Fiber Reinforced Quasi-Solid Polymer Electrolytes Enabling Stable

Li-metal Batteries

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Experimental Section

Synthesis of PPES, rQPE and tQPE

Typically, the poly[poly(ethylene glycol) methyl ether methacrylate)-*r*-(2-ethylhexyl acrylate)-r-sodium (p-styrene sulfonate)] with polyethylene glycol dimethacrylate as crosslinker (PPES) is synthesized as follows: 950 mg (2 mmol) of poly(ethylene glycol) methyl ether methacrylate) (PEGMEMA), 613.7 mg (3.33 mmol) of 2-ethylhexyl acrylate) (2-EHA), 412.4 mg (2 mmol) of sodium (p-styrene sulfonate) (SPSS) and 363.2 mg (1.1 mmol, 15 mol%) of polyethylene glycol dimethacrylate (PEGDMA) were dissolved in 16.5 ml of N,N-Dimethylformamide (DMF) with 6.92 mg (0.5 mol%) of azodiisobutyronitrile (AIBN) as initiator. The solution was purged with N_2 for 20 min to remove any O_2 in the solvent in the room temperature and then the flask was sealed and the reaction was performed at 65 °C for 24 h with magnetic stirring. After the reaction, the PPES film can be obtained after removing the solvent by rotary evaporation and vacuum drying. The PPES@PPF film was prepared by imbedding the poly(propylene) fiber (PPF) into the PPES solution with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as filler, followed by drying in the vacuum oven. The rQPE was prepared by immersing PPES@PPF in ether-based electrolytes consisting of 1 M lithium the bis(trifluoromethanesulfonyl)imide in 1,3-dioxolane/dimethyl ether (v/v=1:1) with 2 wt% LiNO3 as an additive for several minutes. The tQPE was prepared via the similar method with ultra-thin film as reinforcing wire.

Materials Characterization

¹H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with DMSO-d as solvent. FT-IR spectra were performed on a Bruker Tensor II FT-IR Spectrometer with the scanning range of 400-4000 cm⁻¹. The thermogravimetric analysis measurements were performed on a Rigaku TG-DTA8122 thermogravimetric analyzer in the temperature range of 30-800 °C in N2 with a heating rate of 10 °C/min. The glass transition temperature (Tg) was measured by Differential Scanning Calorimetry (TA Instruments DSC 2500). The samples were equilibrated at 120 °C for 30 min to remove the thermal history. And then the sample were measured from -80 °C-200 °C in N₂ with the cooling or heating rate of 3 °C. Small angle X-ray scattering (SAXS) measurements were performed on an Anton Paar SAXSess mc² at the Center for Nanophase Materials Sciences (CNMS) of the Oak Ridge National Laboratory. The SAXS images were collected with a CCD detector (PI-SCX, Roper) at a pixel resolution of 2084×2084 and pixel dimensions of 24×24 μ m². For the measurements, X-rays were generated at 40 kV/50 mA at a beam wavelength of λ = 1.541 Å (Cu Kα radiation), while the data was for 20 min. Tensile analysis using a Universal Testing Machine (Exceed Model E44). Samples were elongated at the rate of 0.1 mm/s till breaks. Rheology measurements of PPS were carried out on an AR2000ex rheometer (TA Instruments) by using 4 mm plates. The loss tangent (tan δ) is calculated based on the equation: $\tan \delta = G''/G$. Scanning electron microscope (SEM, JSM-7800, JEOL, Japan) was used to characterize the morphologies of as-prepared films and electrodes. X-ray photoelectron spectroscopy (XPS) spectrum were record from the Thermo Scientific ESCALAB 250Xi system.

Fabircation of LFP and NMC811 Electrodes

The LFP electrode was prepared by coating the homogenous slurry consisting of LFP active materials, acetylene black and poly (vinylidene difluoride) with a weight ratio of 8:1:1 onto the Al foil. After dyring (in the vacuum oven at 120 °C for 12 h) and cutting process, the LFP electrodes can be obtained with 13.0 mm in diameter and mass loading of \approx 2.5 mg cm⁻². The NMC811 electrodes were preapared via the similar process with the mass loading of \approx 2 mg cm⁻².

Battery Assembly and Electrochemical Measurements

The cells were assembled in an argon-filled glove box with O₂ and H₂O levels lower than 1 ppm. The symmetric cell was assembled with the configurations of Li|rQPE|Li. As a control, commercial separator (Celgard 2400) and 60 µL of liquid electrolyte lithium bis(trifluoromethanesulfonyl)imide consisting of Μ 1 1,3-dioxolane/dimethyl ether (v/v=1:1) with 2 wt% LiNO₃ as an additive were used. The full cell was assembled with the configurations of Li|rQPE|LFP or LiltQPE|NMC811. For control experiments, the PPES or PEO was firstly immersed to the ether-based electrolyte to afford a gel electrolyte, which is utilized to assemble the cell. Electrochemical properties were evaluated with the LAND CT2001A battery test system. The electrochemical impendence spectroscopy (EIS) was measured on the Zennium Pro Electrochemical System with the scanning speed of 0.1 mV s⁻¹ and the frequency range of 10-1-104 Hz at a 5 mV amplitude. The ionic conductivities of the films were evaluated by EIS. Two identical pieces of stainless-steel foil were used as blocking electrodes and a polymer membrane was sandwiched in between. Linear-sweep voltammetry was carried out using LillSS asymmetric cells from 2.5 V to 5.2 V versus Li/Li^+ at a scan rate of 1 mV s⁻¹.

The ionic conductivity (σ) is calculated based on the equation:

$$\sigma = \frac{L}{R_b S} \tag{1}$$

where L (cm), R_b and S are the film thickness, ohmic resistance (Ω) and contact area (cm²), respectively.

The activation energies of HPE were calculated by fitting the conductivity data using the VFT equation:

$$\sigma = A \exp\left(-\frac{E_a}{k_b T}\right) \tag{2}$$

where E_a is the activation energy, A is the pre-exponential factor, k_b is the Boltzmann constant and T the absolute temperature.

The t_{Li^+} was calculated according to Equation (3)

$$t_{Li} += \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)} \tag{3}$$

where I_0 and I_s are the initial and the steady-state currents, respectively. ΔV is the potential applied across the cell and is 10mV, R_0 and R_s are the initial and steady-state resistances of the lithium metal battery.



Figure S1. The digital photos of PPES polymers with different molar ratios of crosslinkers.



Figure S2. ¹H NMR spectrum of PEGMEMA, 2-EHA and SPSS.



Figure S3. The digital photo of rQPE and commercial separator before and after heating at 150 °C for 3 minutes.



Figure S4. The temperature-dependent ionic conductivity of rQPE.



Figure S5. XPS spectra of Li electrodes from Li/LE/LFP cell after cycled for 50

cycles.



Figure S6. Li/rQPE/LFP cell after peeling off the aluminum foil.



Figure S7. (a) Top-surface SEM image of the ultra-thin film. (b) Cross-sectional SEM image of the ultra-thin film.

Table S1. Electrolyte uptake ratio of FFES@FFF min.						
	Electrolyte (mg)	Solvent (mg)	Uptake ratio (%)			
	41	75	82.9			
	47	88	87.2			
	52	94	80.8			
	50	92	84.0			
	49	90	83.7			
Average			83.7			
Standard deviation	on		2.1			

Table S1. Electrolyte uptake ratio of PPES@PPF film.

Table S2. The cationic transport number (t_{Li^+}) of rQPE

			1				
	$R0(\Omega)$	$Rs(\Omega)$	I0 (mA)	Is (mA)	$\Delta V(V)$	t	
1	46.60	58.22	0.11	0.07	10		0.55
2	65.47	84.44	0.09	0.07	10		0.68
4	90.78	90.28	0.08	0.06	10		0.54
Average							0.59
Standard							
deviation							0.07

Electrolytes (Polymer matrix)	Battery (Tempera ture)	Electrochemical performance	Battery type (Temperature)	Electrochemical performance
PPES@PPF(Poly(PEGMEM A-r-(2-EHA)-r-SPSS-r-PEG MA)@ PP fiber) This work	Li /LFP (25 °C)	91%@900 cycles (0.5 C); 77 %@650 cycles (1 C);	Li /Li (25 °C)	1800 h@0.1 mA cm ⁻²
Si@LATP/PVDF/PVC ¹	Li /LFP (25 °C)	99.9%@200 cycles (0.5 C); 94.1%@200 cycles (1 C);	Li /Li (25 °C)	500 h@0.1 mA cm ⁻²
QSE-P ₁ I ₂ ² (PEGMEM and VBIM-TFSI)	Li /LFP	96%@200	Li /Li	1000 h@0.1
	(60 °C)	cycles (0.1 C);	(25 °C)	mA cm ⁻²
PAL-3-C12 ³ (PAN/PLLA)	Li/LFP	97.63 %@140	Li /Li	1000 h@0.15
	(25 °C)	cycles (1 C)	(25 °C)	mA cm ⁻²
DMC/DME/PEGMEA +10%FEC ⁴	Li /LFP (30 °C)	92.7%@300 cycles (0.5 C); 90.2 %@600 cycles (1 C);	Li /Li (30 °C)	350 h@0.1 mA cm ⁻²
PDEGDA/PVDF FMs ⁵	Li /LFP	76.5 %@800	Li /Li	2000 h@0.05
	(60 °C)	cycles (0.5 C)	(60 °C)	mA cm ⁻²
PPLT ⁶ ((PEO-b-PA ₆)/LiTFSI/	Li /LFP	700 cycles (0.5	Li /Li	1200 h@20.1
TEGDME))	(28°C)	C);	(28 °C)	mA cm ⁻²
NH ₂ -UiO-66@BC ⁷ (MOF/	Li /LFP	200 cycles (1	Li /Li	1200 h@0.5
bacterial cellulose)	(25°C)	C);	(25 °C)	mA cm ⁻²
PTLL ⁸ (PEO TPU 3:1 with 10	Li /LFP	96.1 %@100	Li /Li	500 h@0.3 mA
wt% LLZO)	(60°C)	cycles (0.5 C)	(60 °C)	cm ⁻²
IGE ⁹ (PEGDGE, D-400 and	Li /LFP	96.1 %@50	Li /Li	1000 h@0.1
EMITFSI)	(60°C)	cycles (0.1 C)	(60 °C)	mA cm ⁻²
PPLB ₁₀ -GPEs ¹⁰ (P(PEGDA-co -LiBMAB)@PVDF-HFP)	Li /LFP (25 °C)	82%@300 cycles (0.2 C); 85%@150 cycles (0.5 C);	Li /Li (25 °C)	700 h@0.1 mA cm ⁻² 330 h@0.2 mA cm ⁻²

 Table S3. Summary of different types of polymer electrolytes.

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