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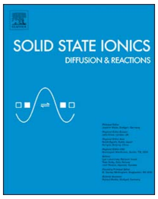

Hybrid solid electrolytes composed of poly(1,4-butylene adipate) and lithium aluminum germanium phosphate for all-solid-state Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cells

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ABSTRACT

Solid polymer electrolytes based on poly(1,4-butylene adipate) (PBA) and $LiClO_4$ were hybridized with Li^+-conductive lithium aluminum germanium phosphate ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, LAGP) to obtain highly conductive and flexible solid electrolyte film. Ionic conductivity, mechanical property and electrochemical stability were enhanced by incorporating an appropriate amount of LAGP into the PBA-based solid polymer electrolyte, and the optimum content of LAGP in the hybrid solid electrolytes was approximately 60–80 wt%. The all-solid-state Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cell employing the optimized hybrid solid electrolyte exhibited an initial discharge capacity of 169.5 mAh g^{-1} with good capacity retention at 55 °C.

1. Introduction

Lithium-ion battery (LIB) has been a leading energy storage technology over the past decades because of its high energy density and long cycle life, and it is being widely used in portable electronics, electric vehicles and energy storage systems [1–5]. However, highly flammable solvents used in the liquid electrolyte still prevent the full utilization of LIBs for existing small power sources and future large-scale applications due to the risk of solvent leakage and fire explosions. In this respect, the all-solid-state lithium batteries employing solid electrolytes have been actively studied in order to enhance the safety of current LIBs [6–13]. Among a variety of solid electrolytes, solid polymer electrolytes possess a lot of potential advantages, including the absence of solvent leakage, good interfacial contacts with electrodes, low cost, easy processing, flexibility and good film formability [6–9]. Solid polymer electrolytes based on poly(ethylene oxide) (PEO) have been intensively studied so far, because PEO can solvate various lithium salts through interaction of its ether oxygens with cations. However, their low ionic conductivities at ambient temperature preclude their practical applications for use in lithium batteries that operate at room temperature. Moreover, the oxidative stability of PEO-based solid polymer electrolytes is still unsatisfactory for applying them to high voltage cathode materials such as $LiCoO_2$, $LiMn_2O_4$ and $LiNi_xCo_yMn_{1-x-y}O_2$ [10]. As an alternative to PEO-based solid polymer electrolytes, polyester-based solid polymer electrolytes have been studied and reported, because ester groups (-COO-) in the polymer backbone can dissolve the lithium salts to produce a sufficient number of free ions and they exhibit higher oxidative stability than ether groups [14–22]. In addition to solid polymer electrolytes, inorganic electrolytes have also been extensively studied as a solid electrolyte for all-solid-state lithium batteries due to their high ionic conductivity, high thermal stability, non-flammability, excellent electrochemical stability and high mechanical strength [11–13]. Among the inorganic electrolytes reported so far, lithium aluminum germanium phosphate ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, LAGP), one of the NASICON-type solid-state lithium ion conductors, has several advantages such as high ionic conductivity, easy synthesis, superior chemical stability with lithium metal and high electrochemical stability [23–27]. However, the lack of flexibility due to their hard and brittle nature results in inferior interfacial contacts and high interfacial resistance with electrode materials in the cells. Therefore, it is great urgency to develop the flexible solid electrolytes satisfying both high ionic conductivity and improved interfacial contact for realization of all-solid-state lithium batteries [28–30].

In the present work, we prepared flexible hybrid solid electrolytes composed of poly(1,4-butylene adipate) (PBA)-based solid polymer electrolyte and Li^+-conductive LAGP, which exhibited superior electrochemical properties and good interfacial contact towards electrodes in the cell. The hybrid solid electrolyte in the form of flexible thin film was employed for fabricating the all-solid-state Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cells, and their cycling performance was evaluated. In our work, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ was chosen as an active material in the composite positive electrode, because it exhibits a high operating voltage and has

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Table 1
Composition of LAGP, PBA and $LiClO_4$ in different solid electrolytes.

Electrolyte	LAGP (g)	PBA (g)	$LiClO_4$ (g)	[BA]: [Li^+]
PBA/$LiClO_4$	0	2.0	0.177	6: 1
LAGP-60	1.2	0.8	0.071	6: 1
LAGP-70	1.4	0.6	0.053	6: 1
LAGP-80	1.6	0.4	0.035	6: 1
LAGP-90	1.8	0.2	0.018	6: 1

a higher specific capacity and lower cost than $LiCoO_2$. To the best of our knowledge, we report for the first time the cycling characteristics of all-solid-state lithium cells employing a high-voltage $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material and polyester-based hybrid solid electrolyte.

2. Experimental

2.1. Hybrid solid electrolyte

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ powders were synthesized by solid solution method, as reported earlier [31]. PBA (average $M_w = 12{,}000$), lithium perchlorate ($LiClO_4$) and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich. A hybrid solid electrolyte was prepared using LAGP, PBA and $LiClO_4$, with a composition given in Table 1. PBA and $LiClO_4$ were mixed with a fixed molar ratio of 6:1 for [BA]: [Li^+] in anhydrous DMC at 60 °C for 12 h. LAGP powder with a different weight ratio (60, 70, 80 and 90 wt%) was added to the polymer solution, and the resulting solution was further mixed for 24 h. After complete mixing of the solution, it was cast with a doctor blade onto a flat Teflon plate, and left to evaporate the solvent slowly at room temperature in a glove box under argon atmosphere. The cast film was further dried in a vacuum oven at 60 °C for 12 h to completely remove remaining DMC. After drying process, the free-standing flexible thin film was obtained as a solid-state electrolyte, as depicted in the right side of Fig. 1.

2.2. Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cell

A composite positive electrode on aluminum current collector consisted of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, PBA, $LiClO_4$ and Super P carbon in the weight ratio of 60: 27.56: 2.44: 10. Solid polymer electrolyte (PBA/$LiClO_4$) in the composite positive electrode was used as a Li^+-conducting electrolyte as well as a polymer binder. The mass loading of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ in the composite positive electrode was approximately 6.0 mg cm^{-2}. A lithium foil (200 µm, Honjo Metal Co., Ltd.) pressed onto a copper current collector was used as a negative electrode. The Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cell was then assembled with hybrid solid electrolyte in CR2032 coin-type cell, as schematically illustrated in the left side of Fig. 1. The cell assembly was conducted in a glove box filled with high-purity argon gas ($H_2O < 20$ ppm).

2.3. Characterization and measurements

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet iS50 spectrometer in the range of 400–4000 cm^{-1}. In order to examine the cross-sectional morphologies of the hybrid solid electrolyte, it was cut using a cross section polisher (JEOL IB-09020CP) at constant power in an inert Ar atmosphere. The cross-sectional image was obtained using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F). Energy dispersive X-ray spectroscopy (EDS) was performed to investigate the cross-sectional elemental distribution in the hybrid solid electrolyte. X-ray diffraction (XRD) measurements were performed by X-ray diffractometer (Rigaku M2500) using Cu Kα radiation. The ionic conductivity of the solid electrolytes was determined from AC impedance measurements using a Zahner Electrik IM6 impedance analyzer over the frequency range from 10 Hz to 1 MHz with an amplitude of 10 mV at different temperatures. The solid electrolytes were sandwiched between two disk-like stainless steel blocking electrodes and sealed in Swagelok-type airtight cells. Before the measurements, each sample was stored at the required temperature for at least 1 h. To investigate the oxidative stability of the solid electrolytes, linear sweep voltammetry (LSV) was performed on a platinum working electrode, with lithium metal as reference and counter electrodes, at a scan rate of 1.0 mV s^{-1} at 55 °C. Cycling test of the all-solid-state Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cells was carried out at a constant current rate of 0.2 C within the voltage range between 3.0 and 4.2 V using a battery cycler (WBCS 3000, Wonatech) at 55 °C, unless otherwise specified.

3. Results and discussion

To investigate the ion conduction behavior of PBA-based solid polymer electrolytes, their ionic conductivities were measured as a function of salt concentration at room temperature, and the results are shown in Fig. 2(a). The ionic conductivity reached a maximum value at a salt concentration of 2: 1 for [BA]: [Li^+], followed by a decrease with a further increase in $LiClO_4$ concentration. This result is due to two opposing effects on the ionic conductivity, as previously reported [32–34]. Since the carbonyl group in the PBA backbone is a strong electron donor and it can effectively dissociate the lithium salt, there is a buildup of free ions as the salt concentration increases. However, this is eventually offset by the increase in ion-polymer interactions and the consequential reduction in ionic mobility at high salt concentration. Ion-polymer interactions and the dissociation of the salt in the PBA-based solid polymer electrolytes were examined by ATR-FTIR spectroscopy, and the resulting spectra are shown in Fig. 2(b) and (c). In Fig. 2(b), the main peak observed at 1730 cm^{-1} in pure PBA corresponds to the free carbonyl stretching, and the peak appearing at 1700 cm^{-1} in the solid polymer electrolytes can be assigned to Li^+-coordinating carbonyl stretching [21]. The intensity of the peak at

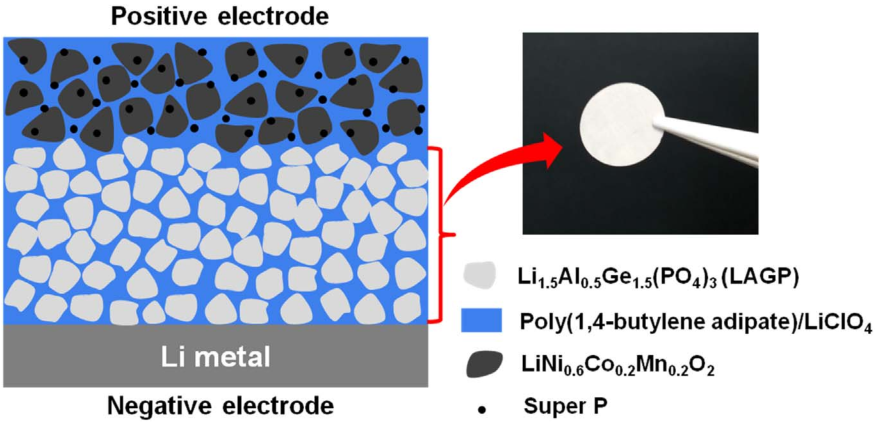

Fig. 1. Schematic presentation of the all-solid-state Li/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cell employing hybrid solid electrolyte and photo image of a representative hybrid solid electrolyte (LAGP-70).