



Electrochemical properties of a ceramic-polymer-composite-solid electrolyte for Li-ion batteries



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ARTICLE INFO

Article history:

Received 3 March 2015

Received in revised form 18 November 2015

Accepted 21 November 2015

Available online 10 December 2015

Keywords:

Composite electrolyte

Li ion batteries

LTAPo

Electrochemical properties

ABSTRACT

This study reports on the fabrication of a ceramic-polymer-composite electrolyte with liquid electrolyte, consisting of $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ (LTAPo) ceramic powder, polytetrafluoroethylene (PTFE) polymer and 1 M LiPF_6 in EC/DMC liquid electrolyte. The morphologies of the LTAPo, LTAPo-PTFE composite membrane, and LTAPo-PTFE- LiPF_6 -EC/DMC composite electrolyte were analyzed using a scanning electron microscopy (SEM). The effect of the liquid electrolyte on the ionic conductivity of the prepared ceramic-polymer electrolyte was investigated using electrochemical impedance spectroscopy (EIS). The room temperature ionic conductivities of the LTAPo-PTFE- LiPF_6 -EC/DMC composite electrolyte and the LTAPo ceramic electrolyte exhibited 2.94×10^{-4} S/cm and 8.36×10^{-4} S/cm, respectively. The first charge capacity of the LTAPo-PTFE- LiPF_6 -EC/DMC composite electrolyte cell reached 118 mAh/g at 0.06 mA/cm² current density. The electrochemical performance of the ceramic-polymer-composite electrolyte cell was better than that of the ceramic solid electrolyte cell.

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1. Introduction

Rechargeable lithium ion batteries are widely used for portable electrochemical energy conversion and as storage devices because they have a higher energy density than other commercialized rechargeable batteries [1–4]. However, since lithium ion batteries use an organic liquid electrolyte, there is a risk of explosion and environmental pollution, which restricts any development of the large size Li batteries. Solid-state lithium ion batteries have the potential to achieve higher energy density with better safety than conventional liquid-based lithium batteries [1,5]. Usually, two-types of solid electrolytes are explored for solid-state lithium batteries: the ceramic solid electrolyte, and the solid polymer electrolyte [6–14]. Ceramic solid electrolytes such as $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ (LTAPo) have a high ionic conductivity, a high lithium transference number ($t_{\text{Li}} \approx 1$), and are non-flammable. However, the ceramic electrolyte displays drawbacks such as brittleness and high interface resistance to electrodes [15]. On the other hand, the solid polymer electrolyte has high flexibility and is lightweight but shows low ionic conductivity with a low lithium transference rate ($t_{\text{Li}} = 0.3\text{--}0.6$) and poor electrochemical stability at high voltages [16–19].

To overcome the disadvantages of ceramic and polymer solid electrolytes, a composite solid electrolyte using polymer and ceramic is introduced. This shows a higher mechanical flexibility and a lower

interface resistance than the ceramic solid electrolyte [20,21]. Furthermore, we report on a composite electrolyte formed by mixing LTAPo pellets with an organic liquid electrolyte [22]. The composite electrolytes decrease the instability of a solid-on-solid interface, which is induced by the volume change of the electrode materials during lithium ion insertion/extraction. However, the electrochemical properties are still lower than those of the liquid electrolyte lithium battery [23, 24]. This may be because ionic conductivity is not sufficient to allow high capacity.

In this study, we design a novel composite solid electrolyte by mixing the LTAPo powder, polytetrafluoroethylene (PTFE) and an organic liquid electrolyte (1 M LiPF_6 in EC/DMC). Uniform LTAPo particles prepared by the sol-gel process are homogeneously mixed with PTFE of 15 wt.% and liquid electrolyte of 15 wt.%. A good ionic conductivity and flexibility are obtained in its solid electrolyte. A solid-state lithium battery is constructed by combining the composite electrolyte, a LiMn_2O_4 cathode, and a LiMn_2O_4 anode. The use of LiMn_2O_4 on both electrodes is because the stable electrochemical window of the composite solid electrolyte reaches only 2.5–4.5 V by reducing Ti^{4+} to Ti^{3+} in the LTAPo. The charge/discharge performance of the solid-state lithium battery has been investigated and the results confirm that it can function effectively as a lithium battery.

2. Experimental method

The flowchart for the preparation of $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ is shown in Fig. 1. Powders of LTAPo were synthesized by a sol-gel process of

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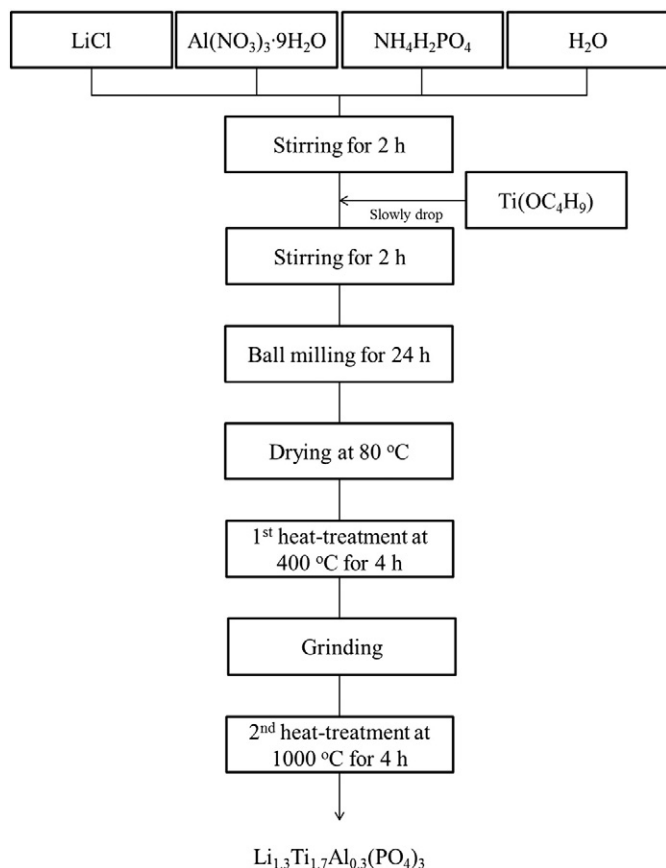


Fig. 1. Schematic diagram for Nasicon LTAPO powder preparation.

stoichiometric amounts of the starting materials. Lithium chloride (LiCl), titanium butoxide ($\text{Ti}(\text{OCH}_2(\text{CH}_2)_2\text{CH}_3)_4$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were employed as starting materials for LTAPO. Starting materials LiCl, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in water. After all the solutes were completely dissolved, titanium butoxide solution was slowly added to the prepared solution while stirring constantly. Precipitation of the LTAPO precursor occurred when titanium butoxide was added to the solution mixture. The resultant solution was stirred for several hours and ball milled for 24 h. The dried powders were heated at 400°C for 4 h and then ground by using an agate mortar and pestle. Next, the powders were re-heated to 1000°C for 4 h. LTAPO and polytetrafluoroethylene (PTFE) powders were used to make a

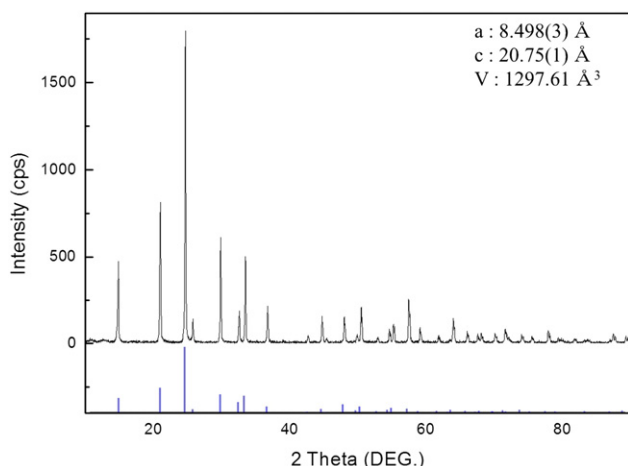


Fig. 2. Powder X-ray diffraction patterns of synthesized LTAPO by the sol-gel process.

ceramic-polymer composite membrane. A LTAPO-PTFE composite electrolyte was fabricated from a 80:20 (wt.%) mixture of 80% LTAPO and 20% PTFE. The two materials were completely mixed by using an agate mortar and pestle. The mixture was rolled into thin sheets and punch stamped into 16 mm diameter circular disks. The thin sheet composite membrane was then soaked in organic liquid electrolyte (1 M LiPF_6 in EC/DMC) and any excess liquid electrolyte was removed resulting in a solid-state. In the final composite electrolyte, the weight percentage of LTAPO:PTFE:liquid electrolyte is 70:15:15.

The negative and positive electrodes were concocted from a 70:10:20 (wt.%) mixture of 70% LiMn_2O_4 as active material, 10% Super P carbon as current conductor, and 20 wt.% PTFE as binder. The flexible film electrodes were fabricated by the same method as that used to make the LTAPO-PTFE composite membrane. The electrochemical cells were prepared in a standard 2032 coin-cell and the solid-state

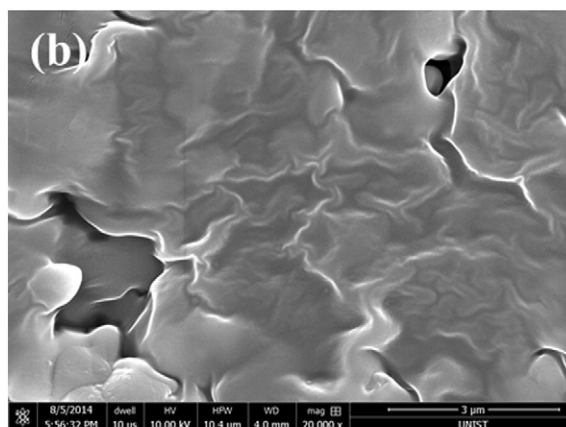
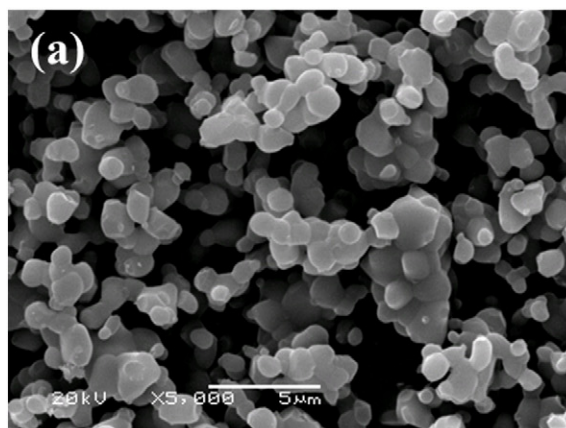


Fig. 3. Microstructure of (a) LTAPO powder, (b) LTAPO-PTFE composite solid electrolyte with 1 M LiPF_6 in EC/DMC, and image of (c) flexible LTAPO-PTFE composite electrolyte.

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