

Electrolytic Reduction of 1 kg-UO₂ Using a Graphite Anode

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1. Introduction

Developing anode materials has been a critical issue of electrolytic reduction in pyroprocessing because of the extremely high price of Pt, which is the most common anode material. Recently, the feasibility of a C anode as a potential alternative to a Pt anode was suggested through a small-scale experiment (~50 g-UO₂) [1]. Accumulation of Li₂CO₃, a major byproduct in the C anode system, can be prevented, enabling the repeatable use of LiCl electrolyte. Cl₂ gas is expected to be dominantly generated at the anode surface during the reaction to eliminate the Li₂CO₃ byproduct. In this study, a larger-scale electrolytic reduction experiment was conducted using 1 kg of UO₂ pellets with graphite as the C anode.

2. Results

An identical reactor, which was used to test the Pt anode at the same scale (1 kg-UO₂), was used for comparison [2]. Pure LiCl was used as the initial electrolyte, which was heated to 650°C. One cathode basket containing 1 kg of UO₂ pellets and two graphite anodes were used in this experiment.

With the graphite anode, the maximum cell current was 220 A under 7-7.5 V with a constant current operation. On the other hand, the Pt anode system operated at a constant voltage of 3.4 V can only transfer 30-35 A. This implies the superiority of the graphite anode in terms of the cell current, which directly determines the reaction time. Such a high current is originated from the application of higher voltage and the higher concentration of the major anion species participating in the electrochemical reaction. Since Pt is ionized to be dissolved in a LiCl electrolyte above 3.4 V ($\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$), it is difficult to apply high voltage with a Pt anode. However, C does not suffer from an anodic dissolution, and a higher voltage can be applied to

result in an increased cell current. A Cl₂ evolution ($2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$) and O₂ evolution ($2\text{O}^{2-} \rightarrow \text{O}_2(\text{g}) + 4\text{e}^-$) are regarded as the major anodic reactions in a graphite anode and Pt anode, respectively. LiCl is the dominant phase in the electrolyte, and hence an excessive amount of Cl⁻ should exist around the graphite anode, which is advantageous over an electrochemical reaction.

The surfaces of the UO₂ pellets were reduced to U metal after the reaction, as shown in Fig. 1. However, the cores of several pellets remained UO₂, even though a 150-200% theoretical charge was supplied. The relatively low conversion rate was due to the limited diffusion of metallic Li, formed at the cathode surface to reduce UO₂ to U ($\text{UO}_2 + 4\text{Li} \rightarrow \text{U} + 2\text{Li}_2\text{O}$), into the core of the UO₂ pellets, and due to side reactions induced by reaction byproducts dissolved in the electrolyte. The conversion rate can be increased by supplying more charge and optimizing the operation condition to ensure the sufficient diffusion time for the metallic Li.

After the reaction, the reactor corroded severely owing to the evolution of highly reactive Cl₂ and O₂ during the reaction. The corrosion can be reduced by designing an off-gas system to minimize the residence time of the gas species in the reactor. In addition, a ceramic coating or attaching ceramic plate will be effective at prohibiting any corrosion.



Fig. 1. U metal products in a cathode basket after electrolytic reduction using a carbon anode.

3. Conclusion

An electrolytic reduction of 1 kg-UO₂ was conducted using a graphite anode. The graphite anode can transfer a 7-times higher current to the Pt anode in the same reactor. UO₂ was electrochemically converted into metallic U after the reaction, indicating the feasibility of the graphite anode at the pilot-scale. However, further investigation should be made, such as increasing the conversion rate, and developing anti-corrosion techniques for a scale-up.

REFERENCES

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