr which can be recycled.

Although multiple-step processes are required to separate Nb from the waste, Nb separation via pyrochemical processes is advantageous because all valuable elements can be recycled and the volume of intermediate waste can be reduced significantly. A further investigation would be necessary to optimize the performance of ER process in terms of Nb concentration as well as the applied potential on the electrode.

REFERENCES