An interpenetrating network polycarbonate-based composite electrolyte for high-voltage all-solid-state lithium-metal batteries

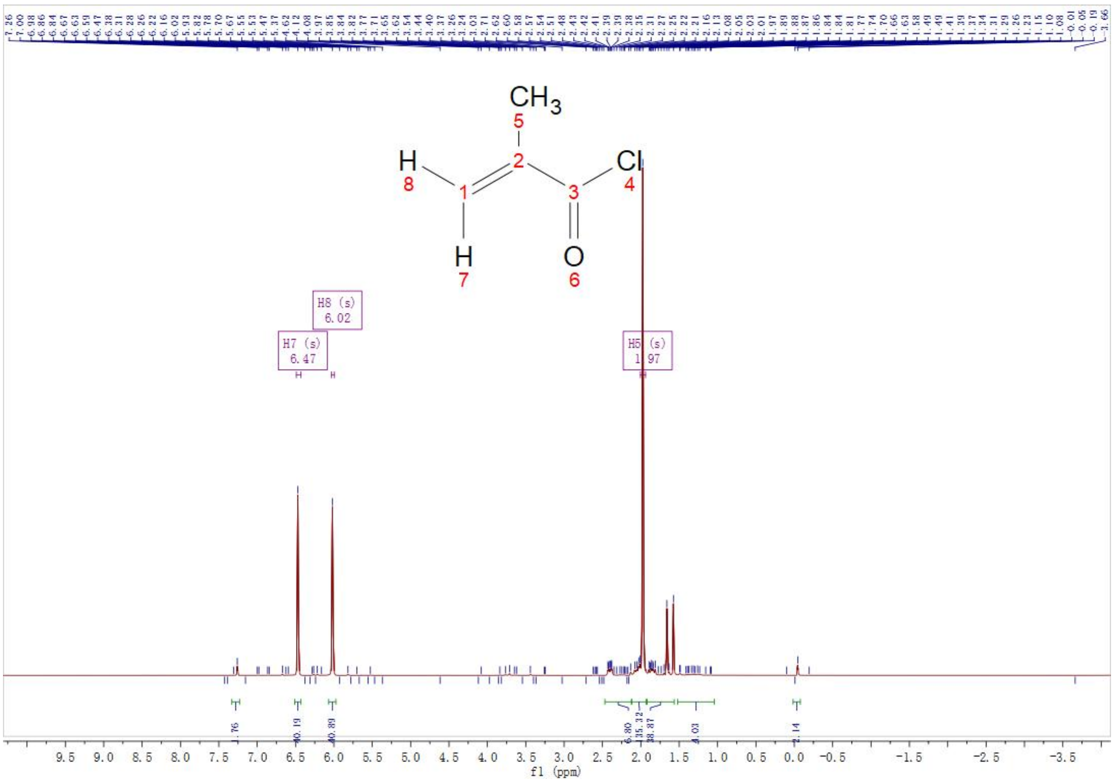
Jiaxin Chen, Chao Wang, Guoxu Wang, Dan Zhou[*], Li-Zhen Fan[*]

Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, Beijing, 100083, China.

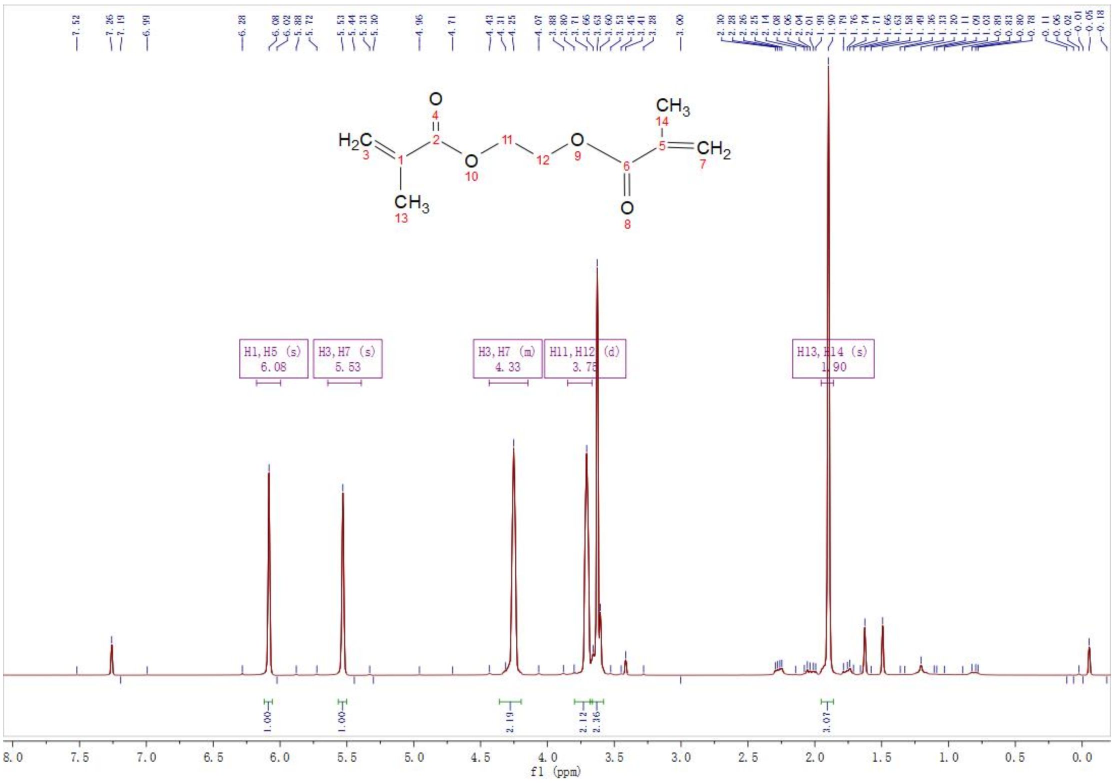
Correspondence to: Prof. Li-Zhen Fan, Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083, China. E-mail: fanlizhen@ustb.edu.cn; ORCID: 0000-0003-2270-4458; Prof. Dan Zhou, Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083, China. E-mail: zhoudan@ustb.edu.cn; ORCID: 0000-0002-5051-9682

Preparation process of positive electrode:

Prepare positive electrode material active material ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$/$LiFePO_4$), binder (PVDF), conductive agent (acetylene black) and solid electrolyte, and weigh them according to the mass ratio of active material, binder PVDF, conductive agent acetylene black and solid electrolyte of 7:1:1:1. Put the positive active material and acetylene black into a mortar and grind for 15 minutes. Then add binder PVDF to the mortar and continue wet grinding for 20 minutes. Finally, the polymer electrolyte was added into the mortar and wet ground for 20 minutes to obtain a uniform positive electrode slurry. Scrape the positive paste onto the positive current collector (aluminum foil coated with carbon layer) with a thickness of 200 microns, put it into the oven and dry it for 12 hours, and set the oven temperature to 60 ℃. After the pole piece is completely dry, take it out of the oven, cut the pole piece into a round piece with a diameter of 14mm, then put it into the vacuum drying oven for standby.

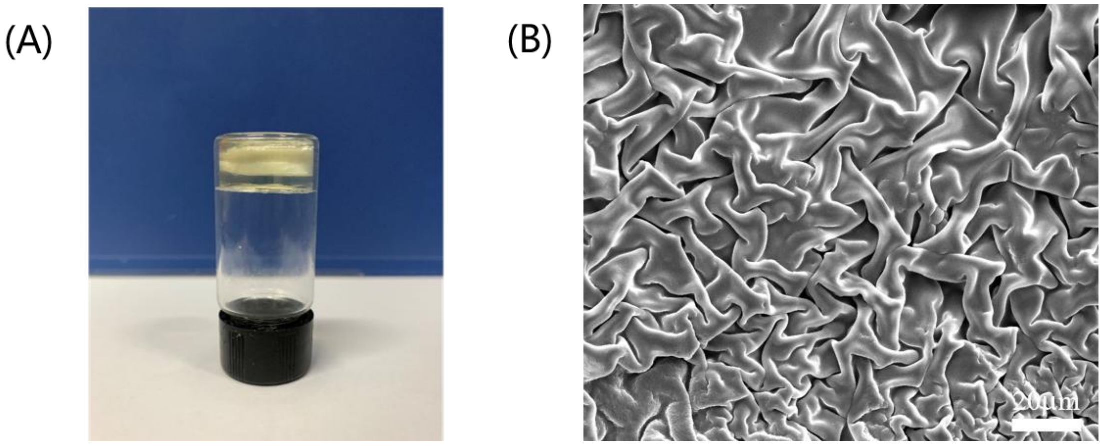


Supplementary Figure 1. ^{1}H NMR spectra of methacryloyl chloride in $CDCl_3$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 1H), 6.02 (s, 1H), 1.97 (s, 3H).

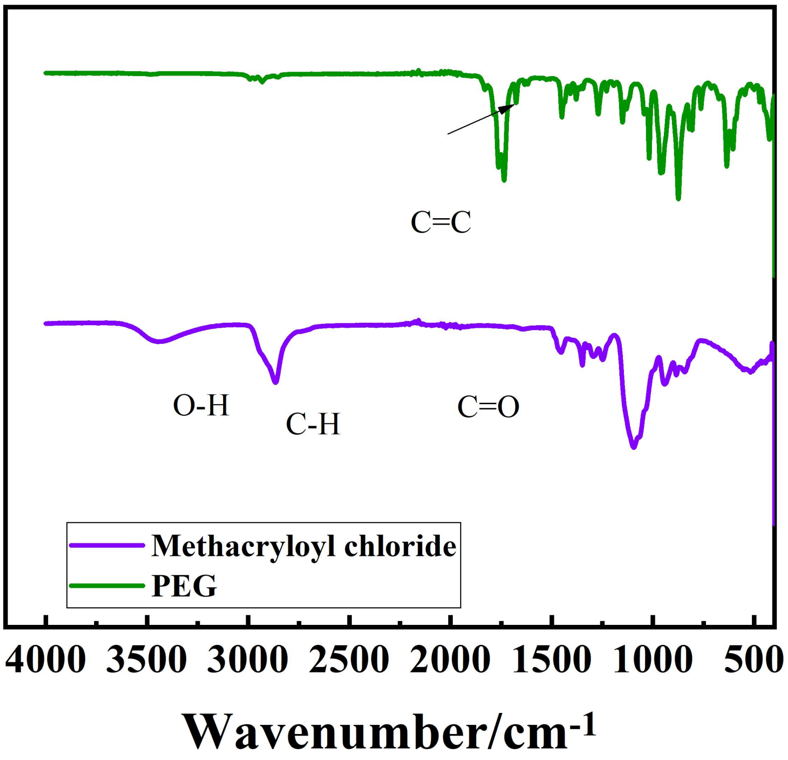


Supplementary Figure 2. ^{1}H NMR spectra of symmetrical monomer in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.53 (s, 1H), 4.25 (s, 2H), 3.69 (d, *J* = 15.5 Hz, 2H), 3.68 - 3.57 (m, 2H), 1.90 (s, 3H). (Because the polyethylene glycol chain segment is too long, only two hydrogen sites are listed here, namely H11 and H12.)

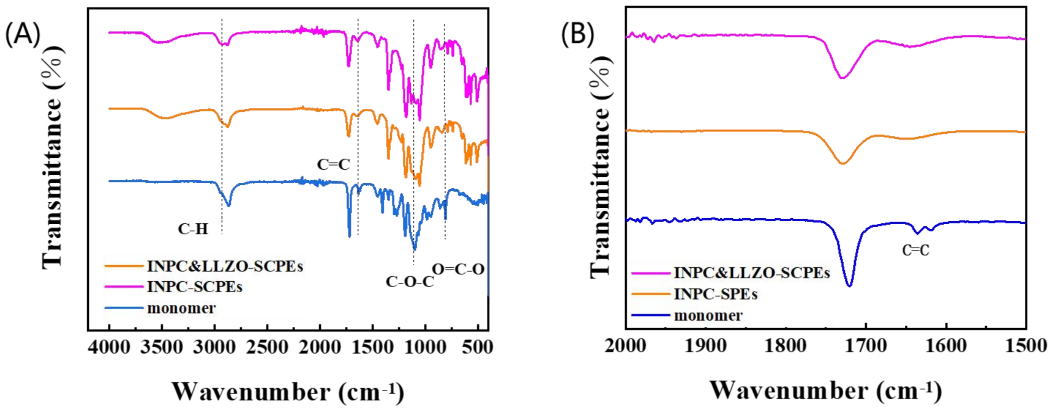
The symmetrical polycarbonate monomer possesses ethylene oxide units and carbonate units alternately, with monomer terminated by methacryl. It was proven by ^{1}H-NMR that the monomer was synthesized successfully. In methacryloyl chloride, the proton peaks at 6.47 and 6.02 ppm correspond to -C=C-, and the proton peak at 1.97 ppm corresponds to $-CH_3-$ (as shown in Supplementary Figure 1). After the nucleophilic substitution reaction, the proton peak at 5.4 ppm disappeared, while the peaks at 1.90, 5.53 and 6.08 ppm appeared in the product, which proved that the hydroxyl functional group was replaced by the halogen atom in methacryloyl chloride. Therefore, symmetric structure monomers that terminated by methacrylic acid groups were successfully synthesized by the nucleophilic substitution reaction. The proton peaks that appeared at 4.26 and 3.70 ppm were assigned to $-OCOOCH_2-$ and-OCH_2CH_2O-, respectively (as shown in Supplementary Figure 2)



Supplementary Figure 3. (A) Photograph of the INPC-SPEs. (B) SEM image of INPC-SPEs.

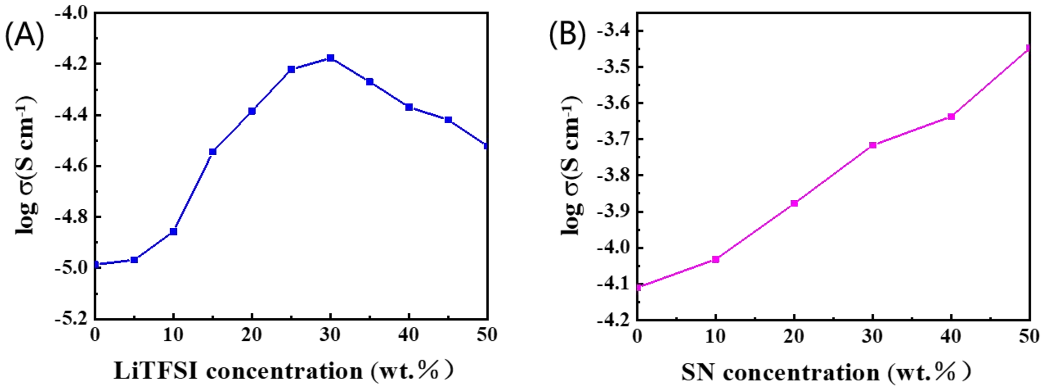


Supplementary Figure 4. FTIR spectra of Methacryloyl chloride and PEG.

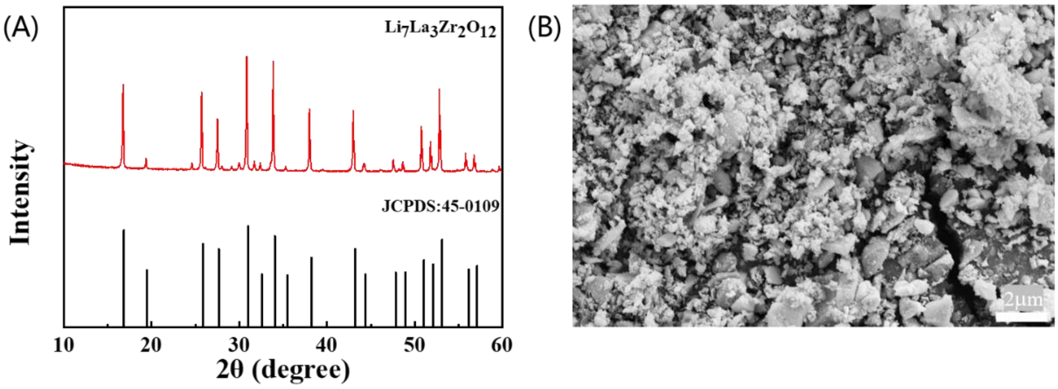


Supplementary Figure 5. (A) FTIR spectra of monomer and solid electrolyte. (B) Partial schematic diagram.

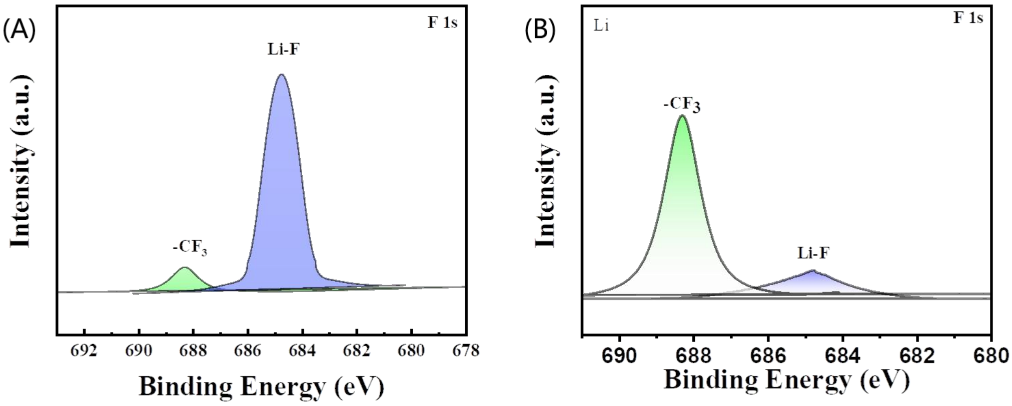
The FTIR spectra comparison in Supplementary Figure 5 shows that the absorption peak at 1634 cm^{-1} disappeared after the polymerization. This means that C=C double bonds at the end of the macromonomer changed to C-C single bonds. Analysis of FTIR spectrum is conducted as follows. "…the appearance of peaks at 2872,1634, and 1128 cm^{-1} are the stretching vibration of C-H, C=C, and C-O-C from ether, respectively, and the appearance of peak at 786 cm^{-1} is the bending vibration of O=C-O from carbonate.



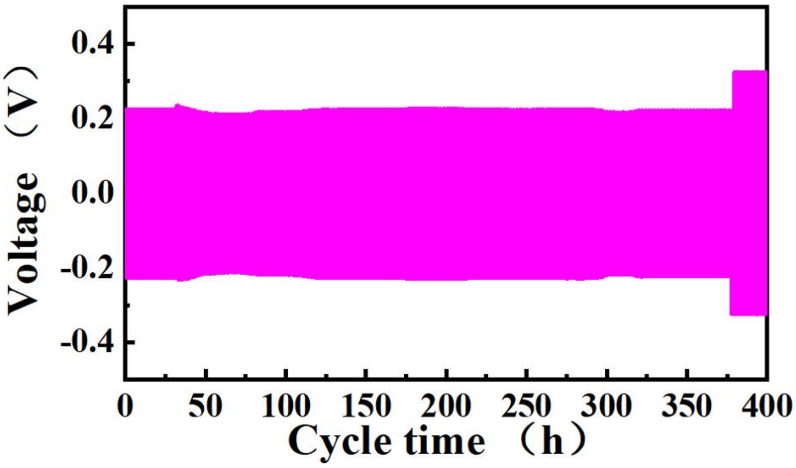
Supplementary Figure 6. (A) Ionic conductivity dependence on LiTFSI concentration for the composite electrolyte of INPC&LLZO-SCPEs at 25 °C. (B) Ionic conductivity dependence on SN concentration for the composite electrolyte of $LiFePO_4$/INPC&LLZO-SCPEs at 25 °C.



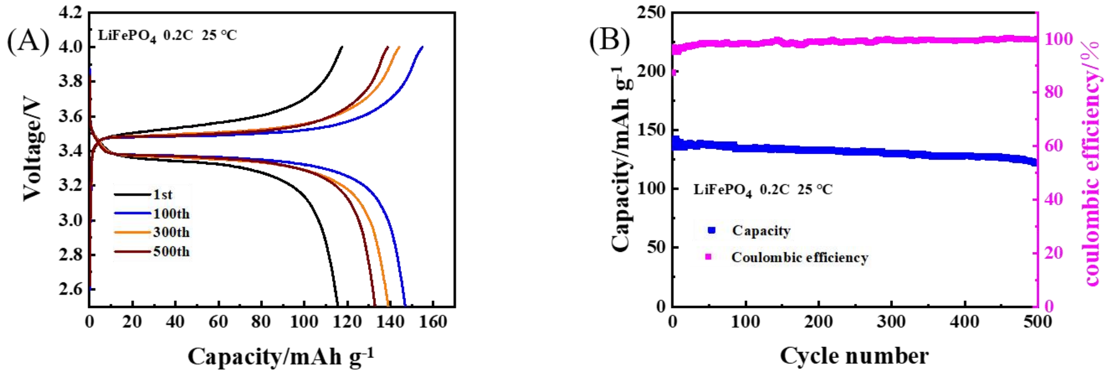
Supplementary Figure 7. (A) XRD patterns of LLZO. (B) SEM image of LLZO.



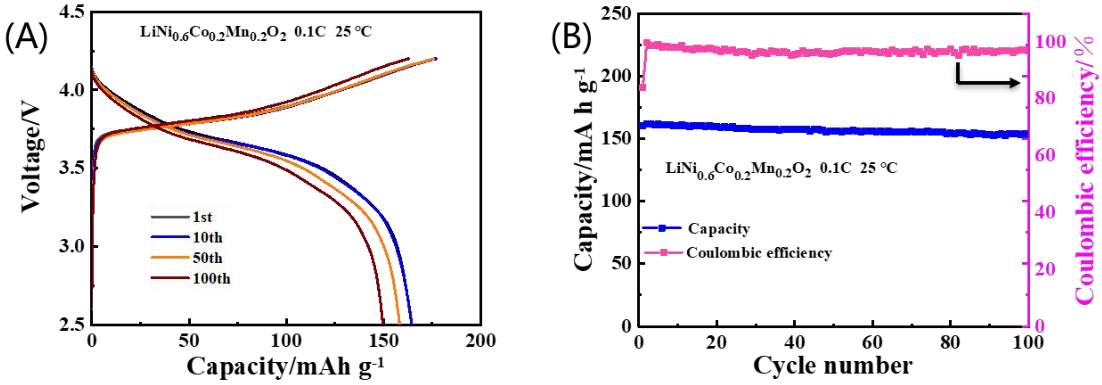
Supplementary Figure 8. XPS spectrum of the surface of (A) Li-FEC and (B) Li.



Supplementary Figure 9. Galvanostatic cycling curves of the symmetric Li-FEC batteries with INPC&LLZO-SCPEs at 0.5 mA cm^{-2}.



Supplementary Figure 10. (A) Charge and discharge profiles of the LiFePO$_4$/INPC-SPEs/Li battery after different cycles at 0.2 C and 25 ℃. (B) Cycling stability of the LiFePO$_4$/INPC -SPEs/Li battery at 0.2 C and 25 ℃.



Supplementary Figure 11. (A) Charge and discharge profiles of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$/INPC-SPEs/Li battery at 0.1 C and 25 ℃. (B) Cycling stability of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$/INPC-SPEs/Li battery at 0.1 C and 25 ℃.