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Rapid communication

Enhanced ionic conductivity of the solid electrolyte for lithium-ion batteries

Artur Tron[a,b,*], Alexander Nosenko[b], Yeong Don Park[a], Junyoung Mun[a]

[a] *Department of Energy and Chemical Engineering, Incheon National University, 12-1, Songdo-dong, Yeonsu-gu, Incheon 22012, Republic of Korea*
[b] *Ukrainian State University of Chemical Technology, Gagarin Ave., 8, Dnipro 49005, Ukraine*

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ABSTRACT

In this study, we demonstrate the influence of the additives molybdenum trioxide (MoO_3) and phosphorus oxynitride (PON) on the ionic conductivity of the oxide solid electrolyte $Li_2O–LiF–P_2O_5$. The latter is used for surface modification of the lithium-ion batteries electrode materials and as the solid electrolyte with higher ionic conductivity for all-solid-state batteries. Furthermore, we report the optimal content of the additives MoO_3 and PON of 1.5 wt% and 10 mol%, respectively, in the structure of the solid electrolyte $Li_2O–LiF–P_2O_5$ which provides higher ionic conductivity (9.15 10^{-6} S cm^{-1} and 2.61 10^{-6} S cm^{-1}, respectively) compared to the solid electrolyte Li_2O-LiF-P_2O_5 without additives (4.4 10^{-7} S cm^{-1}) at room temperature.

1. Introduction

Conventional lithium-ion batteries (LIBs) with non-aqueous electrolytes have been widely used in the various applications such as portable devices, electric vehicles (EVs) and energy storage systems (ESSs) due to their high specific energy and power, high voltage, and long lifecycle [1]. However, using the non-aqueous electrolytes in conventional LIBs results in lithium dendrites growing on the interface between the anode and electrolyte. This leads to puncture in the separator wherein separating the anode and cathode leads to short-circuits and magnified fire hazard [2]. Despite significant advances in LIBs, the issues related to the use of non-aqueous electrolyte, their high cost and also fire hazard forced further progress in seeking and developing new lithium-battery-systems [2–4]. Among the lithium-battery-systems, all-solid-state batteries are the most perspective ones for next-generation technologies, e.g., in automobile industry where they can provide safe green vehicle performance at attractive cost. Yet using an inorganic solid electrolyte in all-solid-state batteries should satisfy the following multiple criteria such as high ionic and low electronic conductivity, the chemical stability in a contact with the electrode materials, the electrochemical stability window in the operation of all-solid-state batteries, and also the combination of environmentally benign low cost materials and easy preparation [5]. In this respect, the inorganic oxide solid electrolytes present potential advantages compared to conventional non-aqueous electrolytes. However, the low ionic conductivity of the solid electrolytes, forced to seek the way to increase the ionic conductivity via various additives such as transition metals MoO_3, WO_3, As_2O_3, V_2O_5 while keeping low electronic conductivity [6–9]. It should be noted that oxide solid electrolytes containing transition metals have attracted attention because of their applications in various fields of electrochemical, electronic and electro–optical devices [10,11]. However, adding the high concentration of transition metal oxide leads to decrease in the ionic conductivity of the oxide solid electrolyte where electronic conductivity is predominant to ionic conductivity due to the presence of various valence ions which can have the mix ionic-electronic conductivity [6]. Therefore, to keep the high ionic and low electronic conductivity optimal concentration of transition metals should be present in the composition of the oxide solid electrolytes for their successful application in lithium-battery-system [12]. As of today "LIPON" is the most frequently used oxide solid electrolyte in all-solid-state batteries [13]. Owing to a good chemical and electrochemical stability to lithium metal and cathode materials, the high ionic conductivity (10^{-6} S cm^{-1}) and the low electronic conductivity (10^{-13} S cm^{-1}) at room temperature [11,14]. It is worth noting that the presence of the high electronic conductivity is a critical parameter for all-solid-state battery performance. Therefore, in this study we used a lower amount of MoO_3 to increase the ionic conductivity while keeping the electronic conductivity low and implemented a partial replacement of P_2O_5 on the PON in the composition of $Li_2O–LiF–P_2O_5$.

2. Experimental

Synthesis of $Li_2O–LiF–P_2O_5$ (in molar ratio 50:10:40 and 50:20:30) was carried out using the reagent-grade chemicals (Aldrich) Li_2CO_3, LiF, H_3PO_4, $NH_4H_2PO_4$, $LiPO_3$ (Li_2CO_3 + H_3PO_4), MoO_3 and PON (H_3PO_4 + CH_4N_2O) as starting materials. The amorphous $LiPO_3$ was obtained by mixing amounts of Li_2CO_3 and

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* Corresponding author at: Department of Energy and Chemical Engineering, Incheon National University, 12-1, Songdo-dong, Yeonsu-gu, Incheon 22012, Republic of Korea.
E-mail address: artur84tron@inu.ac.kr (A. Tron).

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Table 1
Ionic conductivity and activation energy (*E*a) of the solid electrolyte $Li_2O–LiF–P_2O_5$ (50:20:30) at room temperature.

Starting materials			Composition	Ionic conductivity, σ × 10^{-7}, S cm^{-1}	Activation energy, Ea, eV	Reference
Li_2CO_3	LiF	H_3PO_4	H-LFP	0.47	0.611	this work
		$NH_4H_2PO_4$	N-LFP	1.17	0.591	
		$LiPO_3$	L-LFP	4.40	0.567	[15]

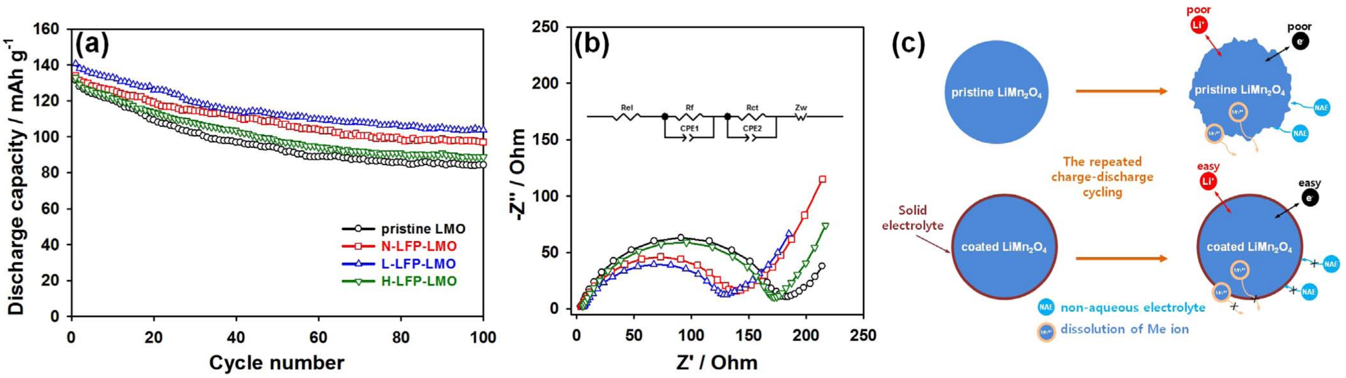

Fig. 1. (a) Cyclic performance of the pristine and coated $LiMn_2O_4$ electrodes at 1 C rate (148 mAh g^{-1}) in the non-aqueous electrolyte of 1 M $LiClO_4$ EC/DMC in the potential range of 3.0–4.5 V, (b) Nyquist plots of the pristine and coated $LiMn_2O_4$ electrodes after 50th cycle. $LiMn_2O_4$ electrode was coated by a 1-μm solid electrolyte layer, (c) Schematic illustration the role of the solid electrolyte on the surface of the $LiMn_2O_4$ materials during the repeated charge-discharge cycling.

H_3PO_4 (Aldrich) with further drying at 270 °C and then heat treatment at 900 °C for 30 min in air which was rapidly cooled using a twin-roller quenching technique. To synthesize PON, H_3PO_4 and CH_4N_2O were used as starting materials at heat treatment of 400 °C until the termination of the gas evolution. Then the PON was cooled, after that crushed and again forced to a heat treatment at 800 °C for 30 min in air. MoO_3 was introduced for the preparation of the solid electrolyte $Li_2O–LiF–P_2O_5–MoO_3$ in the weight percent (wt%) of 0–2. PON in 0–20 mol% was a partial replacement of P_2O_5 in the $Li_2O–LiF–P_2O_5$ solid electrolyte composition. Then, the solid electrolytes were synthesized by a high-temperature solid-state reaction at 900 °C for 30 min in air by melt quenching technique.

To determine the ionic conductivity of the solid electrolyte with the thickness of 1 μm between two symmetric blocking electrodes (stainless steel) AC impedance method (VoltaLab 40, PGZ 301) was used in the frequency range from 100 kHz to 1 Hz with voltage amplitude of 10 mV at room temperature of 25 °C.

To evaluate electrochemical performance of the pristine and coated by a 1-μm-thick-layer of the solid electrolyte $LiMn_2O_4$ electrodes as cathode, 2325-type coin cell was assembled in glove box with argon atmosphere using porous polyethylene membrane (Celgard) as the separator and lithium electrode as anode in the non-aqueous electrolyte of 1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate (EC: DMC = 7:3). The cathode materials were prepared by mixing 90:5:5 wt% of the pristine $LiMn_2O_4$ electrode, acetylene black and PVdF binder, respectively, for getting uniform slurry on the Al foil as a current collector. The $LiMn_2O_4$ electrodes with a diameter of 12 mm and the electrode mass of approximately 2 mg were dried at 120 °C in a vacuum for 12 h. After that, the pristine $LiMn_2O_4$ electrodes were coated by a 1-μm-thick-layer of the solid electrolyte $Li_2O-LiF-P_2O_5$. The repeated charge-discharge cycling was performed in the potential range of 3.0–4.5 V at a current density of 1 C rate (148 mAh g^{-1}). The electrochemical impedance spectroscopy (EIS) measurements were conducted using the impedance analyzer of VoltaLab 40 (PGZ 301) in the frequency range from 100 kHz to 100 mHz at the voltage amplitude of 10 mV. The chemical composition of non-aqueous electrolytes after 50 cycles and the Mn ion concentration in $LiMn_2O_4$ electrodes were measured by inductively coupled plasma optical emission spectrometer (Thermo Scientific iCAP 7000 series ICP-OES).

3. Results and discussion

In order to examine the impact of starting materials on the ionic conductivity of the solid electrolyte $Li_2O–LiF–P_2O_5$ (50:20:30 mol%), we have synthesized the solid electrolyte using the reagent-grade chemicals Li_2CO_3, LiF, H_3PO_4, $NH_4H_2PO_4$, $LiPO_3$. For convenience solid electrolytes were named H-LFP, N-LFP, L-LFP in conformity with Table 1. It should be noted that using the $LiPO_3$ (L-LFP) for synthesis of the solid electrolyte $Li_2O–LiF–P_2O_5$ results in higher ionic conductivity of the L-LFP (4.40 10^{-7} *S* cm^{-1}) compared to the H-LFP and N-LFP (0.47 10^{-8} and 1.17 10^{-7} *S* cm^{-1}, respectively). Thus, the use of $LiPO_3$ also expands the region of the solid electrolytes containing more than 60 mol% of Li_2O and increases their homogeneity thanks to reducing the temperature of the synthesis of the solid electrolytes (and, consequently, also reduce the volatilization of oxides) and it leads to increasing the ionic conductivity as shown in Table 1.

To further determine the influence of the composition of $Li_2O–LiF–P_2O_5$ (50:20:30 mol%) on the ionic conductivity, we have tested the solid electrolyte in conventional LIBs in the non-aqueous electrolyte with anode material of lithium metal and cathode material of $LiMn_2O_4$ which was coated by the three types of the solid electrolytes (H-LFP, N-LFP, L-LFP; refer to Table 1) with thickness of 1 μm. The charge-discharge cycling performance of these materials was examined as shown in Fig. 1. It is noteworthy that the L-LFP-coated $LiMn_2O_4$ (abbreviated as L-LFP-LMO) shows higher discharge capacity of 103.8 mAh g^{-1} after 100 cycles compared to other materials such as the pristine (abbreviated as pristine-LMO), H-LFP-coated $LiMn_2O_4$ (abbreviated as H-LFP-LMO) and N-LFP-coated $LiMn_2O_4$ (abbreviated as N-LFP-LMO) with discharge capacity of 84.2, 88.6, 96.9 mAh g^{-1}, respectively. In addition, the solid electrolyte (L-LFP) on the surface of $LiMn_2O_4$ material improves the cycling performance of $LiMn_2O_4$ material and reduces the electrode resistance (Rf) which results in the stabilization of the electrode structure as presented in Fig. 1b. The Nyquist plots of the samples were obtained in a fully charged state of 4.5 V after 50th cycle and fitted by the equivalent circuit. Detailed discussion about the influence of each element on the surface stability is described in [15]. After the 50th cycle, the electrode resistance of the L-LFP-LMO is lower (27.4 Ω) than that for the pristine (76.4 Ω), H-LFP-LMO (70.2 Ω) and N-LFP-LMO (39.1 Ω). This indicates the