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A perovskite-structured aluminium-substituted lithium lanthanum titanate as a potential artificial solid-electrolyte interface for aqueous rechargeable lithium-metal-based batteries

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An aluminium-doped lithium lanthanum titanate (A-LLTO) solid electrolyte was prepared using a simple citrate-gel method, and this was followed by a pelletization and the conventional sintering process. When the sintering time was varied at 1350°C for the synthesis of the A-LLTO, the A-LLTO ceramic that was sintered at 1350°C for 6 h exhibited the highest ionic conductivity of $3.17 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 25°C. In addition, the stability and durability of the synthesized A-LLTO ceramic was tested through a one-month aqueous-solution immersion for which the pH values were varied between 0 and 14. The stability of the A-LLTO is the highest in the alkaline environment; furthermore, for its use in the aqueous-electrolyte environment, a protected lithium electrode (PLE) structure was made by combining the lithium (Li) metal, a lithium phosphorous oxynitride (LiPON) interlayer, and the A-LLTO, whereby the LiPON interlayer prevented a direct reaction between the Li metal and the A-LLTO. The Li-$LiCoO_2$ and Li-O_2 cells comprising the PLE exhibited a superior electrochemical performance when they were used in the alkaline 1 M $LiNO_3$-electrolyte environment. After 100 cycles of the charge-discharge at the 1C rate, the aqueous Li-$LiCoO_2$ cells maintained 59.3% of the initial capacity with a coulombic efficiency of 98.3%. In addition, the aqueous Li-O_2 cell operated stably for 40 cycles under the limited capacity mode of $0.5\,\mathrm{mAh\,cm^{-2}}$. The outstanding performance of the Li-metal-based cells originates from the A-LLTO solid electrolyte, due to the latter's high stability, ionic conductivity, and an effective suppression effect regarding the dendritic growth of the Li.

1. Introduction

With the increasing mobile electrical-energy demand regarding electronic devices, the further development of battery systems with a high safety and energy density is urgently needed [1–3]. Currently, the rechargeable lithium-ion batteries (LIBs) for which organic electrolytes are employed have been the main energy resource for portable equipment, consumer electronic devices, and high-power applications such as electric vehicles and the energy storage for renewable energy [4]. Despite the excellent performance of the organic LIBs, their application as a large-scale energy-storage system has been limited by a number of issues regarding the specific energy, fabrication cost, and safety concerns (toxicity and flammability of the liquid electrolytes). The use of aqueous electrolytes has consequently been proposed as a promising alternative for the organic electrolytes, since a water-based battery system is economical, safe, and environmentally friendly [5].

To date, lithium (Li) metal has been considered as the most-promising anode material for rechargeable batteries owing to its extremely high theoretical specific capacity ($3860\,\mathrm{mAh\,g^{-1}}$), low density ($0.59\,\mathrm{g\,cm^{-3}}$), and the lowest-known electrode potential (-3.04 V vs. standard hydrogen electrode) [6–8]. The development of rechargeable batteries for which the Li-metal anode is employed, however, has not yet materialised, since the Li-metal electrode suffers from the following drawbacks, among others: (i) The formation of Li dendrites during the charge-discharge process, leading to internal short circuits in the batteries; (ii) a low coulombic efficiency due to the formation of dead Li [7], and (iii) the corrosion or contamination of the Li metal by impurity gases for open-type batteries such as the lithium-air (Li-air) battery. To solve these issues, several solutions have been proposed. Among them, the suppression of the Li-dendrite growth through the use of solid electrolytes has been demonstrated [9–11]. In particular, for

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the rechargeable Li-metal-based batteries for which aqueous electrolytes are used, such as the aqueous Li-air batteries [12,13] and the aqueous LIBs [14], it is necessary to protect the Li-metal electrode from water or the impurity gases through the employment of a solid-electrolyte membrane with a high stability and ionic conductivity.

Aqueous electrolyte batteries with Li metal electrodes were first investigated by Littauer and Tsai [15,16], in whose system a protective LiOH film was formed. This film acted as an artificial SEI membrane for the Li metal electrode. However, it existed in a state of quasi-equilibrium over a wide range of current densities in 3.8–5 M LiOH solutions. Several categories of lithium-ion conducting solid electrolytes have been subsequently developed to protect Li metal electrodes from aqueous environments. These include LISICON [17], NASICON [18], Garnet [19], Si wafers [20], and Perovskite [21]. To date, the most successful Li-air battery solid electrolytes are commercial NASICON-type glass-ceramics $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or LTAP, Ohara Inc., Japan) with ionic conductivities of 1 to 4×10^{-4} S cm^{-1} [22]. LTAP solid electrolytes are popular because of their high Li^+-ion conductivities and mechanical strengths, as well as their chemical stability in water. Unfortunately, they are stable only in mild acids and bases [22]. Meanwhile, the electrolyte is alkalised during the operation of aqueous Li-air batteries due to the formation of LiOH (in alkaline media) or consumption of H^+ (in acidic media) via the following reactions:

Negative electrode: $Li \leftrightarrow Li^+ + e^-$ (1)

Positive electrode: $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ (acidic media) (2)

$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$ (alkaline media) (3)

The over cell reaction: $4Li + O_2 + 4H^+ \leftrightarrow 2Li^+ + 2H_2O$ (acidic media) (4)

$4Li + O_2 + 2H_2O \leftrightarrow 4LiOH$ (alkaline media) (5)

An alternative to LTAP that is stable in highly basic electrolytes is necessary for long-term battery operation.

Although perovskite-structured $Li_{3x}La_{(2/3)-x}\square_{(1/3)-2x}TiO_3$ (LLTO) exhibits a high bulk ionic conductivity of 10^{-3} S cm^{-1} at room temperature, the conductivities of most solid electrolytes are relatively low, often less than 10^{-4} S cm^{-1}, due to high grain boundary resistance. A derivative (A-LLTO) of the LLTO solid electrolyte was obtained by doping LLTO with aluminium and adding excess Li_2O. The total ionic conductivity of the resulting material can be comparable to that of commercial LTAP [23]. Inaguma and co-workers recently demonstrated the successful use of LLTO ceramics in aqueous Li-air batteries that use an alkaline solution as an electrolyte. In addition, comprehensive investigations of LLTO stability in various aqueous media have been insufficient.

In the previous work, the effect of excess Li_2O addition on the ionic conductivity of Al-doped LLTO (denoted as "A-LLTO") was reported [10]. The addition of the excess Li_2O facilitated a crystalline-grain growth in the A-LLTO ceramics, leading to the improved conductivity of the A-LLTO; alternatively, it is expected that the Li content as well as the grain size of the A-LLTO can be controlled by the varying of the sintering time that is an important process parameter. In this study, influence of the sintering time on the microstructure and ionic conductivity of the A-LLTO ceramic was examined. Further, the stability and durability of the A-LLTO in the aqueous solutions ranging from acidic, neutral and basic media were evaluated. The electrochemical performance of the A-LLTO as an artificial solid-electrolyte interface (SEI) layer for the Li-metal electrode in terms of rechargeable Li-metal-based batteries for which the aqueous electrolytes are employed was investigated also.

2. Experimental

2.1. Preparation of the A-LLTO

The aluminium-substituted lithium lanthanum titanate (A-LLTO) was synthesised using the citrate-gel method. Nitrate salts comprising $LiNO_3$, $Al(NO_3)_3 \cdot 9H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and citric acid (CA) were weighed for a $(Li_{0.33}La_{0.56})_{1.005}Ti_{0.99}Al_{0.01}O_3$ stoichiometry, dissolved into deionised (DI) water, and then blended with a mixture solution of titanium isopropoxide and ethylene glycol (EG) to form the A-LLTO sol. Extra 20 mol.% $LiNO_3$ was also introduced to compensate for the lithium loss that is due to the volatilization of the lithium-oxide during the synthesis. The EG:CA:total cation molar ratio was controlled to approximately 15:3:1. Then, the sol solution was gelated at 70°C for 12 h and dried at 100°C until it was transferred into brown resin. The A-LLTO powder was obtained by calcining the resin at 350°C for 6 h, followed by an annealing at 750°C for 3 h. Lastly, the A-LLTO powder was pressed into pellets at 350 MPa and then sintered at 1350°C for various times from 3 h to 12 h. To prevent the lithium loss, the pellets were covered with the sacrificial powders of the same composition prior to the sintering.

2.2. Microstructural and electrochemical characterization

The crystalline phase of the A-LLTO ceramic pellets was identified using X-ray diffraction (XRD; D/MAX Ultima III, Rigaku diffractometer with a Cu Kα radiation source). The microstructure of the ceramic samples was observed using field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700). The actual compositions of the A-LLTO ceramics were determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES; OPTIMA 8300 DV). The A-LLTO ceramic pellets were ground into powder, and then dissolved in the melt of NaOH and Na_2O_2 in a zirconium crucible and cooled to room temperature. Finally, concentrated aqueous HCl and DI water were added to form transparent solutions prior to ICP-AES analysis. In addition, the volumetric density of the A-LLTO was measured using Archimedes method. All samples were weighed using high quality digital balances with accuracies of 10^{-4} g, then completely coated with a varnish layer before being weighed again in both air and deionised water. The relative density of the A-LLTO was calculated based on the experimental (volumetric) and theoretical densities, the latter of which was calculated from the A-LLTO XRD patterns after Rietveld refinement using X'Pert HighScore Plus software.

For the electrical measurements, Pt layers were sputter-deposited on both surfaces of the ceramic pellets before they were connected to the Cu wire using an Ag paste. The Li-ion conductivity of the ceramic samples was computed using an impedance spectrometer (ZIVE SP2) in the frequency range of 1 Hz to 100 kHz at temperatures from 5°C to 65°C.

For the electrochemical characterization, a 200-μm-thin A-LLTO ceramic pellet with a 16 mm diameter was used as an artificial SEI layer for the protection of the Li-metal electrode. In addition, to address the chemical instability of A-LLTO when in contact with Li metal, which is driven by reduction of Ti^{4+} in the A-LLTO into Ti^{3+} by Li [10], a thin layer of lithium phosphorous