Electronic Supplementary Information

High-performance poly(methylethyl α-cyanoacrylate) composite polymer electrolyte for 5 V high-voltage lithium batteries

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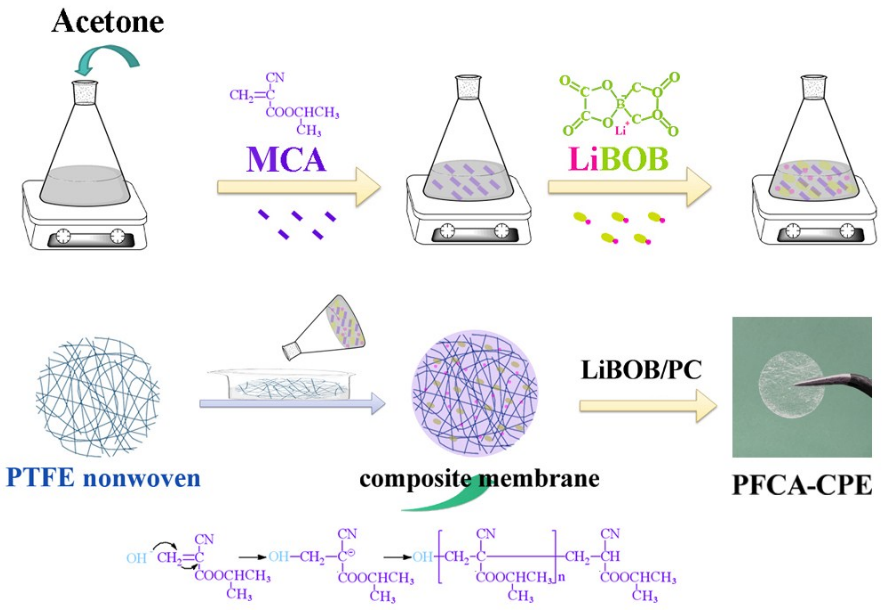

Fig. S1 A schematic illustration for the preparation of PFCA-CPE.

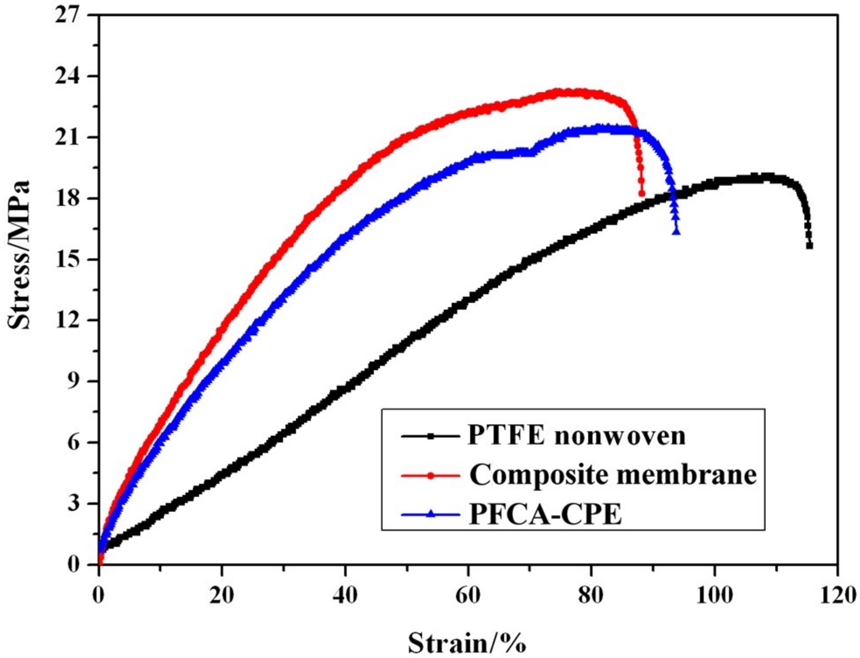

Fig. S2 Stress-strain curves of PTFE nonwoven, composite membrane and PFCA-CPE.

The low mechanical strength is a general problem that almost all of polymer electrolytes face. PTFE shows a tensile strength which can be up to 18.5 Mpa, and a rupture elongation of 112 %. That is to say, PTFE, can be used as a desired framework material in composite polymer electrolyte. So, composite membrane shows a higher tensile strength of 23.8 Mpa, while the rupture elongation decreases to 85 %. After immersed in LiBOB-PC, the tensile strength of PFCA-CPE decreases to 21.1 MPa, while the rupture elongation increases slightly.

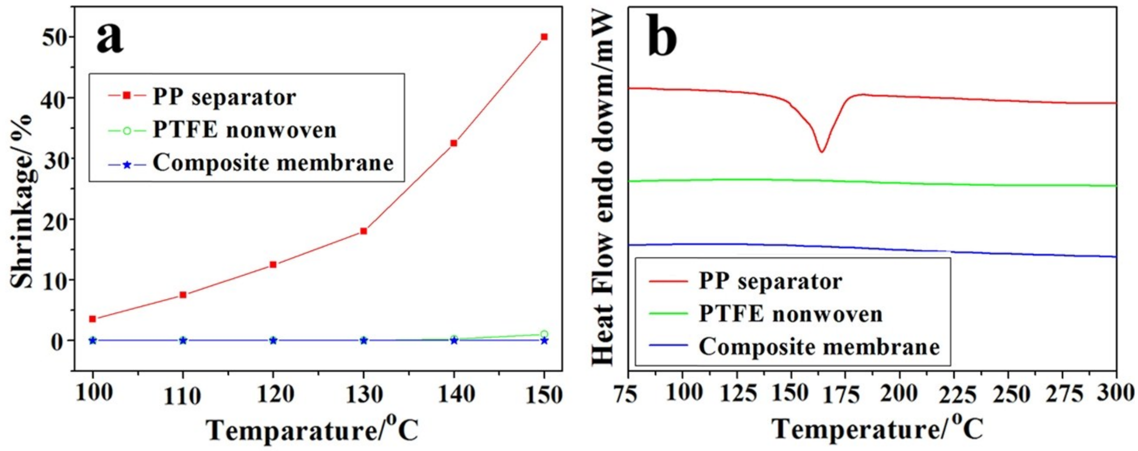

Fig. S3 a) The thermal shrinkage properties for PP separator, PTFE nonwoven and composite membrane at the temperature ranging from 100 ^{o}C to 150 ^{o}C. b) DSC curves of the PP separator, PTFE nonwoven and composite membrane.

The thermal shrinkage of membranes is an important factor for battery safety. It has been reported that PTFE possesses a very strong thermal resistance. The thermal resistance of PP separator, PTFE nonwoven and composite membrane are illustrated in Fig. S3. As shown in Fig. S3a, PTFE nonwoven and composite membrane can maintain dimensionally thermal stability at 150 oC, without any obvious shrinkage. In contrast, the thermal shrinkage ratio of PP at 150 oC reaches to 50 %. The DSC curves (Fig. S3b) indicates that the PP separator has an endothermic peaks at 165 °C ascribed to its melting point. The PTFE nonwoven and composite membrane do not show any obvious endothermic peak below 300 °C.

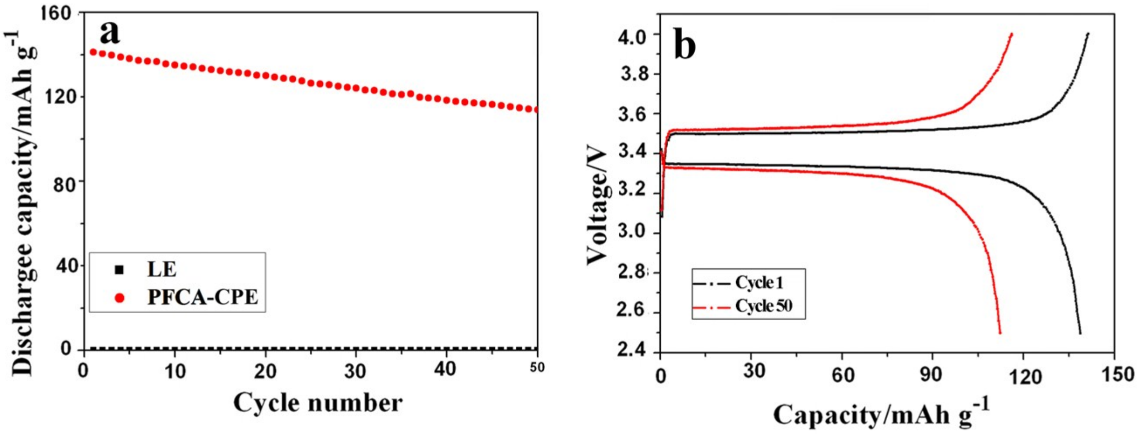

Fig. S4 a) Cycle performance (2.0 C) of $LiFePO_4$/Li cells using PP separator and PFCA-CPE at 160 °C. b) Charge/discharge curve of $LiFePO_4$/Li cells using PFCA-CPE at 160 °C.

In order to testify that PFCA-CPE can endure high temperature tolerance, $LiFePO_4$/Li half cells are assembled with LE and PFCA-CPE. The cells operate at 160 °C. As can be seen from Fig. S4, PFCA-CPE based cells can still be charged/discharged, while, LE based cells are totally incapable of working due to the shrinkage of PP. So, PFCA-CPE not only shows a good heat endurance, but also can be used at high temperature.

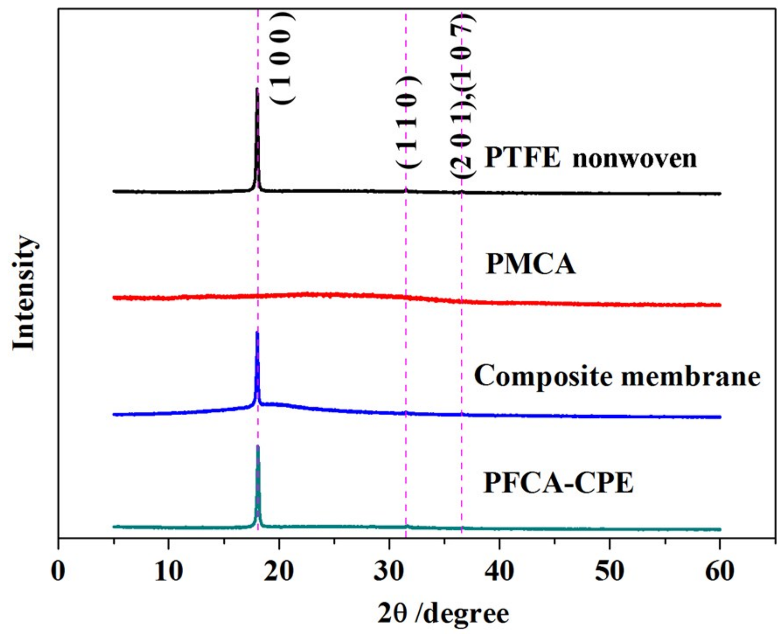

Fig. S5 XRD patterns of the PTFE nonwoven, PMCA, composite membrane and PFCA-CPE.

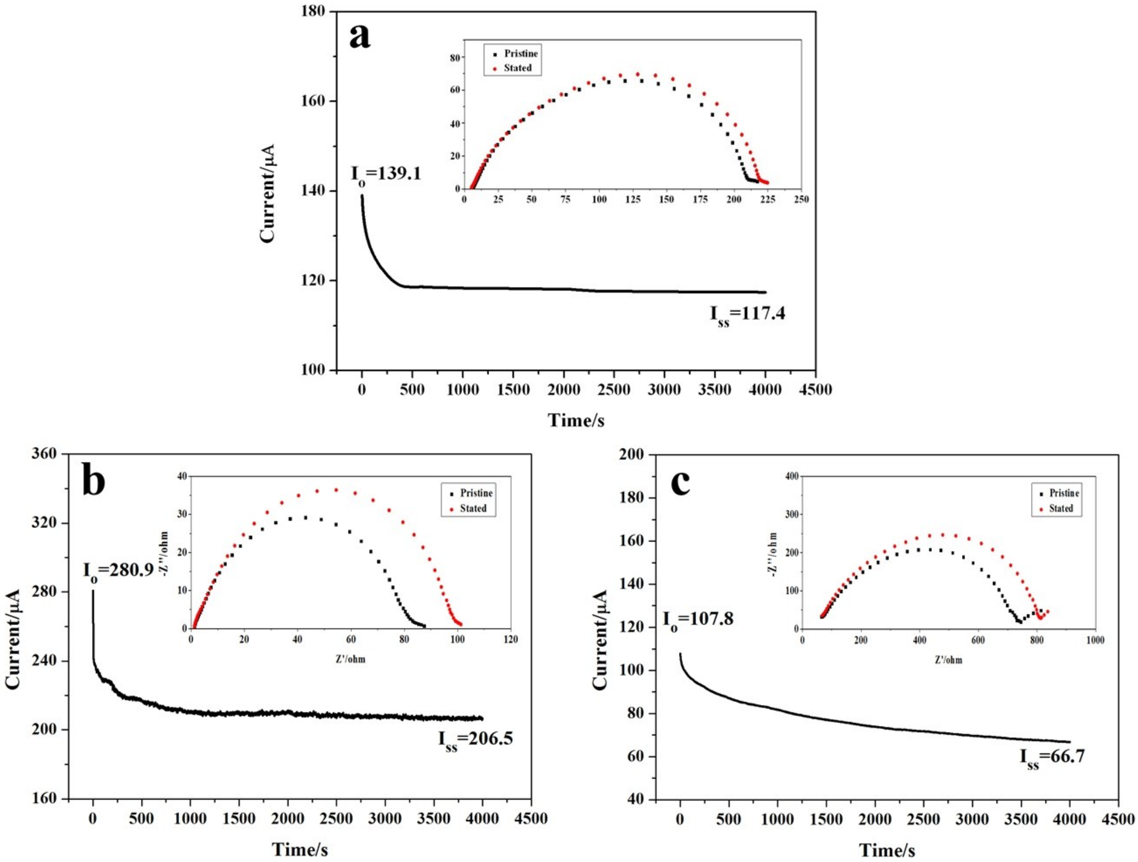

Fig. S6 Current-time curve following a DC polarization of (a) liquid electrolyte using PP separator, (b) PMCA polymer electrolyte and (c) liquid electrolyte using PTFE nonwoven. Insets were Nyquist profiles of the cell electrochemical impedance spectroscopy response before and after polarization.

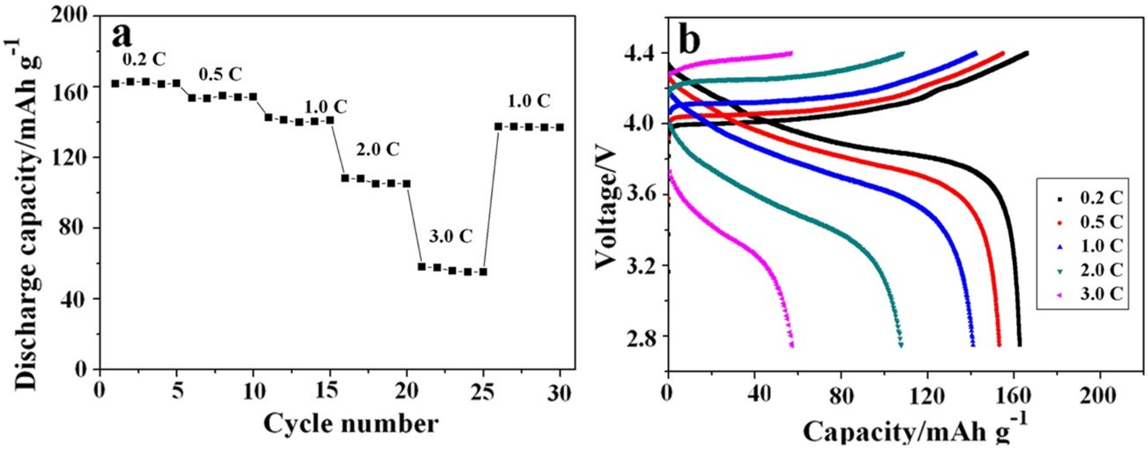

Fig. S7 a) Rate capability and b) charge/discharge curves of $LiCoO_2$/Li cells using PFCA-CPE at varied current density between the voltage range of 2.75 V and 4.40 V at 25 ^{o}C.

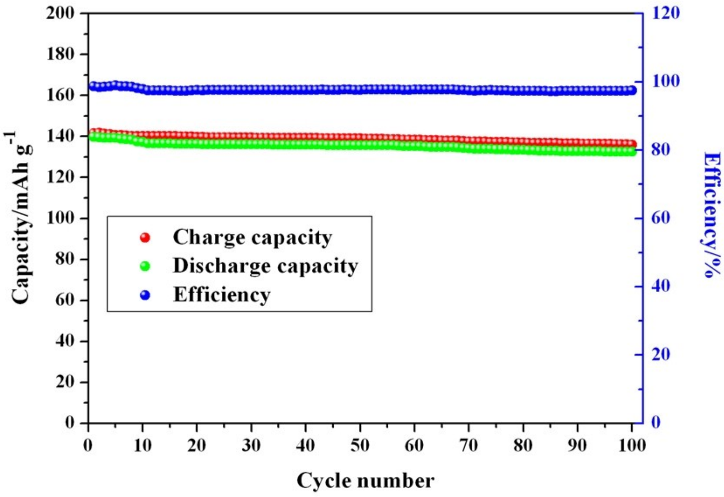

Fig. S8 Cycle performance of $LiCoO_2$/Li cells using PFCA-CPE at 1.0 C between the voltage range of 2.75 V and 4.40 V at 25 ^{o}C.

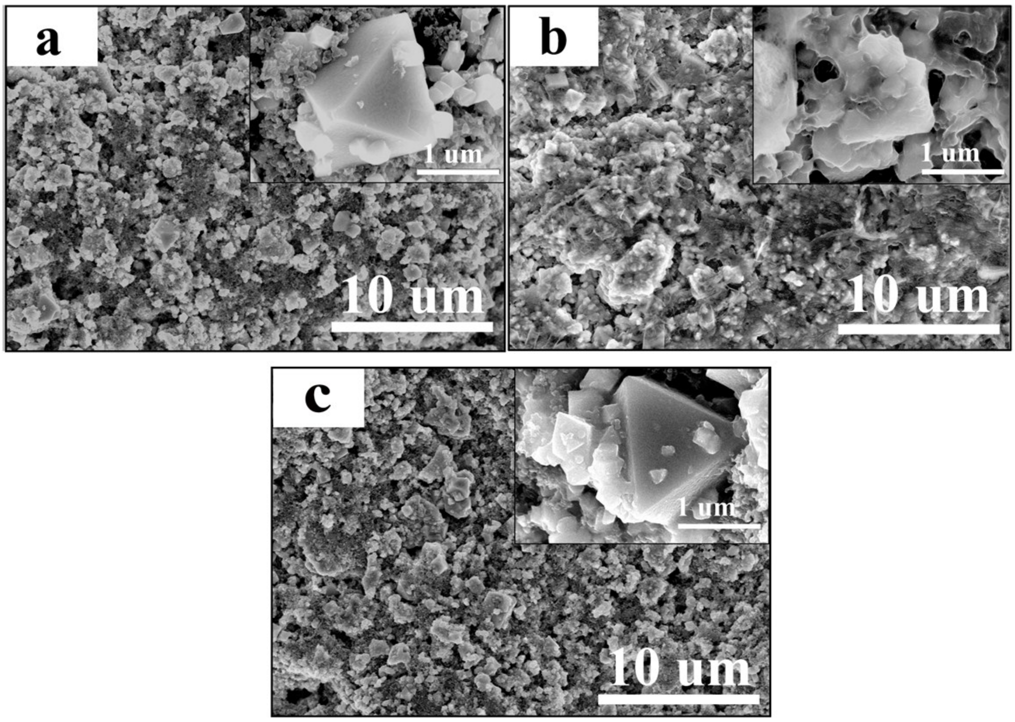

Fig. S9 Typical SEM images of $LiNi_{0.5}Mn_{1.5}O_4$ cathode after 200 cycle of the batteries using a) LE and b) PFCA-CPE. c) Original $LiNi_{0.5}Mn_{1.5}O_4$ cathode before charge/discharge testing. Insets showed the magnified patterns.

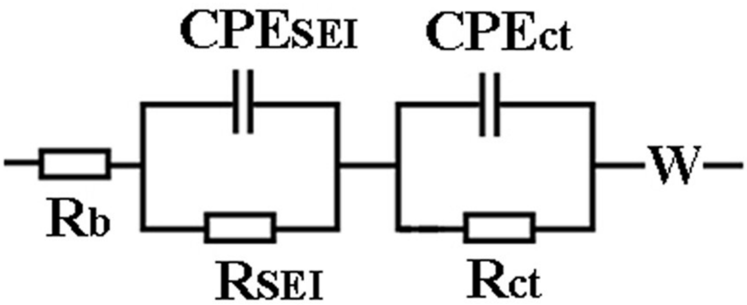

Fig. S10 The equivalent circuit for the impendence plot of $LiNi_{0.5}Mn_{1.5}O_4$/graphite full cells assembled with PFCA-CPE.

Table S1. Physical and electrochemical parameters of PP separator, PTFE nonwoven and PFCA-CPE.

Sample	PP separator	PTFE nonwoven	Composite membrane
Thickness (μm)	25	30	30
Wight (mg)	2.42	4.80	10.71
Porosity (%)	45	76	12
Gurley value (s/100cc)	600	50	>8000
Electrolyte uptake (%)	100	69	181
Ionic conductivity at 25 ^{o}C (S/cm)	5.7×10^{-4}	2.8×10^{-5}	1.24×10^{-3}

After polymerization of methylethyl α-cyanoacrylate on PTFE nonwoven, we can get the content of PMCA on composite membrane.

Content = (10.71 - 4.80) / 10.71 × 100 % = 55.2 %

Table S2. The values of fitting parameters of ionic conductivity of LE and PFCA-CPE.

Sample	A	E_a	T_o
LE	6.17×10^{-3} S cm^{-1}	5.871 KJ mol^{-1}	-
PFCA-CPE	6.79×10^{-3} S $K^{1/2}$ cm^{-1}	0.705 KJ mol^{-1}	246.8 K