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Complete reduction of high-density UO_2 to metallic U in molten $Li_2O-LiCl$

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ABSTRACT

The large size and high density of spent fuel pellets make it difficult to use the pellets directly in electrolytic reduction (also called as oxide reduction, OR) for pyroprocessing owing to the slow diffusion of molten $Li_2O-LiCl$ salt electrolyte into the pellets. In this study, we investigated complete OR of high-density UO_2 to metallic U without any remaining UO_2. Only partial reductions near the surface of high-density UO_2 pellets were observed under operation conditions employing fast electrolysis rate that allowed previously complete reduction of low-density UO_2 pellets. Complete reduction of high-density UO_2 pellets was observed at fast electrolysis rate when the pellet size was reduced. The complete reduction of high-density UO_2 pellets without size reduction was achieved at slow electrolysis rate, which allowed sufficient chemical reduction of UO_2 with the lithium metal generated by the cathode reaction.

1. Introduction

Accumulation of spent nuclear fuel from nuclear power plants is a core challenge in nuclear energy technology. Pyroprocessing technology has been developed for recycling of the spent fuel into metal fuel for fast nuclear reactors by converting the spent oxide fuel into U/TRU (uranium/transuranium) metal ingots via electrochemical processes utilizing high-temperature molten salt. These electrochemical processes employ electrolytic reduction (also referred to as oxide reduction, OR) for the reduction of spent oxide fuel to metal, and electrorefining for the recovery of U/TRU [1–9].

Generally, molten LiCl containing Li_2O at 650 °C is used as the electrolyte in the OR process. The spent oxide fuels, loaded in a permeable basket, and platinum (Pt) are used as the cathode and anode, respectively. The cathode reactions (1–3) can be summarized as follows:

$$Li^+ + e^- \rightarrow Li \quad (1)$$

$$MO_2 + 4Li \rightarrow M + 2Li_2O\ (\textit{salt phase}) \quad (2)$$

$$MO_2 + 4e^- \rightarrow M\ (\textit{actinide}) + 2O^{2-}\ (\textit{salt phase}) \quad (3)$$

Li_2O produced by reaction (2) in molten LiCl dissociates into Li^+ and O^{2-}:

$$Li_2O \rightarrow 2Li^+ + O^{2-}\ (\textit{salt phase}) \quad (4)$$

The anode reaction can be described as follows:

$$2O^{2-}\ (\textit{salt phase}) \rightarrow O_2\ (\textit{gas}) + 4e^- \quad (5)$$

When the electrical potential to produce the Li metal without the decomposition of LiCl is applied, the actinide metal oxide is reduced to metal and remains at the cathode. The oxygen ions (O^{2-}) produced at the cathode are transported through the salt and discharge at the anode to form O_2 gas [10–17]. Hence, the diffusion of O^{2-} ions from the inside of the oxide fuel to the bulk salt affects significantly the reduction rate and current efficiency during the OR process [18].

Since the spent cylindrical oxide fuel pellets separated from the cladding is large and dense [19,20], they are unsuitable for direct use in the OR process as a result of the slow diffusion of $Li_2O-LiCl$ salt into the pellets. Hence, a head-end process is typically required to convert the pellets into an appropriate feed material, with

Abbreviations: EDX, energy dispersive X-ray; OR, oxide reduction; SEM, scanning electron microscopy; SS, stainless steel; TG, thermogravimetry; TRU, transuranium.

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smaller size or lower density, in order to ensure fast diffusion of the salt from the inside of the fuel to the bulk salt, and thus also efficient OR reactions. In our previous works [17,21,22], we demonstrated the excellent reduction of porous UO_2 pellets with small size and low density (compared to those of spent oxide fuel pellets), which were prepared using a head-end process. Nevertheless, the head-end process, which involves powdering, pelletizing under high pressure (>200 MPa), and sintering at high temperature (>1200 °C) is inevitably associated with loss of fuel material. Moreover, the steps associated with the head-end process increase the cost of pyroprocessing. Motivated by the disadvantages of porous pellets, we wished to probe the reducibility of original, high-density spent oxide fuel. To this end, therefore, we investigated in this study the possibility of complete OR of high-density UO_2 to U metal. The dimensions and density of the UO_2 pellets employed here were ϕ 8.3 mm × 9.9 mm (H) and 10.67 g/cm^3, respectively—i.e., values that are similar to those of the spent fuel pellets obtained from pressurized water reactors [19,20]. The conducted OR runs are listed in Table 1. Initially, the reduction behaviors of UO_2 pellets with low (Run P-1) and high densities (Run D-1) were compared by analyses of the reduction products obtained under similar OR operation conditions. Subsequently, we examined two approaches for the complete reduction of high-density UO_2 pellets: (i) reduction of pellet size (Run D-2 and D-3) and (ii) decrease in electrolysis rate (Run D-4 and D-5).

2. Experimental

LiCl is very hygroscopic, and for this reason all experiments utilizing LiCl were performed in a high-purity argon atmosphere glove box in which the concentrations of oxygen and moisture were controlled to be less than 5 ppm. LiCl (99% purity) and Li_2O (99.5% purity) were purchased from Alfa Aesar. Thermal dehydration of LiCl was performed prior to its use by heating to a temperature of 650 °C at a linear heating rate of 0.5 °C/min under low pressure (<1 Torr), and subsequent cooling. The density and size of the high-density pellets used in this study were 10.67 g/cm^3 and ϕ 8.3 mm × 9.9 mm (H), respectively (inset of Fig. 1a). By contrast, the

Table 1
List of OR runs conducted in this study and their characteristics.

OR run	Purpose	Characteristics of the used UO_2		Voltage for electrolysis			Reduction results	
		Type (density, g/cm^3)	Size (mm)	Cell (V)	On time (min)	Off time (min)	Reduction	Li_2O conc. [wt.%]
Run P-1	Low *vs* high density	Low-density (3.6)	ϕ 6.4 × 6.2 (H)	3.2	10–20	5–10	Complete	1.0 → 0.98
Run D-1		High-density (10.5)	ϕ 8.3 × 9.9 (H)				Incomplete	1.0 → 0.68
Run D-2	Pellet size		ϕ 8.3 × 4–5 (H)				Incomplete	1.0 → 0.90
Run D-3			ϕ 8.3 × 2–3 (H)				Complete	1.0 → 0.97
Run D-4	Electrolysis rate		ϕ 8.3 × 9.9 (H)	3.0	3	15	Incomplete	1.0 → 0.70
Run D-5					5	25	Complete	1.0 → 0.85

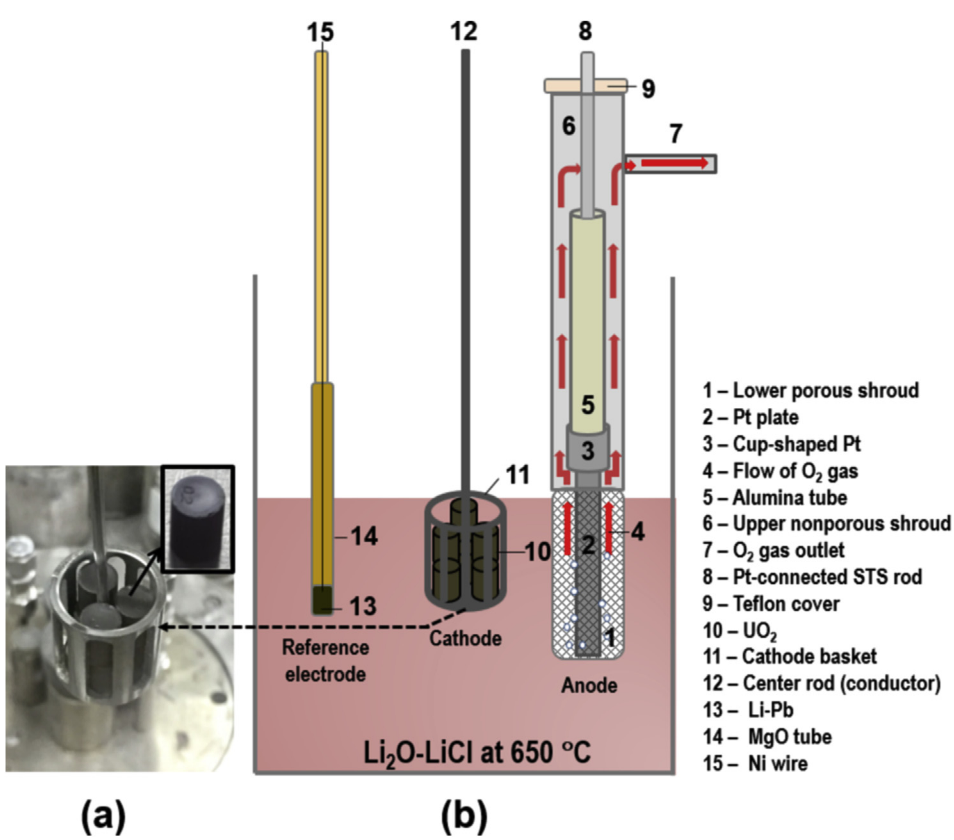

Fig. 1. OR cell set-up: (a) an image of cathode basket containing the cylindrical high-density UO_2 pellets (inset: UO_2 pellet) and (b) its schematic representation.