# Supporting Information for

# "Insight into Fast Ion Migration Kinetics of A New Hybrid Single Li-Ion Conductor Based on Aluminate Complexes for Solid State Li-Ions Battery"

Yancong Feng,‡[a,b] Rui Tan,‡[b] Yan Zhao,[b] Rongtan Gao,[b] Luyi Yang,[b] Jinlong Yang,[b] Hao Li,[a] Guofu Zhou,[a] Haibiao Chen[b] and Feng Pan*[b]

[a]*Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, P. R. China.*

[b]*School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, P. R. China.*

Corresponding Author
*E-mail address: panfeng@pkusz.edu.cn (Feng Pan).

‡ These authors contributed equally.

Keywords: *Single Li-ion conductor, Solid state Li-ions battery, Aluminate complex, Conductive behavior, Li-ion migration kinetics*

**Section 1. Characterizations and measurements of materials**

**Section 2. Computational details**

## Section 1. Characterizations and measurements of materials

### 1.1. Materials characterization

The morphology of the LiAl–PEG/PEO membrane was observed by field-emission scanning electron microscopy (SEM, ZEISS Supra 55) and elemental mapping was analyzed by energy dispersive spectroscopy. Thermogravimetric analysis was conducted in a $N_2$ atmosphere at a heating rate of 5 °C $min^{-1}$ by a TGA/DSC1 system to analyze the thermal stability. The glass transition temperature ($T_g$) and melt temperature ($T_m$) was identified by DSC (DSC1). The characteristic spectrum of PEG and LiAl–PEG was studied by FTIR (Frontier). Nuclei magnetic resonance (NMR) spectrometers (1H NMR) with chloroform solvent were recorded on a Bruker DPX 400 MHz spectrometers.

### 1.2. Electrochemical measurements

The electrochemical characterization tests were conducted by a CHI 660E electrochemical workstation. For the EIS and ionic conductivity, electrolyte membranes were caught sandwiched between two block electrode stainless steels in coin cells (Fig. S1a), which were measured from 10 kHz to 0.1 Hz. To test electrochemical stability of hybrid membranes, single-ion conductors were sandwiched between block electrode (stainless steel) and lithium metal as an integration sealed in coin cells shown in Fig. S1b. This cells were studied at a scan of 0.2 mV $s^{-1}$ between 0 V and 8 V. Regarding the transfer number of Li-ions, the targeted electrolyte membranes were sandwiched between two lithium metal slices and then sealed in coin cells seen in Fig. S1c. Thereafter, by potentiostatic method, the current changes of cells were recorded at a constant voltage 10 mV.

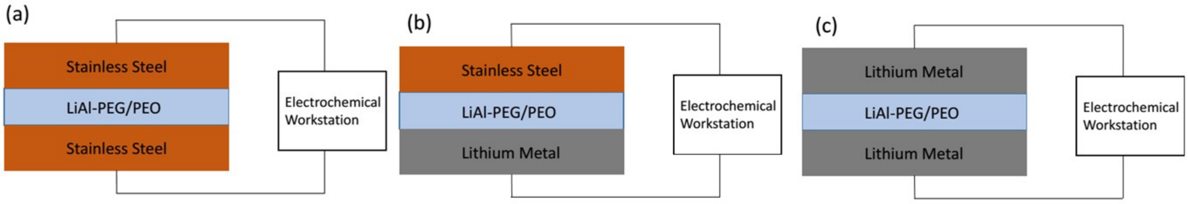

**Fig. S1** Configurations of electrochemical tests for (a) ionic conductivity, (b) electrochemical window and (c) transfer number.

The charge/discharge tests were carried out on a Land instrument (Wuhan Land electronic Co., Ltd. China) in potential range from 2.0 V (discharge) and 4.2 V (charge). The specific capacity of batteries are present in Fig. S2.

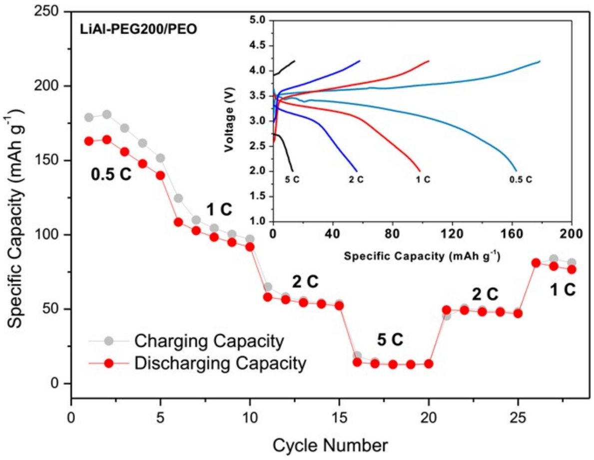

**Fig. S2** Electrochemical performance of batteries.

## Section 2. Computational details

### 2.1. Model of LiAl–PEG

The schematic of LiAl–PEG is displayed in Fig. S3a. One Al atom links four PEG chains by Al–O bonds. In the simulation, one LiAl–PEG chain contain 17 Al atoms (shown in Fig. S3b), and each PEG segment insists of 4 repeat units, corresponding to Mw = 200.

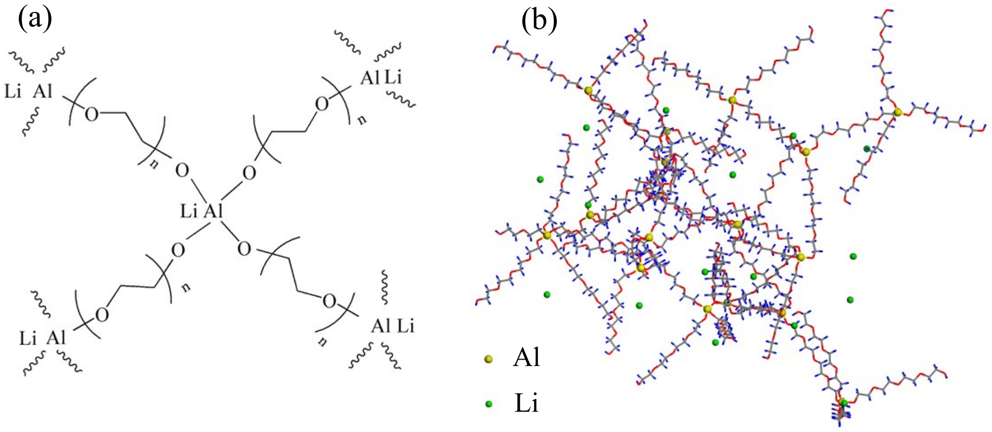

**Fig. S3** (a) Chemical structure and (b) model of LiAl–PEG.

## 2.2. Simulated detail

In the simulation with *NVT* ensemble, the systems were run for 50–100 ns to make sure the chains were fully relaxed. Take the $LiClO_4$/PEO system as the example. The mean square radius of gyration ($R_g^2$) of PEO chain and the potential energy of system were calculated for judging whether the system reached the equilibrium state. The mean square radius of gyration ($R_g^2$) is express by

$$R_{\mathrm{g}}^{\ 2} = \left\langle \frac{\sum_i m_{\mathrm{i}} (r_{\mathrm{i}} - r_{\mathrm{c.m.}})^2}{M} \right\rangle \tag{1}$$

The position of atom *i* with mass $m_{\mathrm{i}}$ is indicated by $r_{\mathrm{i}}$ and the center of mass $r_{\mathrm{c.m.}}$ of each chain is $r_{\mathrm{c.m.}} = \sum m_{\mathrm{i}} r_{\mathrm{i}} / M$, where $M$ is the total mass of chain. The data of following 350–450 ns were collected for analyses.

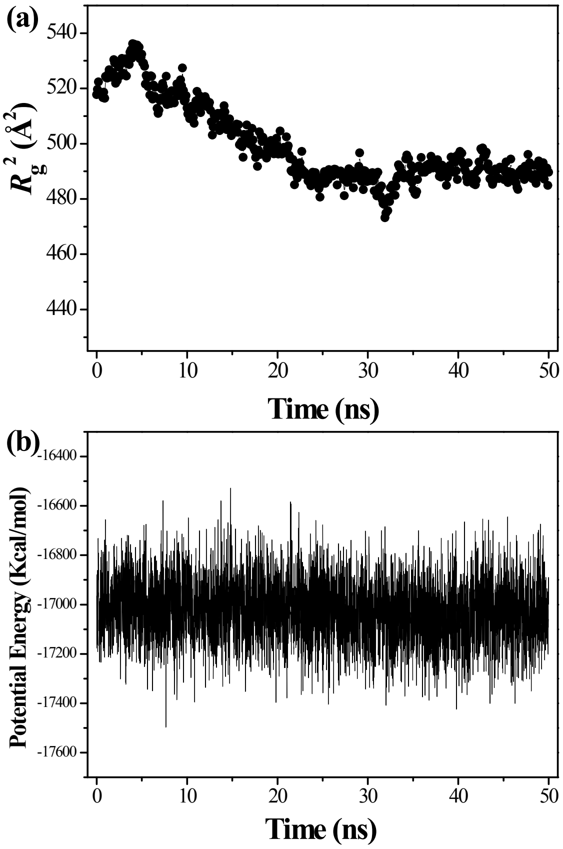

**Fig. S4** (a) The mean square radius of gyration ($R_g^2$) of PEO chain and (b) the potential energy of $LiClO_4$/PEO system during the relaxed process. Both the values fluctuate around the constant values respectively, which is indicative of a fully relaxed system.

## 2.3. Kinetic analysis of the three systems

The kinetic analyses are based on the self-diffusion coefficients ($D$), which is expressed by

$$D_i = \lim_{t\to\infty} \frac{\left\langle [R_i(t) - R_i(0)]^2 \right\rangle}{6t} \tag{2}$$

where $R_i$(t) is the displacement of the ion $i$ during time $t$. For simplicity of statistics, we calculated the Al atom to represent the anion cluster, and Cl atom to represent the $ClO_4^-$. Fig. S5 presents the MSDs of Li-ions and anions of LiAl–PEG, LiAl–PEG/PEO and $LiClO_4$/PEO systems, respectively. Fig. S6 shows that the $LiClO_4$/PEO system presents the highest self-diffusions coefficients $Li^+$ and anion, whereas the LiAl–PEG system has the lowest ones. The qualitative comparison of self-diffusions coefficients is the same as that of calculated ionic conductivity.

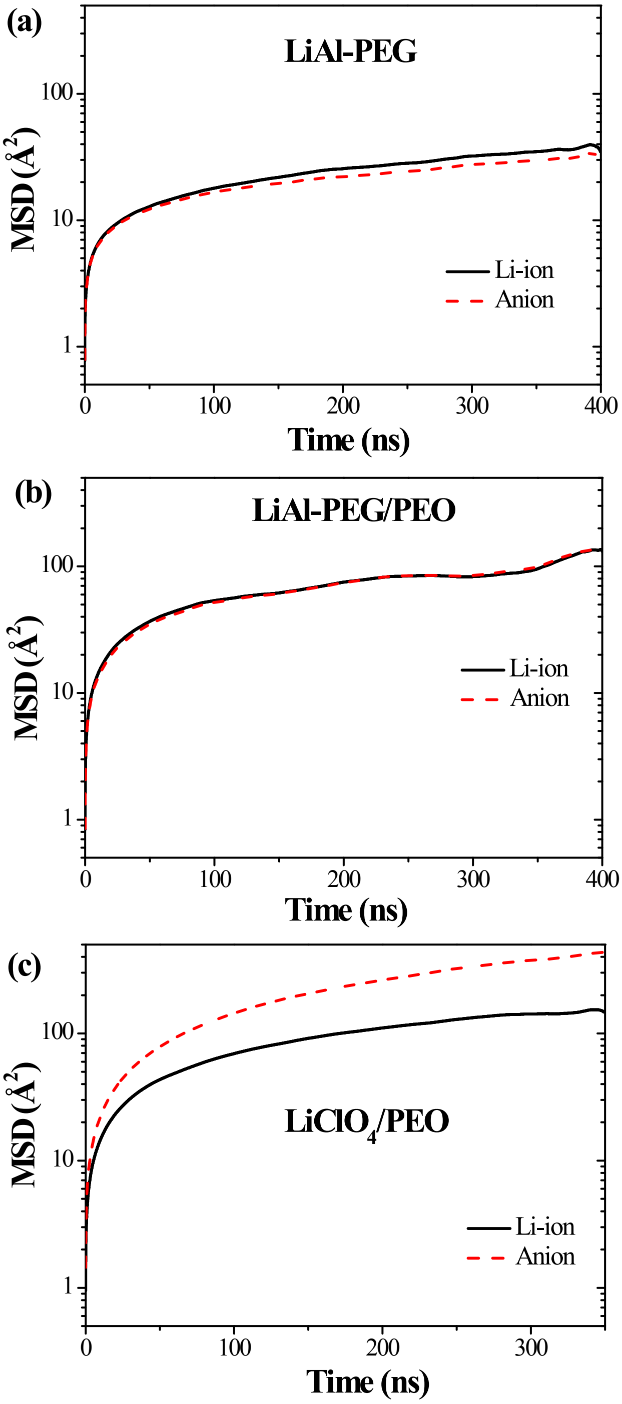

**Fig. S5** The MSDs of Li-ions (black solid lines) and anions (red dash lines) of (a) LiAl–PEG, (b) LiAl–PEG/PEO and (c) $LiClO_4$/PEO systems, respectively.

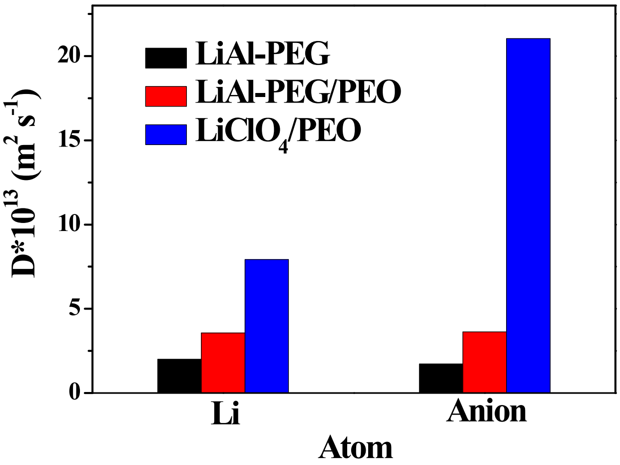

**Fig. S6** Self-diffusion coefficients ( $D$ ) of Li-ion and anion.

## 2.4. Process of Li transport under electric field

For verifying the Li transport mechanism, the simulated systems were added electric field in the Z-direction with the electric field intensity equal to 0.2 V $\text{Å}^{-1}$. Fig. S7 shows the displacements of ions at different directions under the electric field (Z-direction) in LiAl–PEG and $LiClO_4$/PEO systems, respectively. The ions have the obvious displacement in the electric direction, while they move very slowly in the other direction. For the LiAl–PEG system, only the Li-ions transport fast in the electric direction while the anions seem to fix at the original locations. This phenomenon agrees well with the behavior of most Single Li-Ion Conductor in experiment. For the $LiClO_4$/PEO system, the anions migrate faster than the Li-ions, which is in accord with the self-diffusion coefficients displayed in Fig. S6.

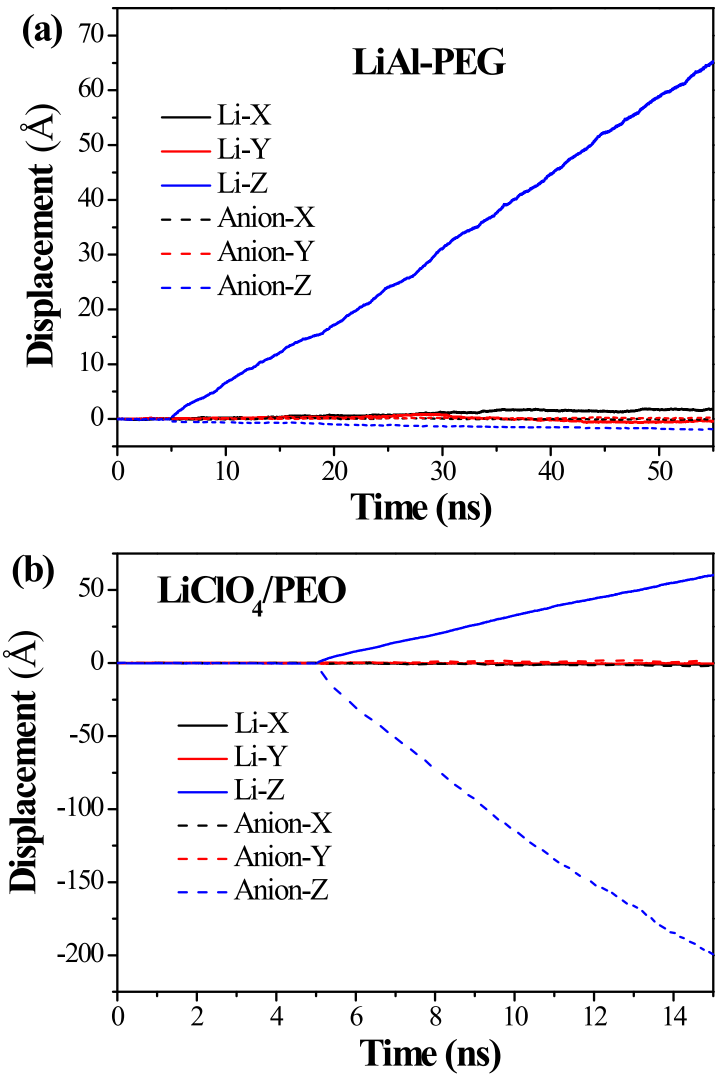

**Fig. S7** Displacements of ions at different directions under the electric field (Z-direction) in (a) LiAl–PEG and (b) $LiClO_4$/PEO systems, respectively.

### 2.5. Role of PEO in the LiAl-PEG complex Lithium

From the high resolution Li1s XPS spectra of LiAl–PEG (Fig. S8a) and LiAl–PEG/PEO (Fig. S8b), the main peak of Li shifts from 56.1 to 54.9 eV, attributing to the addition of PEO. Specifically, in LiAl–PEG, Li-ions are located around aluminum-ions contributing to the high binding energy, which is corresponding to our results of molecular dynamics simulation.

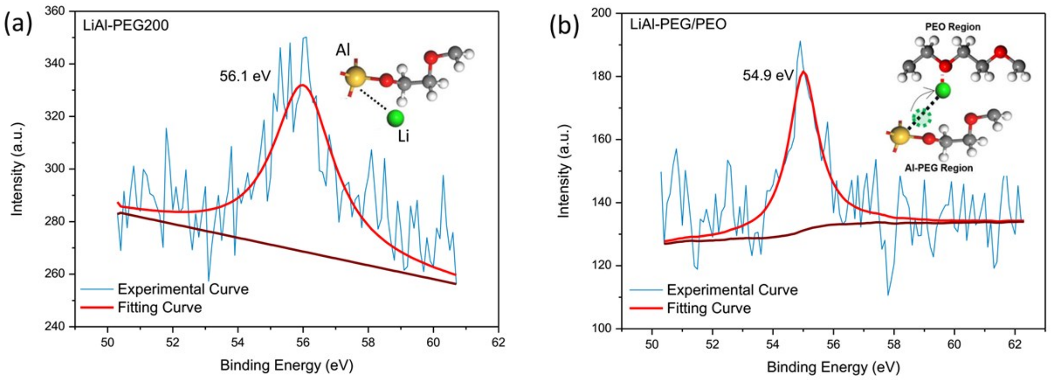

**Fig. S8** (a) Li1s XPS spectrum of LiAl–PEG200 and (b) Li1s XPS spectrum of LiAl–PEG200/PEO. Fitting curves (red lines) are obtained from software XPS PEAK, the purple lines are substrate lines automatically provided by this software.

With the addition of PEO chains, the Li atoms located around Al atoms tend to coordinate with the oxygen of PEO chains shown in the inset of Fig. S8b. In other words, the electron clouds from Li atoms and O atoms overlaps with each other, in which equivalently increasing outer electrons enhance the shielding effects on inner electrons. This results into the binding force from nuclear charges on inner electrons. Thus added PEO weakens the binding situation between nuclear charges and inner electrons, well explaining the low value of binding energy (54.9 eV). This part corresponds to calculation of uncorrelated motion ($\alpha_d$) or ionicity in our manuscript. Low ionicity means the strong interaction between ions and anions, resulting into the high migration barrier of Li-ions, such as in the LiAl–PEG system ($\alpha_d$ = 0.18). PEO acts as a good solvent for the Li-ions, improving the ionicity ($\alpha_d$ = 0.37 in the LiAl–PEG/PEO blend).