Reaction Rate of Porous UO_2 Pellets for Electrolytic Reduction

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1. Introduction

In order to adopt the previously established metal fuel based pyroprocessing in PWR (Pressurized Water Reactor) oxide fuels, electrolytic oxide reduction (OR) step is essential. The OR process under intensive research at KAERI employs LiCl salt with 1 ~ 3 wt% of Li_2O. It is widely accepted that Li_2O is electrochemically decomposed to produce metallic Li and oxygen gas and then Li reacts with UNF (Used Nuclear Fuel) oxides to produce Li_2O as following equations.

Cathode:

$2Li_2O + 4e^- \rightarrow 4Li + 2O^{2-}$ (electrochemical) (1)

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

Anode:

$2O^{2-} \rightarrow O_2(g) + 4e-$ (electrochemical) (3)

This reaction scheme is very attractive because the amount of Li_2O is kept constant until the reactant (UNF) is depleted. However, unlike direct electrochemical reaction, actual reduction rate is determined by the chemical reaction (2), which is not detectable in-situ. In the present study, the reduction reaction rate of porous UO_2 pellets was quantitatively investigated.

2. Experimental

Each experiment was performed with 9 porous UO_2 pellets (average 15.7 g) at 650°C using LiCl salt containing 1.4 ~ 1.5 wt% of Li_2O. The pellets had cylindrical shape with 7.65 mm (H), 5.74 mm (D), and 8.79 g/cm^3 (density). Reaction rate was analyzed by producing samples which undergone various number of charge cycles, where one cycle is composed of 30 minutes of 3.2 V cell potential and 10 minutes of power-off. Largest amount of charge applied was 45,000 C. Degree of reduction was determined by analyzing center-cut image of the samples. The concentration of Li-Li_2O was determined by the HCl titration technique.

3. Results and Discussion

In order for quantitative comparison of the reaction rate, the term 'degree of reduction' was defined as following:

$$\alpha = 1 - \left(\frac{r}{r_0}\right)^2 \quad (4)$$

where r_0 is the radius of a whole pellet and r is the radius of remaining oxide part. Measured values for various Q (applied charge) are shown in Fig. 1.

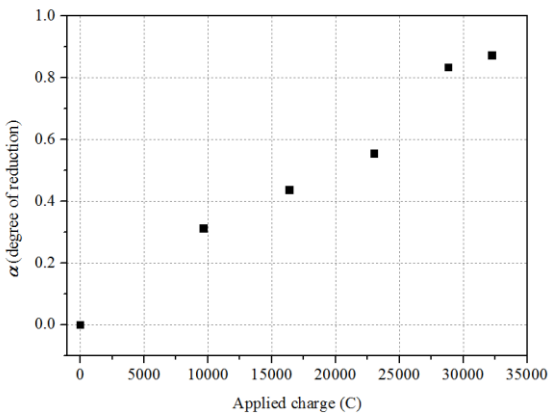

Fig. 1. Degree of reduction as a function of applied charge.

The Sharp-Hancock plot was derived using the data of Fig. 1 to identify the most suitable geometry function [1]. The Sharp-Hancock plotting revealed a slope of 0.88 in the region of $0 \leq \alpha \leq 0.56$. This result suggested reaction models of 1) first-order (slope = 1.00), 2) contracting area (slope = 1.07), and 3) 1-D diffusion (slope = 0.62).

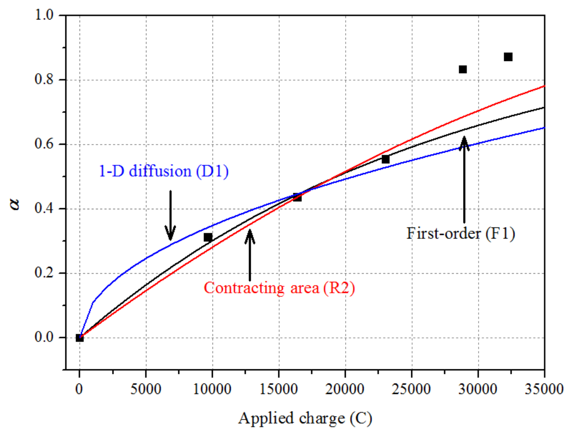

Fig. 2. Fitting results for three geometry functions.

Fitting results for the suggested reaction models are shown in Fig. 2, where the first-order reaction model was identified as the best geometry function to describe the reduction rate of porous UO_2 pellets.

The reduction rate equation of porous UO_2 pellets could be described as:

$$\alpha = 1 - e^{-(3.59 \times 10^{-5} \times Q)} \quad (0 \leq \alpha \leq 0.56) \qquad (5)$$

where Q stands for the amount of applied charge (in C) [2].

4. Conclusion

The reduction rate equation for porous UO_2 pellets was derived using repeated experimental data, which revealed that the first-order reaction model is the geometry function to describe this system.

REFERENCES

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