## Supplementary Materials for

Vertically-aligned and continuous nanoscale ceramic-polymer interfaces in composite solid polymer electrolytes for enhanced ionic conductivity

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Def	Trans of Ciller	Ionic conductivity at room temperature
Kel	Type of filler	(S/cm)
This work	APCE	$5.8 \times 10^{-4}$
<b>S</b> 1	LLTO NWs	$2.4 \times 10^{-4}$
S2	LLZO NWs	$2.5 \times 10^{-4}$
83	<i>in-situ</i> formed SiO <sub>2</sub> NPs	4.4 × 10 <sup>-5</sup> @ 30 °C
S4	Al <sub>2</sub> O <sub>3</sub> NPs	~10 <sup>-5</sup> @ 30 °C
85	Al <sub>2</sub> O <sub>3</sub> NPs	10 <sup>-5</sup> ~10 <sup>-4</sup>
<b>S</b> 6	Al <sub>2</sub> O <sub>3</sub> NPs	$9.39 \times 10^{-7}$
S7	ZrO <sub>2</sub> NPs	$2.65 \times 10^{-4}$
<b>S</b> 8	Graphene oxide	$2.1 \times 10^{-4}$ @ 30 °C
<b>S</b> 9	Y <sub>2</sub> O <sub>3</sub> -doped ZrO <sub>2</sub> NWs	$1.07 \times 10^{-5}$ @ 30 °C
S10	MgAl <sub>2</sub> SiO <sub>6</sub>	~1× 10 <sup>-4</sup>

 Table S1. Comparison of ionic conductivity at room temperature of APCE with that of

 conventional CSPE reported in literatures

To the best of our knowledge, the ionic conductivity of APCE at room temperature was one of the highest among literature reports. Benefitting from its vertically aligned and continuous ceramic-polymer interface, the ionic conductivity of APCE was even higher than conventional CSPE with lithium ion conductor fillers (such as LLTO, LLZO etc.).



Figure S1. (a) Top view SEM image of a AlF<sub>3</sub> coated AAO disc, (b) and (c) side view SEM image and EDX mapping of F element across the entire thickness of a AlF<sub>3</sub> coated AAO disc.

The diameter of nanochannels in the AAO disc did not change significantly after surface modification (Figure S1a). EDX mapping of F element at the cross section of AAO disc shows that the deposition of AlF<sub>3</sub> on the wall of nanochannels is uniform at different depth (Figure S1b and S1c).



Figure S2. The FTIR absorption spectra of C-O ether functional group region for the electrolytes involved in this study: (a) green line for SPE, blue line for CSPE-NPs, Orange line for CSPE-NWs, red line for ACPE-300K-200; (b) red line for ACPE-300K-200, grey line for ACPE-300K-90, and blue line for ACPE-300K-40.

As shown in Figure S2a, the peaks of ether functional group in SPE locate at 1094 and 1052 cm<sup>-1</sup> in SPE. With the addition of nanoparticle or nanowires, this pair of peaks shift to 1096 and 1054 cm<sup>-1</sup>. In the APCE, the 200 nm pore cause an even more obvious shift to 1112 and 1058 cm<sup>-1</sup>. These C-O vibration changes are coincident with C-H changes, indicating the effect of interfaces influence the chain arrangement of PEO polymers. For the APCE with different pore size, we have carefully checked the C-O vibration region; however, there is no obvious peak shift, except a little bit shape variation (Figure S2b).



Figure S3. DSC traces of pure PEO membrane (blue) and the composite, consisting of AAO disc and PEO without lithium salt (green).

For PEO without lithium salt, the effect of the vertically aligned continuous ceramic-polymer interface on inhibiting crystallization of polymer matrix can be observed more clearly. In the composite with AAO disc, the melting/crystallization transition temperature of PEO decreased significantly from 65.3 °C to 23.5 °C. Additionally, an exothermic peak broader than pure PEO membrane is exhibited in the composite consisting of AAO disc and PEO without lithium salt.



Figure S4. FTIR absorption spectra of APCE-300K, APCE-300K-AF, APCE-1.5K, and APCE-1.5K-AF.

FTIR spectra were also recorded for APCE with and without AlF<sub>3</sub> surface modification. Both APCE with and without AlF<sub>3</sub> surface modification show similar bands of PEO in CH asymmetric stretching, CH symmetric stretching, CH scissoring, CH asymmetric bending, and CH wagging in their FTIR spectra. This indicates that the binding behaviors of PEO segments on the surface of ceramic phase were not significantly changed by the AlF<sub>3</sub> surface modification.



Figure S5. (a) Electrochemical impedance spectra measured at room temperature, and (b) Arrhenius plots of ionic conductivity of APCE based on pristine AAO and AAO with surface modification.

Ionic conductivity measurement results of APCE-1.5k with and without AIF<sub>3</sub> surface modifications are shown in Figure S5. The APCE based on low molecular weight polymer (PEG,  $M_w \sim 1500$ ) showed a similar trend of ionic conductivity enhancement induced by surface modification, which was also observed in APCE based on high molecular weight polymer. This suggests that the strategy of enhancing ionic conductivity of APCE by strong Lewis acid surface modifying is effective regardless of the molecular weight of the polymer involved in APCE.



Figure S6. SEM images of pristine AAO (a, c, and e) and APCE (b, d, and f) with different pore size: (a, b) 200 nm; (c, d) 90 nm; (e, f) 40 nm.

AAO discs with different pore sizes were examined using SEM before and after polymer infiltration. The top view images shown direct evidence that all pores have been filled after vacuum infiltration. There was minimum amount of bulk polymer left over on the surfaces of AAO discs.

(a) SPE	(C) APCE 300K	(e) APCE 1.5K
(b)	(d)	(f)
(b)	(d)	
(b)	(d)	

Figure S7. Photographs of solid electrolytes before (upper) and after (lower) baked on a hot plate at 80 °C for 1h: SPE (a, b), APCE-300K (c, d), APCE-1.5K (e, f).

APCE based on the polymers with different molecular weight exhibit superior thermal stability to SPE. After baking at 80 °C for 1h, the sample of SPE would be sticky and shrink in size. On the contrary, APCE did not show any changes in terms of its macroscopic morphology and mechanical hardness.



Figure S8. SEM images of cross section of ceramic-free solid polymer electrolyte membranes

The total thickness of ceramic-free solid polymer electrolyte was also measured using SEM. We controlled the doctor blading process so that it has the similar thickness of 60 um as APCE.



Figure S9. Photographs of solid electrolytes before (left), during (middle) and after (right) burning: SPE (a-c), APCE-300K (d-f), APCE-1.5K (g-i).

The thermal stability of APCE is further demonstrated by the combustion test. As shown in Supplementary Figure 9a-9c, SPE caught fire immediately when touched with the flame of a lighter and only a bit of ashes are left after burning off. In comparison, APCE exhibited a much better thermal stability. Firstly, the combustion of APCE was much less violent than SPE. Additionally, the ceramic framework of APCE maintained its spatial structure and most of mechanical strength although polymer phase was burned off. The combustion test indicates that APCE may provide a hard ceramic barrier to physically block the cathode and anode from shorting, even after burning.

Note S1. Calculation of the specific surface areas of nanoparticles, nanowires, and AAO discs, and porosity of AAO discs



Figure S10. Schematic illustration of the specific surface areas of nanoparticles, nanowires, and AAO discs used for CSPE and APCE. The surfaces are highlighted in red in the planar graph.

The surfaces of nanoparticles, nanowires, and AAO discs used for CSPE and APCE are highlighted in red in Figure S10.

The specific area of nanoparticles per unit volume can be expressed as:

$$A_{NP} = \frac{M_{Al_2O_3}}{\rho_{Al_2O_3}} \times \frac{4\pi r^2}{\frac{4}{3}\pi r^3} / (\frac{M_{PEO}}{\rho_{PEO}} + \frac{M_{Al_2O_3}}{\rho_{Al_2O_3}})$$
(S1)

where *r* is the radius of nanoparticles (~50 nm),  $M_{Al_2O_3}$ ,  $\rho_{Al_2O_3}$ ,  $M_{PEO}$ , and  $\rho_{PEO}$  are the mass and density of Al<sub>2</sub>O<sub>3</sub> and PEO, respectively.

The specific area of nanowires per unit volume can be given as:

$$A_{NW} = \frac{M_{Al_2O_3}}{\rho_{Al_2O_3}} \times \frac{\pi dl + \frac{\pi d^2}{4}}{\pi d^2 l} / \left(\frac{M_{PEO}}{\rho_{PEO}} + \frac{M_{Al_2O_3}}{\rho_{Al_2O_3}}\right)$$
(S2)

where d is the diameter of nanowires (~4 nm), l is the length of nanowires (~300 nm),  $M_{Al_2O_3}$ ,  $\rho_{Al_2O_3}$ ,  $M_{PEO}$ , and  $\rho_{PEO}$  are the mass and density of Al<sub>2</sub>O<sub>3</sub> and PEO, respectively.

In APCE, polymer is infiltrated into the nanochannels of AAO discs. The volume of the composite electrolyte is decided by the dimensions of the AAO discs. The ceramic-polymer interfacial area per unit volume in APCE can be expressed as:

$$A_{AAO} = \frac{2\pi r t}{\frac{\sqrt{3}}{2}a^2 t} = \frac{4\pi r}{\sqrt{3}a^2}$$
(S3)

and the porosity of AAO discs used for APCE can be expressed as:

$$Poro_{AAO} = \frac{\pi r^2 t}{\frac{\sqrt{3}}{2}a^2 t} \times 100\%$$
(S4)

where *r* is the radius of nanochannels in AAO disc (100, 45, and 20 nm), *t* is the thickness of AAO discs ( $\mu$ m), *a* is the side length of the rhombus whose vertices positioned at the centers of 4 nanochannels (255, 125, 65 nm), respectively.

The calculated values of the surface area and porosity are summarized in Table S2.

Table S2. Summary of the calculated specific surface areas of nanoparticles and nanowires used for CSPE, and the calculated specific surface areas and porosities of AAO discs with different pore size used for APCE.

Sample	Specific surface area (cm <sup>-1</sup> )	Porosity (%)
Nanoparticles	3.6×10 <sup>4</sup>	
Nanowires	3.0×10 <sup>5</sup>	
AAO ( <i>r</i> = 100 nm)	1.1×10 <sup>5</sup>	55.76
AAO $(r = 45 \text{ nm})$	2.1×10 <sup>5</sup>	46.99
AAO $(r = 20 \text{ nm})$	3.4×10 <sup>5</sup>	34.33

### Note S2. Calculation of activation energy of SPE, CSPE, and APCE

According to Vogel-Tammann-Fulcher (VTF) theory, the typical curvature of natural logarithm of ionic conductivity versus 1/T can be molded with the following equation:

$$\delta = \frac{A}{T^{0.5}} exp\left[\frac{-E_a}{k(T-T_0)}\right] \tag{S5}$$

where *A* is a preexponential factor, *T* is the absolute temperature, *k* is Boltzmann's constant,  $E_a$  is the activation energy, and  $T_0$  is the reference temperature which is close to the glass transition temperature. The activation energy of the solid electrolytes involved in this study is obtained by nonlinear fitting of Arrhenius plots of measured ionic conductivities versus temperatures (0 °C to 90 °C) by S5. To reveal the different Li<sup>+</sup> conducting mechanisms in polymer electrolytes, the activation energies before and after polymer matrix melts was evaluated based on the ionic conductivities measured at the temperatures lower and higher than their melting points, respectively. The best-fit  $E_a$  are summarized in Table S3.

Sample	E <sub>a</sub> (eV)	$E_a^{1}$ (eV)	$E_a^2$ (eV)	T <sub>melt</sub> (K)
SPE	0.042	0.041	0.057	303
CSPE-NPs	0.059	0.055	0.110	298
CSPE-NWs	0.040	0.039	0.052	299
APCE-300K-200	0.027	0.027	0.016	288
APCE-300K-90	0.028	0.028	0.013	288
APCE-300K-40	0.026	0.026	0.013	288

Table S3. Summary of the activation energy for SPE, CSPE, and APCE<sup>\*</sup>

\*  $E_a$  is calculated based on the VTF fitting of Arrhenius plots of ionic conductivity from 0 °C to 90 °C.  $E_a^{-1}$  is the activation energy after melting (T > T<sub>melt</sub>).  $E_a^{-2}$  is the activation energy before melting (T < T<sub>melt</sub>).

## Note S3. Calculation of the degree of crystallinity of polymer in SPE, CSPE, and APCE

The degree of crystallinity of PEO or PEG ( $X_c$ ) in the presented SPE, CSPE, and APCE is quantified based on the DSC data and the melting enthalpy of 100% crystalline PEO. Specifically,  $X_c$  is given as

$$X_c = \frac{\Delta H_m}{\Delta H_o f_{PEO}} \times 100\%$$
(S1)

where  $\Delta H_m$  is the melting enthalpy of the samples (J/g),  $\Delta H_o$  is the melting enthalpy of the completely crystallized PEO (213.7 J/g)<sup>11</sup> or PEG (262.0 J/g)<sup>12</sup>,  $f_{PEO}$  is the polymer weight fraction of the samples (%). In this study,  $\Delta H_m$  is calculated based on the measured DSC data.  $f_{PEO}$  is determined by the materials ration in composite electrolytes. The calculated degree of crystallinity is summarized in Table S4.

Sample	$\Delta H_m$ (J/g)	$\Delta H_o$ (J/g)	<i>f</i> <sub>PEO</sub> (%)	$X_{c}$ (%)
SPE	38.57	213.7	90	22.7
CSPE-NPs	38.45	213.7	90	20.0
CSPE-NWs	37.84	213.7	90	19.7
APCE-300K-200	9.64	213.7	0.31	14.7
APCE-300K-90	1.13	213.7	0.24	3.36
APCE-300K-40	0.96	213.7	0.15	1.96
APCE-300K-AF	6.40	213.7	0.31	9.79
APCE-1.5K-AF	0.75	262.0	0.31	0.94

 Table S4. Summary of the calculated degree of crystallinity of polymer in SPE, CSPE, and

 APCE.

Note S4. Analysis of ionic transport numbers of composite solid polymer electrolytes involved in this study



Figure S11. Variation of polarization current in SS/electrolyte/SS symmetrical cells at room temperature, with total applied bias of 80 mV: (a) APCE-300K, (b) APCE-300K-AF; (c) APCE-1.5K, (d) APCE-1.5K-AF, (e) SPE, (f) CSPE-NPs, and (g) CSPE-NWs.

The ionic transport number of polymer electrolytes involved in this study was estimated using d.c. polarization technique. The variation of polarization current as a function of time is shown in Supplementary Fig. 10. The ionic transport number was valued by the following relation:

$$t_{ion} = \frac{I_{total} - I_e}{I_{total}} \times 100\%$$
(S6)

The values obtained were summarized in Table S5. One can see that the  $t_{ion}$  of APCE are >99%. This indicates that APCE presented here are predominantly ionic conductor. The low electronic conductivity of APCE is desired for its utility in lithium ion batteries. Additionally, the APCE with AlF<sub>3</sub> surface modified AAO exhibited a slightly higher ionic transport number than its counterparts with pristine AAO. This can be attributed to the AlF<sub>3</sub> surface modification increasing the concentration of ionic carriers in APCE by enhancing the Lewis acid-base interaction on the ceramic-polymer interface.

Sample	I <sub>total</sub> (nA)	$I_{e}(nA)$	$t_{ion}$ (%)
ACPE-300K	910.95	4.95	99.46
APCE-300K-AF	765.96	2.56	99.67
APCE-1.5K	661.63	5.15	99.22
APCE-1.5K-AF	493.96	1.35	99.73
CSPE-NWs	224.56	0.67	99.70
CSPE-NPs	100.50	4.40	95.62
SPE	450.04	2.48	99.45

Table S5. Summary of the ionic transport number  $(t_{ion})$  for APCE with based on pristine AAO and AAO with surface modification, conventional CSPE, and SPE

# Note S5. Analysis of the interfacial and non-interfacial ionic conductivity, and the thickness of interfacial layer in APCE

As depicted in the Figure 4a in the manuscript, we divided the polymer cylinder in a nanochannel into two regions: region I, which is the bulk part far from the ceramic-polymer interface, and region II, which is the interfacial layer formed at the surface of ceramic phase. The overall ionic conductance in APCE can be expressed as:

$$S = \sigma_1 \frac{A\alpha - A\beta d}{t} + \sigma_2 \frac{A\beta d}{t}$$
(S7)

where *S* is the overall ionic conductance of APCE (S), *A* is the cross-sectional area of APCE (cm2), *t* is the thickness of interfacial layer (cm),  $\alpha$  is the porosity of AAO discs (%),  $\beta$  is the specific interface area in APCE (cm<sup>-1</sup>),  $\sigma_1$  is the ionic conductivity of region I (S/cm), and  $\sigma_2$  is the ionic conductivity of region II (S/cm). The Li<sup>+</sup> conducting behaviors in both region I and region II should be abided by VTF model, since only polymer phase contributes to Li<sup>+</sup> conducting in APCE. Therefore,  $\sigma_1$  and  $\sigma_2$  can be given as:

$$\sigma_1 = \frac{A_1}{T^{0.5}} exp\left[\frac{-B_1}{k(T-C_1)}\right]$$
(S8)

$$\sigma_2 = \frac{A_2}{T^{0.5}} exp\left[\frac{-B_2}{k(T-C_2)}\right] \tag{S9}$$

In addition, the interfacial layer is formed because of the polymer segment anchoring and cross-linking at  $Al_2O_3$  surface. The nature of its temperature dependence of thickness should be the interface-effected segments dynamics versus temperature. The VTF model is also very successful in describing the temperature dependent ionic conductivities of composite electrolytes involving ceramic fillers. It is known that the ionic conductance in ceramic-polymer composite electrolytes is partly relied on the mobility of the polymer segments, which is influenced by the interactions between the ceramic phase and polymer segments. This indicates that the VTF model is applicable to describe the dynamic process related to the temperature-dependent mobility of polymer segments, even though the effects of ceramic-polymer interfaces are involved. Thus, we assumed that *t* also can be described by VTF model like ionic conductivities. It should be noted that the coefficient of the exponential term in

VTF equation for *t* should be positive. This is because the segments' mobility of the whole polymer cylinder increases as temperature increases and the effective thickness of the interfacial layer with extraordinary ionic conductivity will become thinner and thinner. Above all, the thickness of the interfacial layer can be expressed as:

$$t = \frac{A_3}{T^{0.5}} exp\left[\frac{B_3}{k(T-C_3)}\right]$$
(S10)

where *T* is the absolute temperature, *k* is Boltzmann's constant,  $A_i$  is a preexponential factor,  $B_i$  is a activation energy related term, and  $C_i$  is the reference temperature which is close to the glass transition temperature (*i*= 1, 2, 3). Combing equation S7-S10, we can obtain an expression for overall ionic conductance in APCE. Through nonlinear fitting of measured ionic conductance versus temperatures by the expression, the parameters ( $A_i$ ,  $B_i$ ,  $C_i$ , *i*=1, 2, 3) can be obtained. Then, the interfacial and non-interfacial ionic conductivity, and the thickness of interfacial layer can be calculated by S8-S10. To study the impact of surface chemistry and molecular weight of polymer on interfacial and non-interfacial ionic conductivity, and the thickness of interfacial layer in APCE, the nonlinear data fitting was conducted for the ionic conductance of APCE-300K, APCE-300K-AF, and APCE-1.5K-AF measured in the temperature range from 0 °C to 90 °C. The best-fit parameters are summarized in Table S6. Note that APCE-300K and APCE-300K-AF have a thermal transition at 15 °C and 1 °C, respectively, according to their DSC traces. Thus, the conductance of APCE-300K and APCE-300K-AF measured at temperatures lower and higher than their thermal transition temperature are fitted separately. Meanwhile, the data fitting of APCE-1.5K-AF was conducted by one run, since its thermal transition temperature is lower than 0 °C

As seen in Table S6, the reference temperature determined by the best-fitting, the value of  $C_i$  (*i*=1, 2, 3), is slightly lower than the reported glass transition temperature of polymer composite<sup>13, 14</sup>, which is corresponding to its definition<sup>15</sup>. Furthermore, the reference temperature of the interfacial part ( $C_2$  and  $C_3$ ) is slightly lower than that of bulk part ( $C_1$ ). This is consistent with the hypothesis on the ceramic-polymer interactions would impede the recrystallization of polymer matrix, which has been noted and proved by previous publications<sup>3, 4, 16, 17</sup>. These consistencies may prove the presented approach for VTF analysis based on data fitting is effective to some extent.

Sample	APCE-300K		APCE-300K-AF		
Paras	Below 15 °C	Above 15 °C	Below 1°C	Above 1 °C	APCE-1.5K-AF
A <sub>1</sub>	3.5877	1.6152	2.4853	1.1476	0.8380
$B_1$	391.1849	369.3368	392.601	365.4448	290.0448
$C_1$	244	244	235.7889	235.7889	235
A <sub>2</sub>	0.20731	0.4852	0.1798	0.4648	0.95861
$B_2$	250.1104	198.4843	235.6047	190.2526	188.4051
C <sub>2</sub>	223	223	215	215	215
A <sub>3</sub>	9.37×10 <sup>-6</sup>	9.03×10 <sup>-6</sup>	8.20×10 <sup>-6</sup>	8.20×10 <sup>-6</sup>	2.13×10 <sup>-6</sup>
B <sub>3</sub>	1×10 <sup>-15</sup>				
C <sub>3</sub>	223	223	215	215	215

Table S6. Best-fit VTF parameters for the conductance of APCE-300K, APCE-300K-AF, and

APCE-1.5K-AF (0 °C to 90 °C)

Note S6. Calculation of the interfacial area per volume of polymer in the APCE with different pore size



Figure S12. Schematic illustration of the interfacial area per volume of polymer in the APCE: the interfaces are highlighted in red in the planar graph, the orange part is the polymer cylinder in nanochannels, and the grey part is the AAO template.

To determine the interfacial area dependence of ionic conductivity, the interfacial area per volume of polymer in APCE should be quantified, since the ionic conductivity in this study is normorlized based on the polymer cross-section area.

The ceramic-polymer interfacial area per unit volume in APCE can be expressed as:

$$A_{inter} = \frac{2\pi rt}{\pi r^2 t} = \frac{2}{r} \tag{S3}$$

where r is the radius of nanochannels in AAO disc (100, 45, and 20 nm), t is the thickness of AAO discs ( $\mu$ m). The calculated interfacial areas per volume of polymer in the APCE with different pore size were summarized in Table S7.

Table S7. Summary of the calculated interfacial areas per volume of polymer in the APCEwith different pore size

Pore size (nm)	interfacial areas per volume of polymer (cm <sup>-1</sup> )
200	$1.00 \times 10^{7}$
90	$2.22 \times 10^7$
40	$5.00 \times 10^{7}$

Note S7. Electrochemical measurements of solid electrolytes based on PEO-LiClO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>



Figure S13. Arrhenius plots of ionic conductivity of SPE, APCE with different polymer molecular weight and surface modified nanochannels based on LiClO<sub>4</sub>.

The ionic conductivity enhancement was not unique to a specific lithium salt such as LiTFSI. With other lithium salts such as  $LiClO_4$  that we have tested, APCE has also shown ionic conductivity improvement using AAO as the backbone in the composite polymer electrolyte. Similar to the LiTFSI system, the ionic conductivity in the  $LiClO_4$  system can be further improved using AlF<sub>3</sub> surface modification and polymer weight optimization.



Figure S14. Electrochemical impedance spectra of APCE with different nanochannel diameters measured at room temperature: 200 nm (red), and 90 nm (blue).

 Table S8. Ionic conductivities and interfacial area of APCE with different nanochannel

 diameters

Diameter (nm)	Interfacial area $(10^5 \text{ cm}^{-1})$	$\sigma$ (10 <sup>-6</sup> S/cm)
200	1.1	1.76
90	2.1	3.25
Ratio (200:90)	1:1.90	1:1.85

For APCE based on LiClO<sub>4</sub>, the quantitative relationship between ionic conductivities and diameter of nanochannels in AAO disc can be observed at room temperature, due to the absence of plasticizing effect from  $ClO_4^-$ . Figure S14 shows the EIS spectra of LiClO<sub>4</sub>-based APCE with the nanochannel diameter of 200 and 90 nm measured at room temperature. Their ceramic-polymer interfacial area and ionic conductivities are summarized in Supplementary Table S8. One can see the ratios of interfacial area and ionic conductivities between APCE with two different nanochannels diameters are roughly equal.

Note S8. Optimization of [EO]/[Li] ratio and molecular weight in APCE



Figure S15. (a) Electrochemical impedance spectra measured at room temperature, and (b) Arrhenius plots of ionic conductivity of LiTFSI-based APCE with different [EO]/[Li] ratios: 24:1 (yellow), 16:1 (red), 12:1 (green), 8:1 (blue).

The ionic conductivity of APCE with different [EO]/ [Li] ratios are studied. LiTFSI- based APCE with the [EO]/ [Li] ratio of 16:1 exhibits superior ionic conductivities in the temperature range from 0 °C to 90 °C. The optimized ionic conductivity at the [EO]/ [Li] ratio of 16:1 may be derived from the balancing of the concentration of ionic carriers and the lithium salt related crystallization behaviors.

Interestingly, comparing to samples with [EO]/[Li] ratio of 16:1. the ionic conductivity of the samples with the higher lithium concentration of [EO]/ [Li] ratio of 8:1 has slightly higher lithium ion conductivity at 90 °C but lower lithium ion conductivity at room temperature. Such phenomena can be well explained by recent discovery by Hsu and his colleagues18, in which they found the local viscosity plays an important role in determining the overall lithium ion conductivity. For samples with higher lithium ion concertation, the high local viscosity may impede lithium ion conduction, especially at low temperature region. When temperature increases, this phenomenon is less pronounced as the viscosity can be greatly reduced at higher temperature. Indeed, we observed higher lithium ion conductivity at higher temperature region for samples with high lithium salt concentration due to higher ion carrier concentration after lithium salt dissociation.



Figure S16. Arrhenius plots of ionic conductivity of APCE with different polymer molecular weight based on LiClO<sub>4</sub>.

It is generally believed that the polymer matrix with lower molecular weight would exhibit a lower crystallinity and higher ionic conductivities. The ionic conductivity of  $LiClO_4$ -based APCE with different polymer molecular weights are studied in the temperature range from 0 °C to 90 °C. The trend of increasing ionic conductivity of APCE with decreasing molecular weight of polymer was observed. As expected, APCE with PEG (M<sub>w</sub> 1500) exhibited superior ionic conductivities over other counterparts.

#### **Supplementary References**

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