Available online at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

Chemical Stability of Conductive Ceramic Anodes in LiCl–Li_2O Molten Salt for Electrolytic Reduction in Pyroprocessing

Sung-Wook Kim [a,b,*], *Hyun Woo Kang* [a], *Min Ku Jeon* [a,b], *Sang-Kwon Lee* [a], *Eun-Young Choi* [a], *Wooshin Park* [a], *Sun-Seok Hong* [a], *Seung-Chul Oh* [a], *and Jin-Mok Hur* [a]

[a] *Nuclear Fuel Cycle Process Development Group, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Republic of Korea*

[b] *Department of Quantum Energy Chemical Engineering, University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea*

ARTICLE INFO

Article history:
Received 28 January 2016
Received in revised form
25 February 2016
Accepted 2 March 2016
Available online 19 March 2016

Keywords:
Anode
Conductive Ceramics
Electrolytic Reduction
Lanthanum Strontium Manganese Oxide
Molten Salt
Pyroprocessing
Spent Oxide Fuels

ABSTRACT

Conductive ceramics are being developed to replace current Pt anodes in the electrolytic reduction of spent oxide fuels in pyroprocessing. While several conductive ceramics have shown promising electrochemical properties in small-scale experiments, their long-term stabilities have not yet been investigated. In this study, the chemical stability of conductive $La_{0.33}Sr_{0.67}MnO_3$ in LiCl–Li_2O molten salt at 650°C was investigated to examine its feasibility as an anode material. Dissolution of Sr at the anode surface led to structural collapse, thereby indicating that the lifetime of the $La_{0.33}Sr_{0.67}MnO_3$ anode is limited. The dissolution rate of Sr is likely to be influenced by the local environment around Sr in the perovskite framework.
Copyright © 2016, Published by Elsevier Korea LLC on behalf of Korean Nuclear Society. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The accumulation of spent oxide fuels used in nuclear power plants has become a global issue because of their long lifetime and radiotoxicity [1,2]. However, spent oxide fuels have several reusable radioactive species such as U, Pu, and other trans-uranic elements that can be recovered. Pyroprocessing is being considered as a method to manage and recycle the spent oxide

* *Corresponding author.*
E-mail address: swkim818@kaeri.re.kr (S.-W. Kim).
http://dx.doi.org/10.1016/j.net.2016.03.002
1738-5733/Copyright © 2016, Published by Elsevier Korea LLC on behalf of Korean Nuclear Society. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

fuels [3–5]. Pyroprocessing includes several electrochemical processes, such as electrolytic reduction, electrorefining, and electrowinning [3]. The spent oxide fuels can be reduced to metallic states through electrolytic reduction. Metal oxides (e.g., UO_2) are electrochemically dissociated into metals (e.g., U) at the cathode, and O_2 gas at the anode, during electrolytic reduction using LiCl–Li_2O molten salt at 650°C [6]. The metal products are then recovered using electrorefining and electrowinning processes for the fabrication of the metal fuels which could be used in next-generation sodium-cooled fast reactors [3–5].

Pt is the most commonly used anode material in electrolytic reduction because of its excellent electrochemical activity and superior oxidation resistance at high temperatures (approx. 650°C) [6,7]. However, the Pt anode is gradually damaged during the electrolytic reduction in the LiCl–Li_2O molten salt, owing to side reactions (e.g., $Pt + 3O^{2-} + 2Li^{+} = Li_2PtO_3 + 4e^{-}$ or $Pt = Pt^{2+} + 2e^{-}$) [6]. Additionally, Pt is one of the most expensive materials, thus alternative anode materials are needed for use in the LiCl–Li_2O molten salt system [8–12].

Conductive ceramics are potential candidates for use as O_2-evolving anode materials because of their stability in the presence of high-temperature O_2 gas [8–10]. Recent studies have revealed that several conductive ceramics such as TiN, Ni_xFeO_y, and $La_{0.33}Sr_{0.67}MnO_3$ can electrochemically reduce metal oxides to metals in the LiCl–Li_2O molten salt at 650°C [8–10]. However, the TiN anode significantly degrades during electrolytic reduction owing to the formation of pores, indicating its poor stability [8]. It has been claimed that Ni_xFeO_y can be chemically transformed to NiO and Li(Ni, Fe)O_2 at the surface (e.g., $NiFe_2O_4 = NiO + 2LiFeO_2$) during electrolytic reduction, without degradation in its electrochemical performance [9]. No noticeable phase change or physical degradation was found in the $La_{0.33}Sr_{0.67}MnO_3$ anode after a small-scale experiment [10]. However, the long-term stability of ceramic anodes is an important issue for the scale-up of the electrolytic reducer.

In this study, we investigated the chemical stability of $La_{0.33}Sr_{0.67}MnO_3$ to evaluate its long-term stability in the molten salt electrolyte. First, $La_{0.33}Sr_{0.67}MnO_3$ was immersed into LiCl–Li_2O molten salt under O_2 bubbling for 7 days. Its structural changes and dissolution behavior was then examined. The chemical stabilities of $SrRuO_3$ and $LaNi_{0.6}Fe_{0.4}O_3$, which have similar crystal structures and elements to $La_{0.33}Sr_{0.67}MnO_3$, were also investigated for comparison.

2. Materials and methods

The chemical stability of sintered $La_{0.33}Sr_{0.67}MnO_3$ (Toshima Manufacturing Co., Ltd, Japan) was evaluated using 300 g of LiCl–Li_2O (1 wt.% of Li_2O; Alfa Aesar, A Johnson Matthey Company, USA) molten salt at 650°C. Rectangular $La_{0.33}Sr_{0.67}MnO_3$ (approx. 6 × 2.5 × 0.6 cm) was immersed into the molten salt (immersion depth: approx. 3 cm) and then stored for 7 days under continuous O_2 bubbling (Fig. 1) to create an oxidative environment. The immersed $La_{0.33}Sr_{0.67}MnO_3$ was rinsed with distilled water to remove any residual salt. X-ray diffraction (XRD; Bruker Corporation, D8 Advances, Germany) and energy-dispersive X-ray spectroscopy (EDS; Horiba, Ltd, X-MAX, Japan) coupled with scanning electron microscopy (Hitachi, Ltd, SU-8010, Japan) were used to identify phase stability and atomic distribution before and after the immersion. Another immersion experiment was performed for 1 day (without O_2 bubbling) to evaluate the cation (e.g., La, Sr, and Mn) dissolution behavior in the molten salt (3.9 g of $La_{0.33}Sr_{0.67}MnO_3$ in 300 g of LiCl–Li_2O). Elemental analysis of the $La_{0.33}Sr_{0.67}MnO_3$-immersed molten salt was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to examine the cation composition of LiCl–Li_2O. Additional 1-day immersion tests were carried out on a sintered $SrRuO_3$ (LTS Chemical Inc., USA) and $LaNi_{0.6}Fe_{0.4}O_3$ powder (Kceracell, Co., Ltd, South Korea) for comparison.

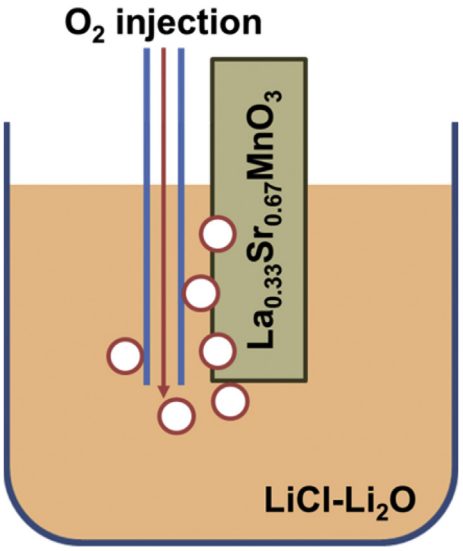

Fig. 1 – Schematic illustration of the experimental set-up for the long-term stability test of $La_{0.33}Sr_{0.67}MnO_3$ with O_2 bubbling.

3. Results and discussion

Figs. 2A and 2B show the mechanical instability of $La_{0.33}Sr_{0.67}MnO_3$ in the LiCl–Li_2O molten salt. The surface of the sintered $La_{0.33}Sr_{0.67}MnO_3$ was destroyed after immersion in the molten salt for 7 days under O_2 bubbling. To investigate the origin of this destruction (either thermal stress or chemical reaction), the chemical stability of $La_{0.33}Sr_{0.67}MnO_3$ before and after the immersion was examined with scanning electron microscopy-EDS and XRD (Figs. 2C and 2D). Surprisingly, no Sr was detected in several regions on the delaminated $La_{0.33}Sr_{0.67}MnO_3$ samples (Fig. 2C), indicating that Sr was dissolved into the molten salt during the immersion. XRD patterns shown in Fig. 2D confirm the structural change of the $La_{0.33}Sr_{0.67}MnO_3$ phase. This implies that the structural change induced by Sr dissolution is the dominant factor in the collapse of the $La_{0.33}Sr_{0.67}MnO_3$ phase.

Pristine $La_{0.33}Sr_{0.67}MnO_3$ possesses a well-known perovskite structure (Fig. 2D). However, it seems that the secondary phase (as indicated by the circle shown in Fig. 2D) appeared around the original peaks during the immersion, and the

Download English Version:

https://daneshyari.com/en/article/1739840

Download Persian Version:

https://daneshyari.com/article/1739840

Daneshyari.com