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Original Article

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

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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.

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

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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.

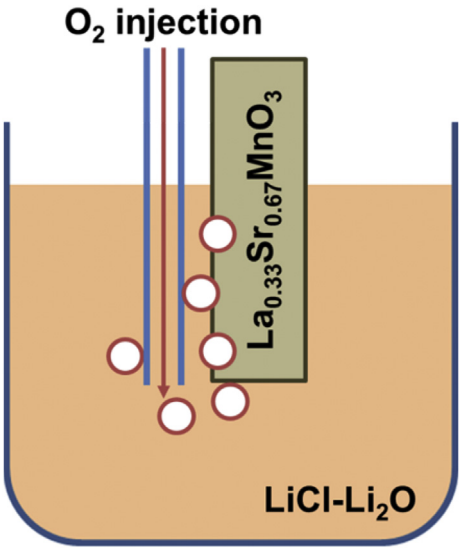

Fig. 1 – Schematic illustration of the experimental set-up for the long-term stability test of $La_{0.33}Sr_{0.67}MnO_3$ with O_2 bubbling.

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

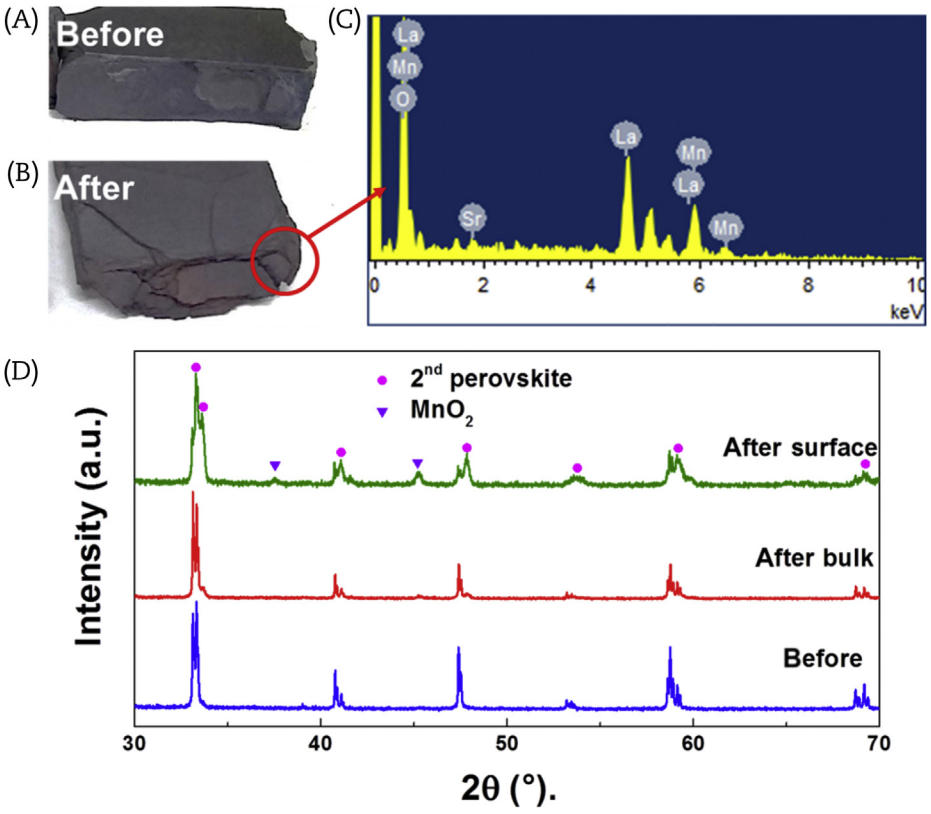

Fig. 2 – Photographs of sintered $La_{0.33}Sr_{0.67}MnO_3$. (A) Before immersion in LiCl–Li_2O for 7 days with O_2 bubbling. (B) After immersion in LiCl–Li_2O for 7 days with O_2 bubbling. (C) Energy dispersive X-ray spectroscopy result of the delaminated region in immersed $La_{0.33}Sr_{0.67}MnO_3$. (D) X-ray diffraction patterns of $La_{0.33}Sr_{0.67}MnO_3$ before and after immersion. a.u., arbitrary unit.

intensity of the secondary peaks became higher in the delaminated area, compared with that in the bulk area after the immersion. Hence, it is thought that the phase change is more favored near the surface, leading to the collapse of $La_{0.33}Sr_{0.67}MnO_3$ at the surface. The overall diffraction pattern of the secondary phase resembles that of the pristine materials, suggesting a similar crystal structure of the secondary phase to the original one. Hence, the secondary phase is believed to be the off-stoichiometric perovskite-like La–Mn–O phase (Sr-free/deficient). In addition, a third phase (as indicated by the reverse-triangle shown in Fig. 2D), whose peak position does not match that of the perovskite, can be seen after the immersion. This phase is likely to be MnO_2 (PDF#42-1169), which can be formed owing to the presence of excess Mn compared with La.

The cation dissolution behavior of $La_{0.33}Sr_{0.67}MnO_3$ was quantitatively studied using ICP-AES, as summarized in Table 1. After a 1-day immersion (without O_2 bubbling), 128 ppm of Sr were detected in the molten salt, while compositions of La and Mn were not less than the detection limit. This result agrees with the EDS analysis, demonstrating the dissolution behavior of Sr (Fig. 2C). The amount of dissolved Sr in LiCl–Li_2O was approximately 0.038 g, while that in the pristine material was approximately 1.10 g (approx. 3.45% loss per day). Such a dissolution rate is likely to be problematic for long-term use of $La_{0.33}Sr_{0.67}MnO_3$ (simply, approx. 50% loss after 20 days).

Table 1 – Summary of the inductively coupled plasma-atomic emission spectrometry results of the LiCl–Li_2O molten salt after immersion of $La_{0.33}Sr_{0.67}MnO_3$ and $LaNi_{0.6}Fe_{0.4}O_3$ for 1 day each (unit: ppm).

Element	La	Mn	Sr	Ni	Fe
$La_{0.33}Sr_{0.67}MnO_3$	N/A	N/A	~128	–	–
$LaNi_{0.6}Fe_{0.4}O_3$	N/A	–	–	~10	~10

For comparison, the dissolution behavior of a Sr-rich perovskite, $SrRuO_3$, was studied. The sintered $SrRuO_3$ was completely lost and a powdered product was obtained after the immersion, as shown in Figs. 3A and 3B. The XRD data depicted in Fig. 3C clearly shows that the $SrRuO_3$ phase was eliminated during the immersion to form a metallic Ru phase. This means that the dissolution rate of Sr in $SrRuO_3$ is much faster than that in $La_{0.33}Sr_{0.67}MnO_3$. Therefore, the dissolution behavior of Sr is not solely affected by the Sr element itself, but is also strongly related to the local environment surrounding Sr.

The chemical stability of the Sr-free perovskite compound, $LaNi_{0.6}Fe_{0.4}O_3$, was also investigated, as shown in Fig. 4 and Table 1. Despite the absence of Sr in the $LaNi_{0.6}Fe_{0.4}O_3$ structure, a more severe structural degradation occurred compared with that seen in $La_{0.33}Sr_{0.67}MnO_3$ (Fig. 4). ICP-AES analysis showed that both Ni and Fe were soluble in the LiCl–Li_2O molten salt, as shown in Table 1. La composition was less than

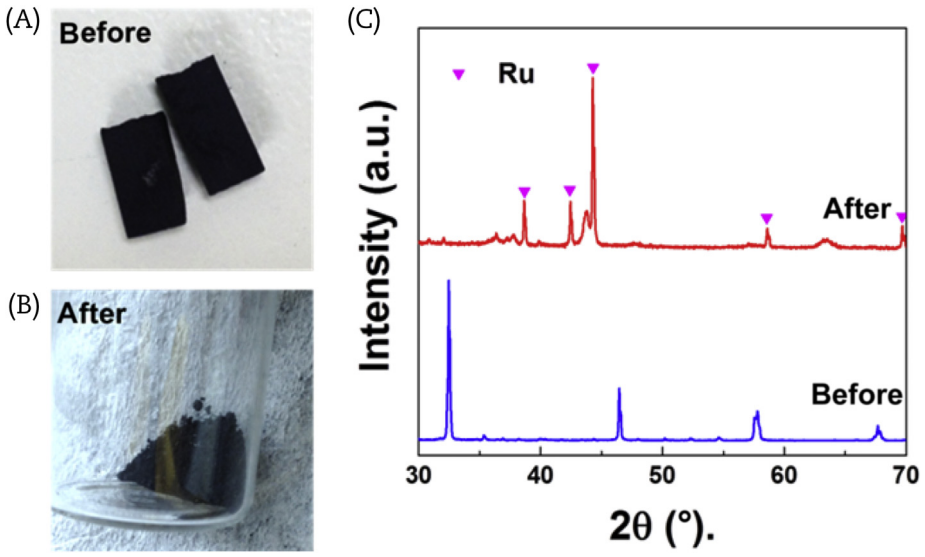

Fig. 3 – Photographs of sintered $SrRuO_3$. (A) Before immersion in LiCl–Li_2O for 1 day. (B) After immersion in LiCl–Li_2O for 1 day. (C) The corresponding X-ray diffraction pattern. a.u., arbitrary unit.

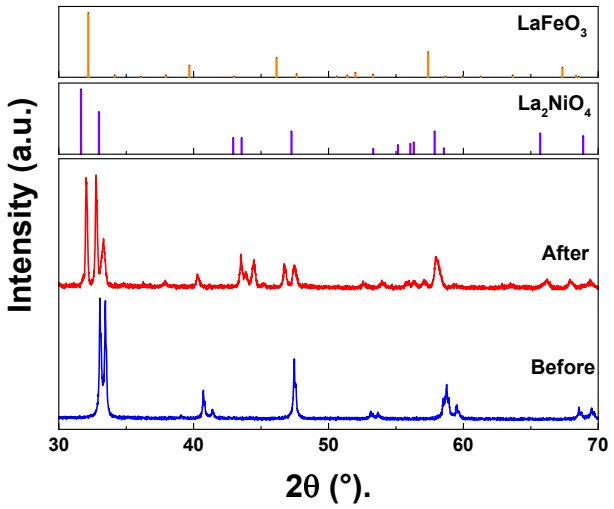

Fig. 4 – X-ray diffraction patterns of $LaNi_{0.6}Fe_{0.4}O_3$ before and after immersion in LiCl–Li_2O for 1 day. a.u., arbitrary unit.

the detection limit after the immersion, similar to $La_{0.33}Sr0_{.67}MnO_3$, implying a high stability of La in LiCl–Li_2O. It is interesting that the structural change of $LaNi_{0.6}Fe_{0.4}O_3$ is more drastic than that of $La_{0.33}Sr_{0.67}MnO_3$ in spite of the lesser amount of Ni/Fe dissolution. This probably occurred because $LaNi_{0.6}Fe_{0.4}O_3$ separated into Ni-rich (La_2NiO_4-like) and Fe-rich ($LaFeO_3$-like) phases. It is thought that the perovskite $LaNi_{0.6}Fe_{0.4}O_3$ phase cannot be stabilized, even with a small amount of cation dissolution.

4. Conclusion

Chemical stabilities of conductive ceramics ($La_{0.33}Sr_{0.67}MnO_3$, $SrRuO_3$, and $LaNi_{0.6}Fe_{0.4}O_3$) in the LiCl–Li_2O molten salt were investigated to examine their feasibility as long-term stable anode materials in electrolytic reduction. Cation dissolution (e.g., Sr, Ni, and Fe) is a dominant factor affecting the chemical instability of these compounds. It seems that the dissolution rate of the cations varies depending on the local environment as well as the type of the elements. La and Mn remained stable in the perovskite structure in the LiCl–Li_2O molten salt. Hence, the Sr-free/deficient La–Mn–O phase may be promising as a long-lasting anode material, but its electrical conductivity, electrochemical activity, and mechanical stability should be considered.

Conflicts of interest

All authors have no conflicts of interest.

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