

Experimental Methods for Determining Li₂O Entrainment in Electrolytic Uranium Oxide Reduction

A. J. Burak, M. F. Simpson

University of Utah, Department of Metallurgical Engineering,

William Browning Bldg., 135 S 1460 E, Rm 412, Salt Lake City, UT 84112

adam.burak@utah.edu, michael.simpson@utah.edu

INTRODUCTION

Reprocessing of spent nuclear fuel is important for the sustainability of nuclear power generation. While PUREX is an established process, high temperature electrolytic reprocessing, or pyroprocessing, has many unique advantages.¹ These include a small footprint, reduced risk of criticality accidents, reduced risk of proliferation of weapons-usable materials, no fuel cooling requirement, and avoidance of organic solvents.

Increasing the efficiency of pyroprocessing oxide fuel is important in order to make it economical for commercial spent fuel. Pyroprocessing of oxide fuel involves electrolytic oxide reduction followed by metal fuel electrorefining. Lithium oxide carried over from the oxide reduction cell to the electrorefining cell would be detrimental to the subsequent electrorefining step, as it would scavenge uranium chloride out of the molten LiCl-KCl.² Therefore, minimization of lithium oxide entrainment in the oxide reduction cathode basket is an important goal aimed at increasing process efficiency.

In order to study the transport behavior of lithium oxide in the oxide reduction cell, a method must be developed to analyze the product of the reduction process. Several experimental techniques have been developed in an attempt to characterize the reduced uranium product and are reported in this paper.

RESULTS

Time-Dependent Titration

The first technique developed was time-dependent titration, intended to measure lithium oxide entrained in the particles. Various particle size fractions were electrolytically reduced at 650°C in a lithium chloride-1 wt% lithium oxide molten salt bath. All reduction operations were performed in an argon atmosphere glovebox with <1 ppm water and oxygen. Pictures of the cathode pouches used in these tests are shown in Figure 1.

The reduced product was then analyzed via time-dependent acid-base titration. To initiate these titrations, a beaker was filled with deionized (DI) water and titrated

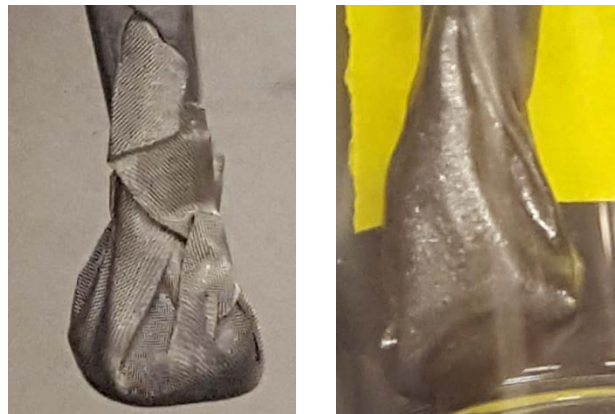
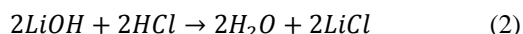
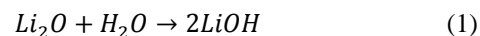


Fig. 1. On the left is the cathode, prior to reduction. On the right is the cathode, after reduction

to a pH of 3 with 0.1 M hydrochloric acid (HCl). Next, the cathode was inserted and the cell was titrated back to 3 pH. The cumulative volume of titrant used was recorded.

The HCl balances the lithium hydroxide produced from dissolving lithium oxide into the water. The volume of HCl can then be related to the moles of lithium oxide. This process is described in Equations (1-4).



$$V_{\text{HCl}} \cdot M_{\text{HCl}} = n_{\text{HCl}} \quad (3)$$

$$\frac{1}{2}n_{\text{HCl}} = n_{\text{Li}_2\text{O}} \quad (4)$$

After an initial fast titration regime, >0.017 ml/s (1 ml/min), the pH was maintained at 3 pH with a slow addition of HCl. The fast regime typically concluded within 1.8×10^3 s (30 min), compared to 1.7×10^5 s (3 days) for the slow regime.

The fast regime was attributed to adhered salt

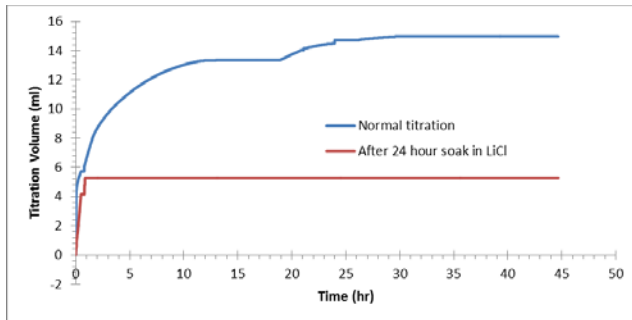


Fig. 2. Validation titration profiles. The upper line is a reduced cathode with no soaking. The lower line is a reduced cathode after soaking in LiCl for 24 hours.

dissolution, whereas the slow regime was attributed to diffusion of lithium oxide out of the particles. This allowed the measurement of lithium oxide entrained within the particles.

Validation of this technique was performed by reducing two cathodes at the same time. One cathode was titrated, as reduced. The second cathode was soaked in pure lithium chloride salt for a day, and then titrated. The slow titration regime was absent from the second titration profile. This supports the hypothesis that the slow regime is attributable to lithium oxide diffusion out of the particles. A comparison of these titration profiles is shown in Figure 2.

Thermogravimetric Analysis

The next technique developed utilized a thermogravimetric analyzer (TGA) to measure reduction extent. In order to establish a baseline, a test was run with pure uranium. A uranium rod was shaved with a diamond coated file in order to remove oxidation. After removing the oxidation layer, a small piece, ~14 mg, was clipped off using wire cutters. This was all performed in an argon atmosphere glovebox with <1 ppm water and oxygen.



Fig. 3. On the left is pure uranium prior to analysis in the TGA. On the right is pure uranium after analysis.

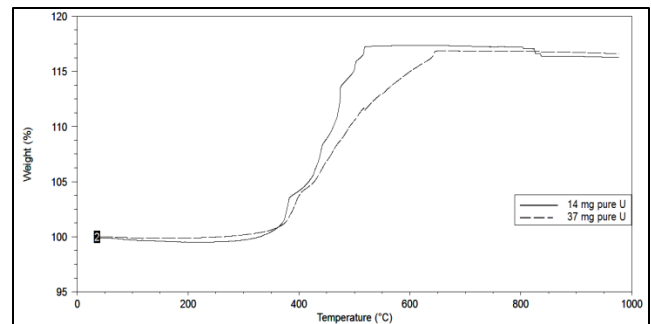


Fig. 4. Change in mass vs temperature for pure uranium samples under flowing air.

The sample was transferred out of the glovebox in a sealed sample container, and then loaded directly into the TGA. It was ramped from ~323 K (50°C) to 1263 K (990°C) at 0.333 K/s (20°C/min), while flowing air at 1.666 ml/s (100 ml/min). Pictures of the sample before and after analysis are shown in Figure 3.

The extent of reduction was calculated by considering the change in mass of the sample from 473-973 K (200-700°C). The final mass can then be related to reduction extent, as shown in Equations (5-8).

$$(m_{\text{initial}} + m_{\text{gained}}) \cdot \frac{\omega_U}{M(U_{238})} = n_U \quad (5)$$

$$M(U_{238}) \cdot (n_U - x) + M(UO_2) \cdot (x) = m_{\text{initial}} \quad (6)$$

$$\frac{m_{\text{initial}} - M(U_{238}) \cdot n_U}{M(UO_2) - M(U_{238})} = x \quad (7)$$

$$\frac{n_U - x}{n_U} = \text{reduction extent} \quad (8)$$

This method of calculation makes a couple of assumptions. It assumes that at the higher temperature, 973 K, the sample has fully converted to U_3O_8 .³ Before the TGA run is initiated, it is assumed that the sample is $U+UO_2$.

The ~14 mg sample was calculated to be 99.5% reduced using this method. Another similar sample of ~37 mg was shown to be 94.0% reduced. This is reasonable, as the second sample was exposed to ambient air while the first test was being performed, ~7200 s (2 hr). The analyses gathered from the TGA using the pure uranium are shown in Figure 4.

Scanning Electron Microscopy

The final technique, still being developed, utilizes energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope (SEM) to characterize oxygen distribution in the cathode product. The cathode basket containing reduced urania is cross-sectioned and mounted onto an SEM stub with a carbon tab.

The locations of the particles are determined using

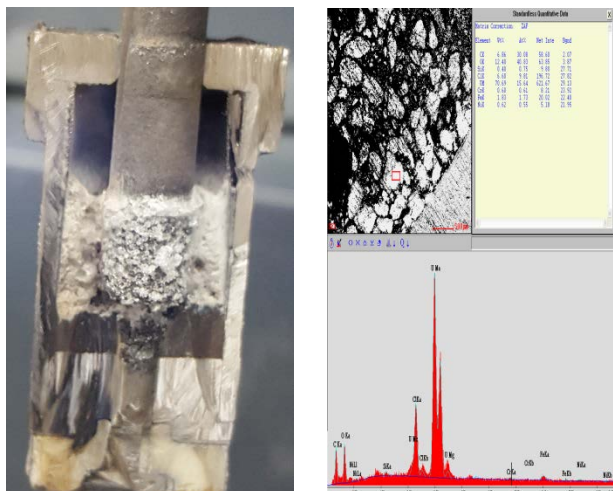


Fig. 5. On the left is a picture of the cathode after it has been cross-sectioned. On the right is the EDS analysis of a particle in the cathode basket.

the backscattered electron detector of the SEM. The oxygen content, with respect to position, can then be measured using EDS. The oxygen distribution of the cathode basket and the individual particles themselves can then be measured. Preliminary work has been completed in an attempt to assess the feasibility of this technique.

Images gathered throughout this process are shown in Figure 5. The optical image clearly shows the different materials—including urania (brownish colored in the middle), salt, ceramics, and stainless steel. The SEM image in the upper right shows the urania particles. An EDS scan of one of the particles gave the result of 71 wt% uranium and 12 wt% oxygen indicating either the reduction efficiency of this cathode product was very low, or significant lithium oxide entrainment.

SUMMARY

Through a combination of these techniques, the cathode product in this process can be effectively characterized. Time-dependent titration may be used alone to assess Li_2O entrainment, or in combination with EDS, to elucidate Li_2O distribution. TGA may be used to determine the composition of the product, post-reduction. Effective characterization of the cathode product will facilitate the study of the transport behavior of lithium oxide in the oxide reduction cell.

NOMENCLATURE

m_j =mass at condition j

M_i =Molarity of species i

$M(i)$ =molecular weight of species i

n_i =number of moles of species i

V_i =Volume of species i

ω_i =mass fraction of species i

x = some variable x

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