Fabrication and impedance analysis for designed composite layers with polymer and inorganic electrolytes leading to high conductivity

Shintaro Kitajima[a,b,*], Hirokazu Kitaura[c,**], Dongmin Im[a], Yunil Hwang[a], Masayoshi Ishida[b], Haoshen Zhou[b,c]

[a] Samsung Advanced Institute of Technology (SAIT), Samsung Electronics Co., Ltd., Samsung-ro, Yeongton-gu, Suwon-si, Gyeonggi-do 443-803, South Korea
[b] University of Tsukuba Graduate Scholl of System and Information Engineering, University of Tsukuba, Tennoudai 1-1-1, Tsukuba 308573, Japan
[c] Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba 305-8568, Japan

ARTICLE INFO

ABSTRACT

This study presents newly designed and produced solid Li-ion conductive composite layers based on polymer electrolytes and Li-ion-conducting particles. The composite layers are studied using AC impedance spectroscopy. The conductivity of the composite layers is 0.14 mS/cm at room temperature. We discuss the Li-ion transfer mechanism via a characteristic frequency of impedance analysis and show that the interior of Li-ion-conducting particles is the major Li-ion path. The activation energy is less than that of polymer electrolytes while being greater than that of the grain boundary of Li-ion–conducting particles. The newly designed composite layers could be utilized in solid-state Li-ion batteries and solid-state Li-air batteries.

1. Introduction

The use of solid electrolytes, which can be classified into polymer and inorganic electrolytes, have attracted much attention over the years due to their advantages of being compact and safe and a high energy density. However, critical problems remain in terms of using solid polymer electrolytes in commercial Li-ion batteries (LIBs) for electric vehicles owing to their low ionic conductivity [1,2]. Alternatively, numerous inorganic electrolytes have been developed [3–10]. Typically, Li-ion-conducting particles (LICP) are sintered to form the inorganic electrolyte disc. However, this disc tends to be brittle and prone to cracking. For this reason, they are not suitable for application to large sizes without increasing excessive thickness, which results in unacceptable weights and higher resistance. Numerous studies have been published with respect to multi-particle thick LICP–polymer composites in order to improve the mechanical strength of the inorganic electrolyte disc. However, this can reduce the lithium ion's mobility owing to high resistance from polymer electrolytes, the LICP–polymer, and the LICP–LICP contact interfaces [11–15].

To overcome these limitations, Aetukuri et al. [16] designed and fabricated one-particle-thick membranes (OPTMs), which have much improved mechanical properties relative to those of inorganic electrolyte disc. OPTMs have a characteristic structure in which LICP is embedded as a single layer into an insulating organic polymer matrix. OPTMs can avoid the impedance issues associated with conductance across the LICP–LICP contact interface. We calculated the conductivity of OPTMs, which is approximately 0.05 mS/cm (the range of inorganic particles: 75–90 μm, diameter: 1/2 in., total resistance: 128 Ω). The oxygen reactive ion etching process (O$_2$-RIE) was needed to remove the insulating polymer on the top and bottom surfaces of the particles with the aim of improving Li-ion conductance. Furthermore, there is also a problem that the interfacial resistance between OPTMs and electrodes might be huge because of impossibility of high temperature sintering, if the OPTMs are used for the bulk-type solid-state Li-ion batteries.

Here, we present the newly designed composite layers (CLs), comprising a polymer electrolyte and LICP as a matrix, with particles arranged in a single layer towards the matrix. In this new concept, the aforementioned problems of OPTMs can be solved. The etching process is not needed because the polymer electrolytes on the top and bottom surfaces of the LICP can conduct the lithium ion. However, polymer electrolytes generally have low ionic conductivities at room temperature. Therefore, in order to reduce the total resistance, it is necessary to make the polymer electrolyte thinner between the LICP and the electrodes. This is the most important point of this concept. In addition, it is anticipated that using flexible polymer electrolytes will help increase contact with the electrodes. Moreover, several other merits are

---

expected. In our method, the CLs can be directly fabricated on the electrodes. Therefore, the CLs can be made as thin as possible without the additional supporting layer to obtain sufficient mechanical strength. Regarding the resistance components of CLs themselves, interfacial resistance should be considered to achieve a lower total resistance except for the bulk resistance of polymer electrolytes as mentioned above. Although CLs have no LICP–LICP contact, like OPTMs, there are LICP–polymer contacts in CLs. Abe et al. [11] suggested that the composite electrolytes using polymer electrolytes and ceramic electrolytes show high interfacial resistance and their contact area should be as small as possible to attain high Li-ion conductivities. In comparison with multi-particle thick LICP–polymer composites, CLs can minimize the LICP-polymer interfacial resistance. In this work, we demonstrate the fabrication of CLs; then, we study the impedance behaviors in order to understand the Li-ion transfer mechanism of CLs.

2. Experimental method

$Li_{1.3}Al_{0.3}Ti_{1.7}P_3O_{12}$ (LATP) was chosen from the viewpoints of its high Li-ion conductivity and stability in ambient air. The LATP particles (Toshima Manufacturing) were sieved from 45 μm to 53 μm-sized particles. By way of comparison, 50 μm-sized ZrO_2-based particles (Niimi NZ beads 50, Niimi Sangyo), which are insulators, were used.

A schematic of the process used to prepare the CLs is shown in Fig. 1(a). The CLs were fabricated in a dry room (temperature: 21 °C, dew point: − 65 °C). Polymer electrolyte, which consists of polyethylene oxide with an electrolyte salt, lithium bis(trifluoromethane sulfonyl) imide (PEO-LiTFSI), is well known as an adhesive for inorganic particles [17]. PEO (average Mw: 60,000, Aldrich) and LiTFSI (Panax) with [Li]/[O] = 18 (i.e., the ratio of the ethylene oxide unit [O] to Li [Li]) were chosen. Anhydrous acetonitrile (AN) containing 0.07 g of PEO-LiTFSI at 8 wt% was dropped on a stainless steel disc (SUS), which was employed as an electrode, and then dried at 80 °C for 30 min in order to remove AN. The thickness of the PEO-LiTFSI layer on

the SUS was approximately 10 μm (SUS/PEO-LiTFSI). Next, sieved particles were dispersed to be arranged in a single layer on the PEO-LiTFSI with the SUS (SUS/PEO-LiTFSI/particles). The arranged ZrO_2-based or LATP particles in the single layer are visible in Fig. 1(b) and (c). Moreover, SUS/PEO-LiTFSI was stacked on SUS/PEO-LiTFSI/particles to obtain the sandwich structure SUS/PEO-LiTFSI/particles/PEO-LiTFSI/SUS, which was encapsulated in a 2032 coin cell with two springs that exert a small pressure on the sample. Finally, samples were placed in an oven at 80 °C, which is over the melting point of PEO (60 °C), for each retention period to embed the particles in the PEO-LiTFSI matrix. The abovementioned conditions for storing the CLs are crucial for the following reasons. First, defoaming of the microbubbles between the particles and the movement of PEO-LiTFSI around the particles enhances adhesion of the particles to the interface. Second, the thickness of PEO-LiTFSI (t-PEO-LiTFSI), which is slightly remained between the SUS electrode and the LATP particles, is decreased. The residual t-PEO-LiTFSI, which may possibly decrease total Li-ion conductivity, was hardly observed as shown in the cross-section SEM image in Fig. S1.

We obtained the ionic conductivities of CLs from AC impedance measurements of the SUS/CLs/SUS sandwich structure at room temperature (21 °C) in a dry room, as Imanishi et al. reported using an Al/LATP disc/Al structure [18]. For the SUS/CLs/SUS with LATP particles (CL-LATP) and the SUS/CLs/SUS with ZrO_2-based particles (CL-ZrO_2), we collected AC impedance measurements using a potentiostat (VMP3, Bio-Logic) in a frequency range from 1 Hz to 1 MHz (with a perturbation voltage of 10 mV) at room temperature for various retention periods. Impedance measurements for Arrhenius plots were performed at temperatures between − 20 °C and 80 °C, controlled by a thermostatic oven (ESPEC).

3. Results and discussion

To clarify the Li-ion transfer mechanism of CL-LATP, impedance
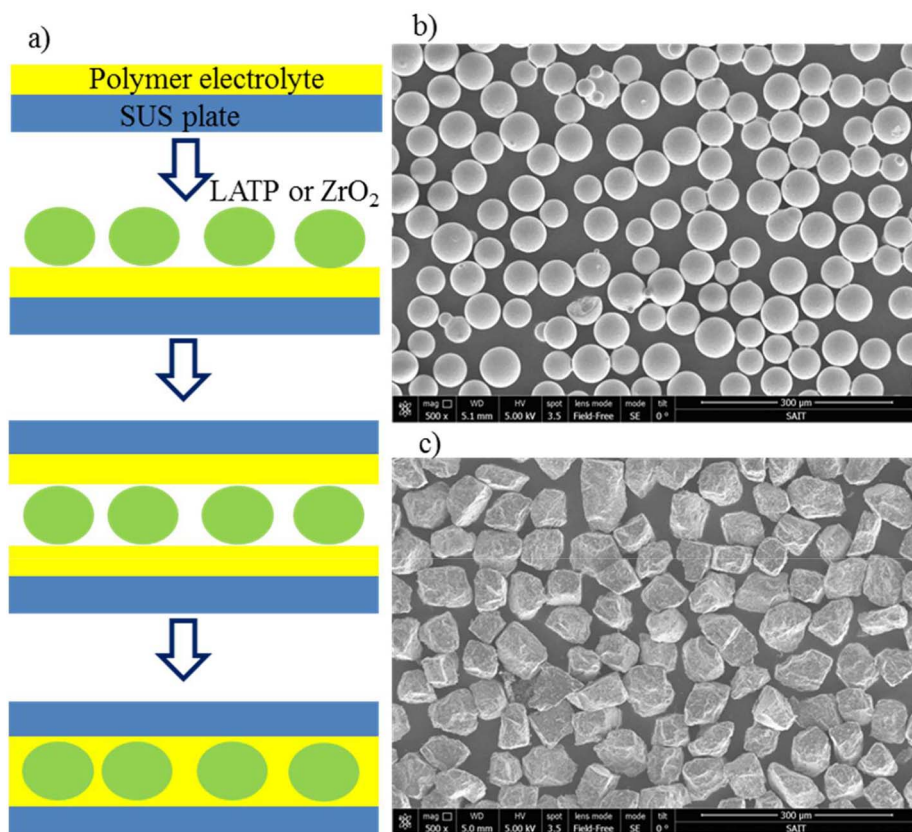

Fig. 1. (a) Schematic of the steps involved in the fabrication of CLs. Plane-view SEM images of arranged particles in a single layer on PEO-LiTFSI in the second step of the schematic: (b) ZrO_2-based particles and (c) LATP particles.