Supplementary Information (SI) for RSC Applied Polymers.

Electronic Supplementary Information for:

Metal Oxide Cluster-Integrated Polymer Networks for Robust Solid-State Single-Ion Conduction at High Temperatures

Jie Deng, [a] Litao Ma, [a] Lu Liu, [a] Weigang Sun, [a] Yuan Liu, [a] and Panchao Yin*[a]

[a] *State Key Laboratory of Luminescent Materials and Devices & South China Advanced Institute for Soft Matter Science and Technology, Guangdong Basic Research Center of Excellence for Energy & Information Polymer Materials, South China University of Technology,*

Guangzhou 510641, P. R. China.

E-mail: yinpc@scut.edu.cn

1. Materials

All of the chemicals used in this work were purchased from Aladdin Reagent Co., Ltd., China. Moreover, the mentioned anhydrous solvents were distilled with CaH_2. All the preparation processes in this paper are shown in Fig.S1.

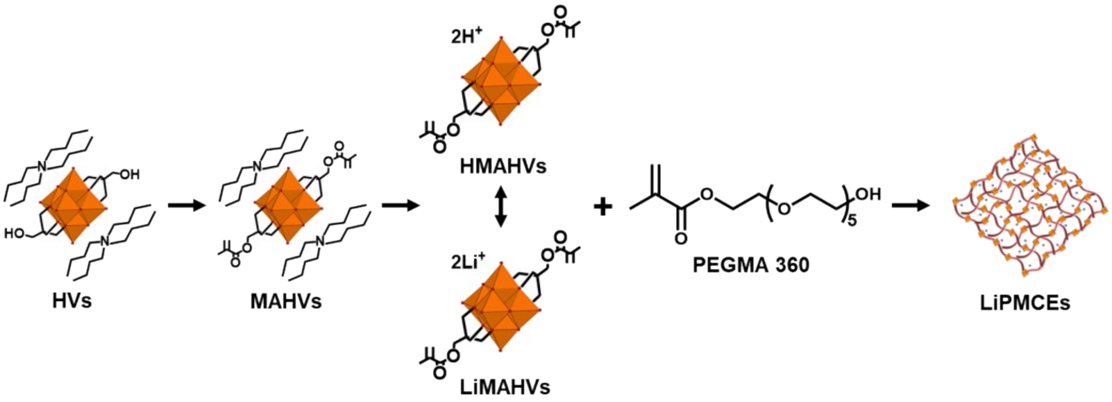

Fig.S1 Roadmap for the synthesis of single-ion polyelectrolyte.

1.1 Preparation of hexavanadates (HVs) (molecular formula: $(Bu_4N)_2[V_6O_{13}((OCH_2)_3CCH_2OH)_2]$).

20 g of sodium metavanadate ($NaVO_3$) was weighed into a round-bottomed flask containing 200 mL of H_2O, heated to 60 °C, stirred until the sodium metavanadate was completely dissolved, and then cooled to room temperature. After filtration, about 210 mL of hydrochloric acid (1 mol/L) was added to the sodium metavanadate solution to adjust the pH to 3, where the color of the solution changed from light yellow to dark red. Add 8 g of pentaerythritol to the dark red solution, heat to 80 °C, stir for 48 h and filter to obtain a dark red filtrate. The above dark red filtrate was added dropwise to tetrabutylammonium bromide aqueous solution (50 g of tetrabutylammonium bromide dissolved in 15 mL of H_2O), the yellow precipitate was collected by filtration, washed with H_2O for three times, and then filtered and dried in a vacuum drying oven for 24 h.

1.2 Preparation of methacrylic anhydride modified hexavanadates (MAHVs) (molecular formula: $(Bu_4N)_2[V_6O_{13}((OCH_2)_3CCH_2OOCC(CH_3)=CH_2)_2]$).

4 g of hexavanadates was weighed in a 250 mL round bottom flask and dried in a blast oven for 60 min, then hexavanadates, methacrylic anhydride (1 mL) and 4-dimethylaminopyridine (20 mg) were dissolved in 100 mL of acetonitrile. After complete dissolution, a clear red color solution was obtained. During the reaction, 0.9 mL of triethylamine (TEA) was added slowly to neutralize the acid produced in the reaction. At the end of the reaction, the precipitate was filtered and collected directly while hot and then dried in a vacuum oven for 24 h.

1.3 Preparation of protonated ethylene modified hexavanadates (HMAHVs) (molecular formula: $H_2[V_6O_{13}((OCH_2)_3CCH_2OOCC(CH_3)=CH_2)_2]$).

The MAHVs are completely dissolved in acetonitrile and H_2O is gradually added to the acetonitrile solution until it becomes turbid, then the filtrate is passed through a strong acid cation exchange resin (H-type) and H_2O is added again to the resulting solution until it becomes turbid, then it is passed through the resin again and the process is repeated several times, then the acetonitrile is removed from the solution by spin evaporation, and the remaining pure aqueous phase is continued to be passed through the resin and the filtrate is collected and lyophilized to remove the solvent water. The filtrate was evaporated and lyophilized to remove the solvent water to obtain the product (red powder).

1.4 Preparation of lithium ionized vinyl-modified hexavanadates (LiMAHVs) (molecular formula: $Li_2[V_6O_{13}((OCH_2)_3CCH_2OOCC(CH_3)=CH_2)_2]$).

Equivalent amounts of Li_2CO_3 were slowly added to the aqueous solution of HMAHVs while stirring, and the solvent water was removed by lyophilization after the reaction was sufficient to obtain LiMAHVs with the counter ions of HMAHVs replaced with lithium ions.

1.5 Preparation of hexavanadate-based polymer metal-oxygen cluster electrolytes (PMCEs).

PMCEs were synthesized by a typical one-step polymerization reaction. PEG 360 monomer (4 mL), H/LiMAHVs (0.34 g), and potassium persulfate (KPS) initiator (20 mg) were dissolved in deionized water (4 mL), and the reactants were added to a vacuum reaction glass vial to undergo a liquid nitrogen freezing-evacuation operation to remove the oxygen in the reaction system (repeated three times). The reaction bottle was then transferred to an oxygen-free glove box and the prepared reaction solution was transferred to a 1 mm thick glass mold, sealed and placed in an oven heated to 70 °C for 24 h.

In addition, the synthesis of the series of samples with different molar percentages (including 0.08%, 0.16%, 0.26%, 0.37% LiPMCEs) was carried out in a similar way as described above, and it was only necessary to adjust the content of the LiMAHVs. Then, the series of polymer electrolyte samples obtained by polymerization were immersed in deionized water and placed on a shaker overnight (repeated three times) to remove the H/LiMAHVs that were not involved in the cross-linking. Finally, the obtained samples were placed in air to evaporate the solvents for 72 h, and then the samples were dried at 50 °C in an electrically heated constant-temperature blast oven for 72 h.

1.6 Preparation of Li|LiPMCEs|Li battery.

Li|LiPMCEs|Li batteries are composed of a negative shell, a diaphragm (i.e., 0.16% LiPMCEs), a pole piece (lithium piece), a steel piece, a shrapnel, and a positive shell. The above components are placed in the transition chamber of the glove box. After three vacuum-argon operations in the transition chamber, the components were transferred into the glove box, where the moisture was kept below 3 ppm. Place the negative shell, steel sheet, shrapnel, positive shell and other components in order, take the lithium sheet into the negative shell, take the diaphragm to cover the lithium sheet, take the lithium sheet to cover the diaphragm, and then put the steel sheet and shrapnel in order and cover them with the positive shell. Use non-conductive tweezers to put the assembled battery on the sealing machine, pressurize it to a certain pressure and keep it for 10–15 s to seal the battery. The assembled cells were annealed for a certain period of time and then used to test the Li^+ transference.

2. Characterization

2.1 Nuclear Magnetic Rasonance (NMR) Tests.

The resulting samples were dissolved in deuterated reagent and tetramethylsilance (TMS) was selected as the internal reference. NMR data were recored on a BRUKER AVANCE 500 instrument at 25 °C.

2.2 Fourier transform infrared spectroscopy (FT-IR) Tests.

Fourier transform infrared spectroscopy (FT-IR) were measured in the range of 600–4000 cm^{-1} through the attenu-ated total reflectance (ATR) mode of a PerkinElmer.

2.3 Thermogravimetric analyses (TGA) Tests.

All the tests were performed under N_2 atmosphere. Thermogravimetric analysis (TGA) was performed with a TA TGA 5500 equipment within a temperature range of 30 °C to 600 °C at a heating rate of 10 °C min^{-1} under an air atmosphere.

2.4 Differential Scanning Calorimetry (DSC) Tests.

Differential scanning calorimetry (DSC) tests were carried out on DSC 2500 from TA instruments with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The temperature range was -80 °C to 100 °C for LiPMCEs. The glass transition temperature was determined from the last temperature-rise period by using a software *TRIOS*.

2.5 Elemental content analysis.

Inductively coupled plasma-optical emission spectrometer (ICP-OES) is an important tool for quantitative analysis of metallic elements. In order to analyze the types and contents of metal elements in the samples, the samples were analyzed by ICP-OES with a Perkin Elmer Optima 7000 instrument. Before measurement, the samples were dissolved in a solution of 67–70% nitric acid (1.0 mL) and 48% hydrofluoric acid (0.1 mL) for 15 min, and then diluted to 35 mL with deionized water.

2.6 Small- and Wide Angle X-ray Scattering (SAXS and WAXS) Characterizations.

Samll-angle X-ray scattering (SAXS) data were collected at the beamline (BL16B1) with an X-ray energy of 10 keV of shanghai Synchrotron Radiation Facility (SSRF). A Pilatus 2M detector was applied to collect the data with the exposure time of 60 s, while the sample-to-detector distance was about 4.7 m. Data analysis was processed with RAW software and the background scattering was subtracted. Wide-angle X-ray scattering (WAXS) data were collected using a two-dimensional wide-angle X-ray diffraction instrument equipped with the HomeLab system of Rigaku.

2.7 Rheology.

Viscoelastic properties of the LiPMCEs nanocomposites were studied using an Anton Paar Rheometer 302 (MCR 302) equipped with an 8 mm diameter cone plate from 30 °C to 100 °C. The thin film is fixed between two parallel plates. The sample is sheared with constant oscillation rates (ω = 10 rad/s), while maintaining stability as the oscillation strain ranges from 0.001% to 10%.

2.8 Alternative Current (AC) Impedance Tests.

Alternating current (AC) impedance analysis is performed using the dual probe method with an electrochemical workstation CHI660E with an input voltage of 10 mV at frequencies between 0.1 Hz and 10^6 Hz. Impedance measurements were taken at 10 °C intervals between 40 °C and 100 °C and data were recorded. Prior to each measurement, the sample was placed in a thermostat at the target temperature and held at that temperature for 1 h. Impedance was obtained by fitting a Nyquist curve. The ions conductivity of the membranes can be calculated by using equation: $\sigma = L/(AR_b)$, Where the R_b is obtained by the intercept of the Nyquist plot with the real axis, A is the area of copper sheet electrodes and the L is distance between two electrodes (*i.e.*, thickness of the membrane), respectively.

2.9 Li^+ Transference Number Tests.

Direct current (DC) polarization measurements were performed on a cell with a voltage of 10 mV and the current response was measured at ambient temperature for approximately 60 min. The electrochemical impedance spectroscopy (EIS) of the cell was measured before and after the DC polarization at an input voltage amplitude of 10 mV between frequencies of 0.1 Hz and 1 MHz. The Li^+ transference number was calculated using the Bruce-Vincent-Evans (BVE) formula, $t_{Li+} = I_s (\Delta V - I_0R_0)/I_0 (\Delta V - I_sR_s)$, where t_{Li+} is the Li^+ transference number, ΔV is the applied potential, I_0 and I_s are the initial and steady state currents, and R_0 and R_s are the initial and steady-state interface impedances. R_0 and R_s were determined by fitting Nyquist plots using EC-Lab software based on previous reports.

2.10 Broadband Dielectric Spectrometer (BDS) Tests.

Broadband Dielectric Spectrometer (BDS) is a phenomenon in which the dielectric constant varies with the frequency of the electromagnetic field, and is generally made as the real part of ε(w) spectrum and the imaginary part of ε''(w) spectrum, respectively. The dielectric spectrum can give important information about the polarization mechanism and lattice vibration of the sample. In this experiment, broadband dielectric spectra were measured using a Novocontrol Concept 80 with an Alpha-ANB impedance analyzer and a Quatro low-temperature temperature system. The frequency range was from 0.001–10^7 Hz and the temperature range of the measurements was from -30 °C to 100 °C. During the tests, the samples were cut into discs of 1.5 cm in diameter and 1 mm in thickness and placed in a sandwich-type pole piece of 2 cm in diameter for the broadband dielectric measurements.

3. Results and discussion

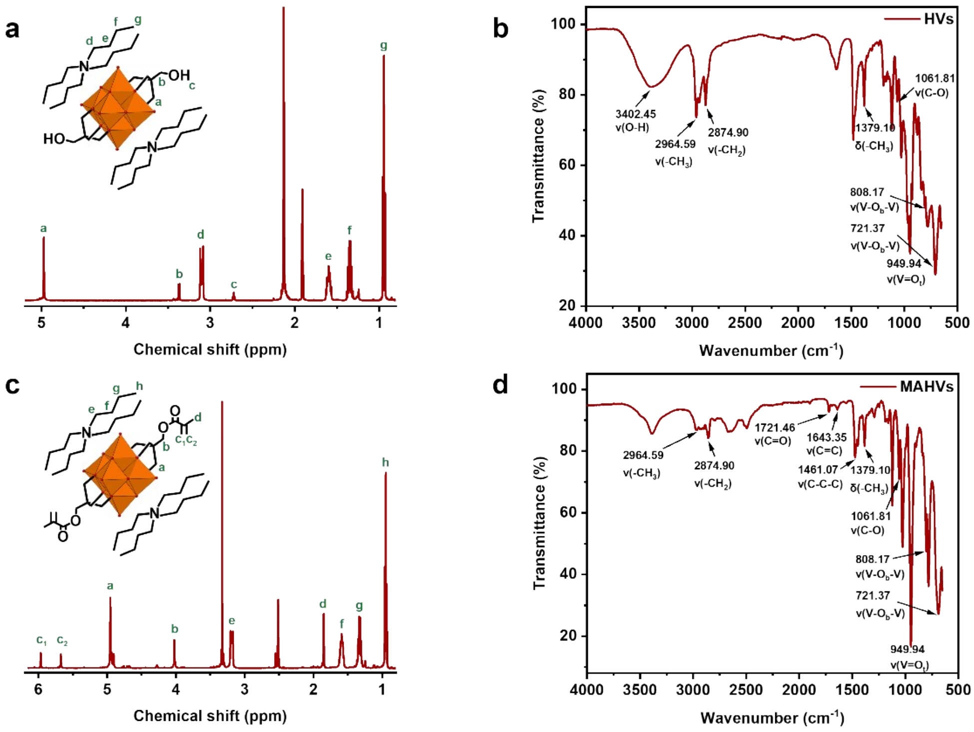

Fig.S2 ^{1}H NMR and FT-IR Spectra of HVs and MAHVs.

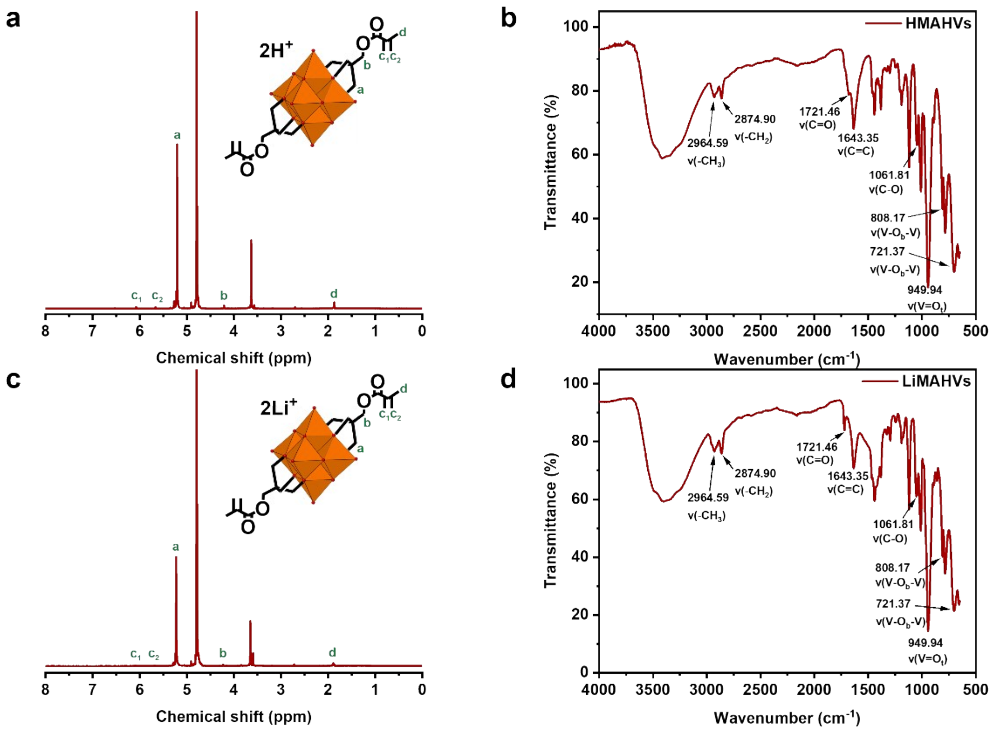

Fig.S3 ^{1}H NMR and FT-IR Spectra of HMAHVs and LiMAHVs.

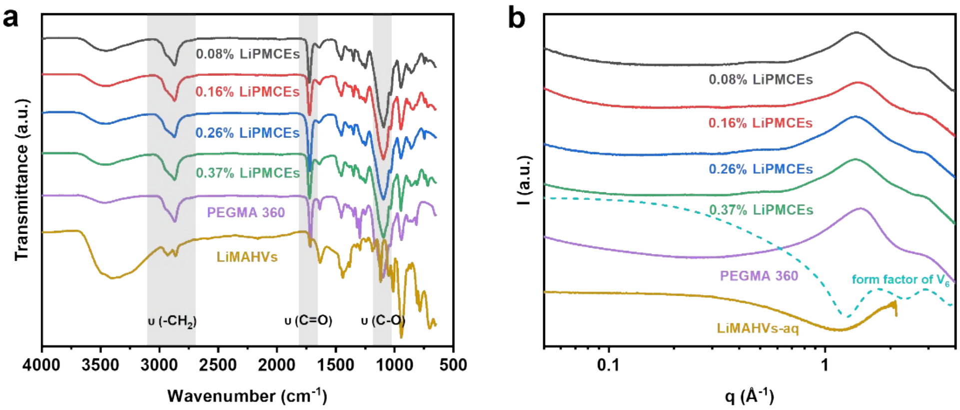

Fig.S4 FT-IR and SAXS-WAXS Spectra of PEGMA, LiMAHVs, and LiPMCEs (0.08%, 0.16%, 0.26%, 0.37%).

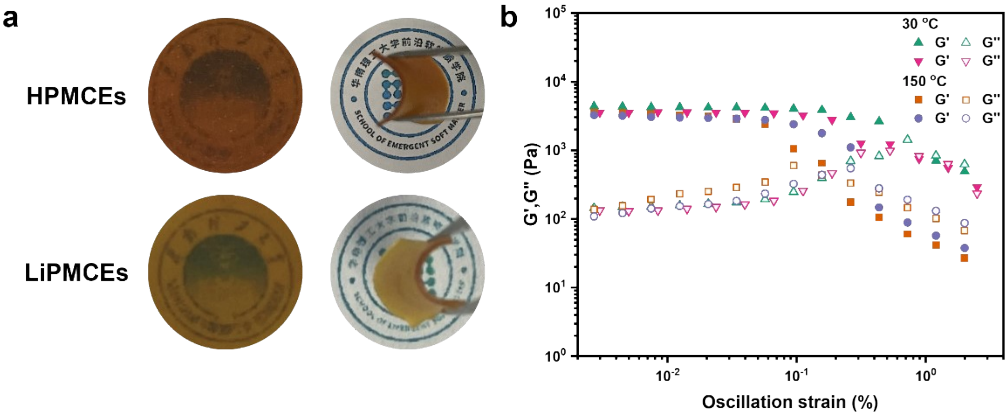

Fig.S5 (a) Photographs of transparent yellowish-brown PMCEs samples in unbent and bent states. (b) The 0.16% LiPMCEs undergoes two amplitude sweeps at 30 °C and then two at 150 °C consecutively to evaluate its flexibility.

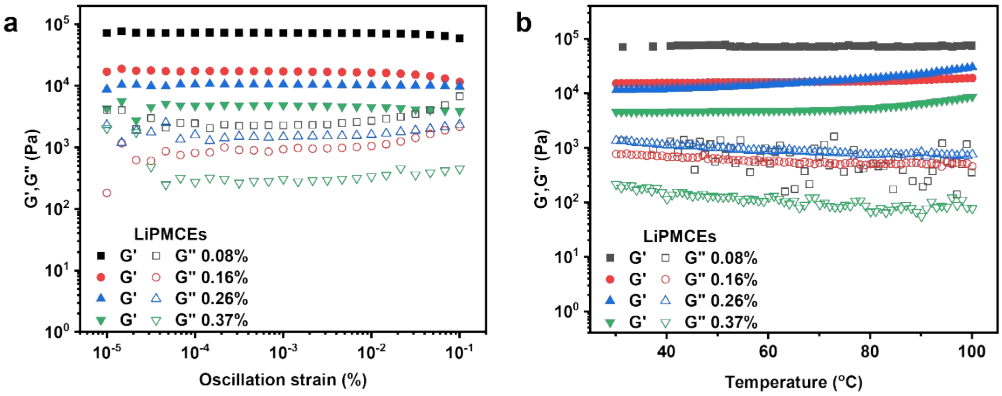

Fig.S6 Amplitude and Temperature Sweep Plots of LiPMCEs (0.08%, 0.16%, 0.26%, 0.37%).

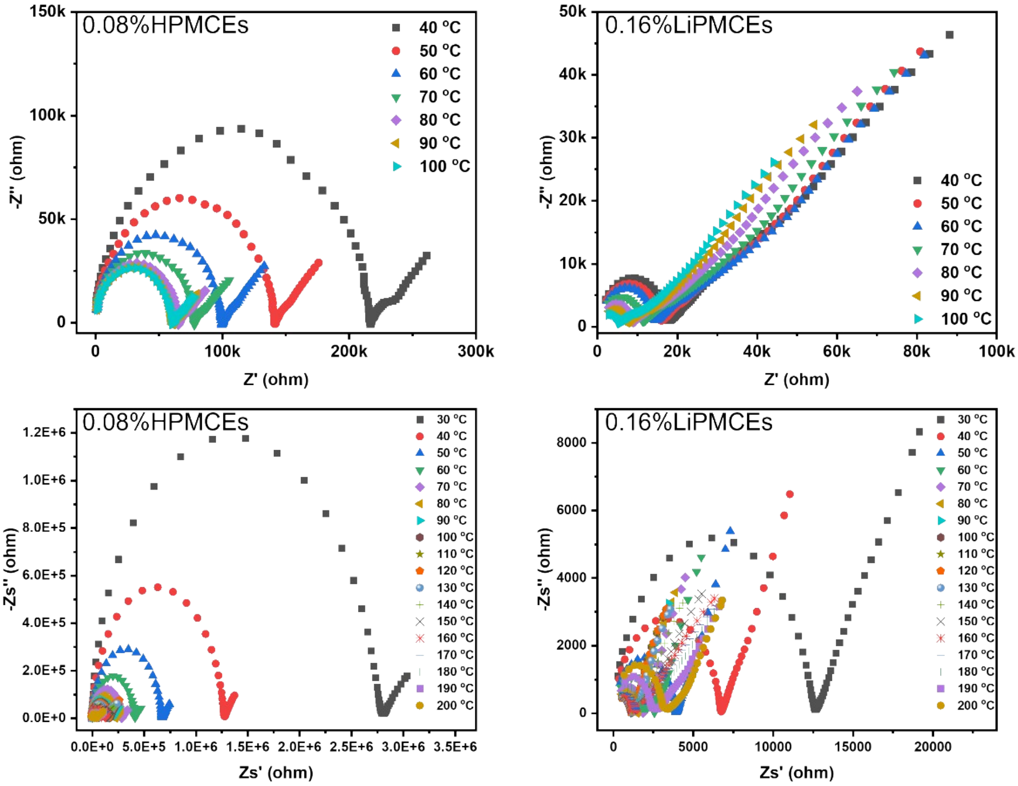

Fig.S7 Ion conducting performance of the PMCEs. (a) Nyquist plots of 0.08% HPMCEs (measured by EIS) from 40 to 100 °C. (b) Nyquist plots of 0.16% LiPMCEs (measured by EIS) from 40 to 100 °C. (c) Complex impedance spectra of 0.08% HPMCEs measured by BDS over 30–200 °C. (d) Complex impedance spectra of 0.16% LiPMCEs measured by BDS over 30–200 °C.

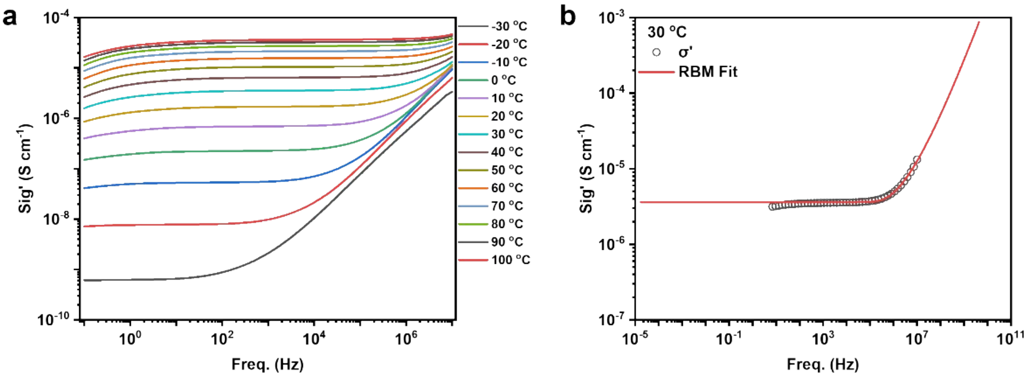

Fig.S8 (a) Frequency dependence of the DC conductivity (σ′) for 0.16% LiPMCEs over the temperature range of -30 to 100 °C. (b) Representative σ′ spectra of 0.16% LiPMCEs at 30 °C (ring symbols) and their fits (red solid lines) modelled via an RBM function.

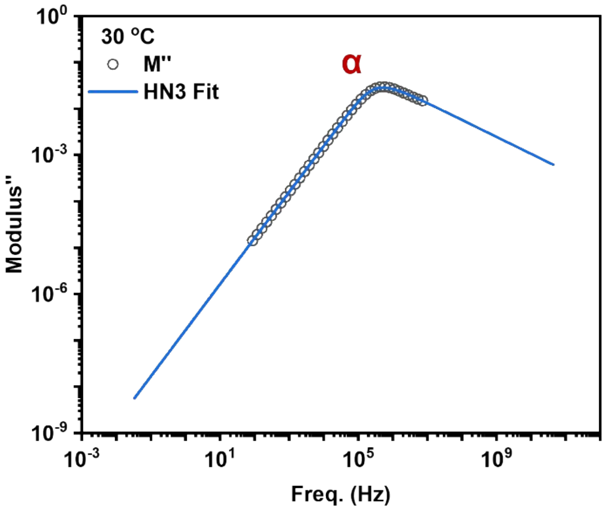

Fig.S9 Frequency dependence of dielectric loss modulus (M″) for 0.16% LiPMCEs at different temperatures (Fig.3c), representative M″ spectra of 0.16% LiPMCEs at 30 °C (ring symbol) and their fit (blue solid line) using a HN function for modulus approach.