

Selection of Surrogate Materials for Oxide Reduction of Used Nuclear Fuel Using Carbon Anode

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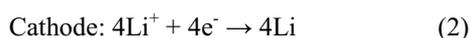
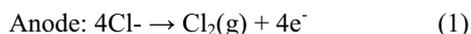
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1. Introduction

Carbon was recently proposed as a new anode electrode material to replace costly platinum for oxide reduction of used nuclear fuels [1]. Employing carbon sacrificial anode enables operation of the cell at a higher voltage than the platinum case where the anode voltage is limited below platinum oxidation potential.

The oxide reduction reaction with carbon anode occurs via two steps of electrochemical and chemical reactions. First, LiCl molten salt is electrochemically decomposed into metallic Li and chlorine gas as follows:



And then metallic lithium produced in the cathode electrode reacts with UNF as follows:



This consequent reaction mechanism suggests that the surrogate material should have similar properties to U or other nuclides in both electrochemical and chemical aspects.

In this work, theoretical calculations were performed to identify the most appropriate surrogate materials for the carbon anode oxide reduction process. Employing surrogate materials will help to

minimize the amount of radioactive waste produced during the research of oxide reduction process.

2. Theoretical calculations

Reduction potentials of various metal oxides were calculated from Gibbs free energy (ΔG) values using the following equation:

$$E = -\Delta G / zF \quad (4)$$

where E is the reduction potential, z is number of electrons involved in the reaction, F is the Faraday constant. In chemical reaction point of view, ΔG values and equilibrium constants were compared with UO_2 and PuO_2 . These calculations were performed using the HSC chemistry code.

3. Results and Discussion

3.1 Surrogate materials for UO_2

Among various metal oxides, four of Al_2O_3 , TiO , ZrO_2 , and BaO exhibited similar reduction potential with UO_2 as shown in Table 1. Comparing ΔG for chemical reaction with lithium, TiO and ZrO_2 were identified as the best surrogate material to replace UO_2 . In addition, it should be mentioned that metallic Al melts at 660°C (close to operation temperature (650°C) of oxide reduction process) and metallic Ba has high solubility in LiCl salt. Although zirconia is

known to react with Li_2O to produce Li_2ZrO_3 , low Li_2O concentration of the carbon anode system might suppress this reaction [2].

Table 1. Theoretical calculation results for UO_2 surrogate candidates at 650°C

Material	E (V)	ΔG for reaction with Li (kcal/mol)
UO_2	2.396	-6.394
Al_2O_3	2.395	-9.757
TiO	2.350	-5.328
ZrO_2	2.394	-6.591
BaO	2.402	-2.929

3.2 Surrogate materials for PuO_2

Identical approach was employed to identify appropriate material to replace PuO_2 . Among various oxides, CeO_2 and Eu_2O_3 were identified to have similar reduction potential and ΔG for chemical reaction. However, it is well known that Eu_2O_3 exhibits high solubility in LiCl salt leaving CeO_2 as the only candidate for PuO_2 .

Table 2. Theoretical calculation results for PuO_2 surrogate candidates at 650°C

Material	E (V)	ΔG for reaction with Li (kcal/mol)
PuO_2	2.281	-17.03
CeO_2	2.327	-12.747
Eu_2O_3	2.358	-14.85

4. Conclusion

Considering both electrochemical and chemical properties, TiO and ZrO_2 were proposed as the best surrogate materials to replace UO_2 . In the case of PuO_2 , CeO_2 was identified as the most appropriate surrogate material.

REFERENCES

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