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Development of manganese-based thin-film probe via hydrothermal process for localized electrochemical impedance analysis of a solid-state electrolyte LiPON

Yi-Hung Liu [a], Sin-Syu Liao [b], Bernard Haochih Liu [b,*]

[a] Department of Greenergy, National University of Tainan, 33, Sec. 2, Shu-Lin St., Tainan 70005, Taiwan
[b] Department of Materials Science and Engineering, National Cheng Kung University, No. 1, University Road, Tainan 70101, Taiwan

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ABSTRACT

A facile low-temperature synthesis process, including the first electrodeposition and the second hydrothermal reaction, has been adopted in fabricating the Li-Mn-O thin-film probe to measure the localized electrochemical impedance of the solid-state electrolyte LiPON. The synthesized thin film is uniformly and densely deposited on the probe, which is composed of layered Li_2MnO_3 and $LiMnO_2$ crystalline phases. In addition to surface topography mapping, using the thin-film probe allows us to discern the dominant charge transfer resistance at the LiPON/Li-Mn-O interface from the electrolyte resistance in nanoscale level, which is different from the results obtained by a conductive probe as well as a MIM cell. It is also found by the thin-film probe that the ion transport in LiPON and charge transfer behavior at the LiPON/Li-Mn-O interface can be facilitated by introducing an external voltage.

1. Introduction

All-solid-state lithium ion batteries recently attract much attention in energy storage application due to its improved flexibility, reduced volume and increased safety [1]. However, solid-state electrolytes generally possess lower ionic conductivity and higher interfacial resistance at the electrolyte/electrode interface, compared with liquid electrolytes, thus limiting the battery power density [2,3]. An amorphous thin film composed of lithium phosphorus oxynitride (LiPON) has been studied as a solid-state electrolyte, which demonstrates good compatibility with lithium metal and favorable ionic conductivity of 2×10^{-6} S cm^{-1} at room temperature [4]. Besides, the advantages of chemical stability, voltage stability, and low electronic conductivity enable LiPON to be one of the most established solid-state electrolytes [5]. To investigate the ion transport capability in LiPON, a Ti/LiPON/Ti sandwich cell structure (MIM cell) has also been used to carry out the electrochemical impedance spectroscopy (EIS) measurements [6], while the impedance information of each local site cannot be obtained but an integral phenomenon of the bulk electrolyte impedance. To overcome this issue, the conductive-probe atomic force microscopy (CP-AFM) has been utilized to study the localized electrochemical behaviors of the target material with a high spatial resolution below 100 nm [7,8]. However, the interfacial impedance at the electrolyte/active material interface, that greatly affects the battery performances, still cannot be locally analyzed.

As an extension of the nanoscale measurement using AFM probe, we herein develop a manganese-based thin-film electrode probe to investigate the ion transport across the electrolyte/electrode interface and in the bulk electrolyte of LiPON. A facile two-step synthesis process at low temperature allows us to fabricate this thin-film probe. The proposed fabrication process and the new insight into the localized EIS measurement obtained by the probe open a new avenue in nanoscale electrochemical analysis.

2. Experimental

The AFM probe prototype of PNP-TR type (NanoWorld) was used as a substrate for the thin-film synthesis process. 0.1 M Mn$(NO_3)_2$ aqueous solution (Alfa Aesar) was firstly added to a bath where the electrodeposition reaction was carried out. The working electrode and counter electrode used were the AFM probe prototype and carbon paper, respectively. The reaction was controlled at a current density of 0.5 mA cm^{-2} by a power supply for 30 min at room temperature, followed by a rinsing with deionized water and a drying at 90 °C. Next, the probe was carefully moved to the bottom of a Teflon lined autoclave with its tip upward.

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* Corresponding author.
E-mail address: hcliu@mail.ncku.edu.tw (B.H. Liu).

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The hydrothermal treatment was performed in a 3 M LiCl or LiOH (J. T. Baker) aqueous solution at 100 °C for 10 h. After the subsequent rinsing and drying operations, the thin-film probe was obtained. The preparation process is summarized in Fig. 1(a). In addition, the preparation details for LiPON can be referred to Table S1.

Morphological and elemental analysis of the thin-film probe were carried out using a scanning electron microscopy (JSM-6700F, JEOL) and an Auger electron spectroscopy (AES) (Microlab 350, Thermo Fisher Scientific), respectively. For the identification of crystalline phases, an X-ray diffraction using an X-ray diffractometer with Cu-Kα radiation (Multipurpose X-ray Thin Film Diffractometer, Rigaku Corporation) was applied. To perform the localized electrochemical measurement, a measurement system combining the AFM (Dimension Icon, Bruker) and potentiostat/galvanostat (Reference 600, Gamry), in which the thin-film probe and platinum layer of LiPON substrate respectively functioned as the working electrode and counter electrode, was utilized. A sinusoidal voltage of 10 mV over the frequency range from 0.1 to 100 kHz was applied for the measurements.

3. Results and discussion

Fig. 1(b–e) show the SEM images of the prototype probe and as-prepared probe. The surface of the prototype probe is smooth and a pyramid-shape probe tip can be observed at the end of the cantilever (b). After the hydrothermal treatment, clearly, the probe is well covered by the synthesized material, while the probe tip can still be recognized with inconspicuous pyramid edges (c). The probes are further treated by focus ion beam, as shown in (d) and (e). The probe remains its original shape and structure after experiencing the thin-film formation process, in which a material layer is uniformly deposited on the surface of the prototype probe with a dense structure (e). The film thickness of the probe tip is *ca.* 0.4 μm.

The thin-film synthesis method is also applied to the other probe prototype and the corresponding SEM observations with the FIB treatment are shown in Fig. 1S(a) and (b). It is evidenced that the synthesized material layer entirely covers the probe tip and cantilever. AES measurement of the tip surface (c–e) further confirms that the thin film is composed of Li-Mn-O active material.

Identification of the crystalline phases of the synthesized material on the nanoscale tip cannot be achieved by XRD due to the measuring limit. Alternatively, a substrate made of silicon nitride with a size of 16 × 18 mm^2 is used to deposit the thin-film via the same synthesis process as the probe, which enables the XRD crystalline analysis, as shown in Fig. 2(a). In the pattern (i), a primary Mn_3O_4 crystalline phase is identified, which constitutes the precursor layer. The precursor almost remains even after the hydrothermal treatment in the LiCl solution (ii), indicating that lithium ions cannot react with the precursor in this neutral reaction condition. Once the reaction solution is replaced by LiOH, it is worth noting that the products change to Li_2MnO_3 and $LiMnO_2$ phases without the precursor remained (iii). On the other hand, the XRD pattern of solid-state electrolyte LiPON is shown in Fig. 2(b). No other peaks can be clearly identified except for the strong Pt peak from the current collector substrate and the minor peak of impurity Li_2CO_3, supporting that the LiPON thin film has an amorphous structure.

Fig. 3(a,b) offer the surface topography information of the LiPON thin film, which is obtained by the Li-Mn-O thin-film probe. It is inevitable that the resolution is sacrificed to some extent due to the increased curvature of thin-film tip. However, with the support of 3D image (b), it can be found that the particles of LiPON are well

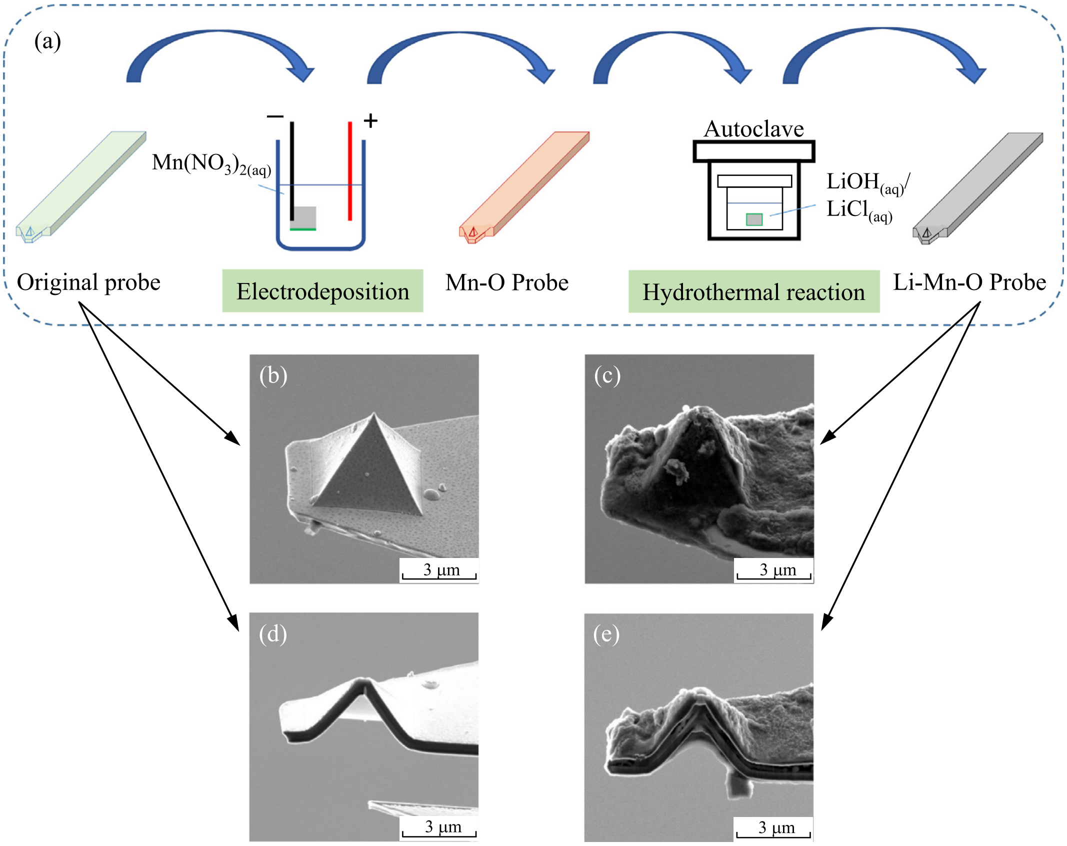

Fig. 1. (a) Schematic fabrication process diagram for Li-Mn-O thin-film probe; SEM images for (b, d) original PNP-TR type probe and (c, e) as-prepared thin-film probe.