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

Min Ku Jeon*, Sung-Wook Kim, Sang-Kwon Lee, and Eun-Young Choi

Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, 34059 Daejeon, Republic of Korea

*minku@kaeri.re.kr

## 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:

Anode: $4Cl^- \rightarrow Cl_2(g) + 4e^-$ (1)

Cathode: $4Li^+ + 4e^- \rightarrow 4Li$ (2)

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

$UO_2 + 4Li \rightarrow U + 2Li_2O$ (3)

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 ($\Delta G$) 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, $\Delta G$ 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 $\Delta G$ 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) | $\Delta G$ 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 $\Delta G$ 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) | $\Delta G$ 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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[2] W. Park, E.-Y. Choi, S.-W. Kim, S.-C. Jeon, Y.-H. Cho, J.-M. Hur, "Electrolytic reduction of a simulated oxide spent fuel and the fates of representative elements in a $Li_2O$-LiCl molten salt", Journal of Nuclear Materials, 477, 59-66 (2016).