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Ionic liquid decorated mesoporous silica nanoparticles: a new high-performance hybrid electrolyte for lithium batteries

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Supporting Information

Experimental details

A. Synthesis

(i) Synthesis of mesoporous silica nanoparticles (MSNs): Firstly, *n*-cetyltrimethylammonium bromide (CTAB, 1.00 g, 2.74×10^{-3} mol) was dissolved in 480 mL of deionized water. NaOH (aq) (2.00 M, 3.50 mL) was added to CTAB solution, followed by adjusting the solution temperature to 80 °C. Tetraethyl orthosilicate (TEOS, 5.00 mL, 2.57×10^{-2} mol) was added dropwise to the CTAB solution. The mixture was allowed to stir for 2 h to give rise to white precipitates, then the solid product was filtered, washed with DI water and methanol, and dried in air.[1]

(ii) Synthesis of MSN-IL-TFSI: The IL precursor (1-methyl-3-trimethoxysilane imidazolium chloride) was synthesized by the reaction between 1-Methylimidazole and (3-chloropropyl)trimethoxysilane at 80 °C for 2 days. The solution was purified via liquid extraction in ether and the solvent was finally evaporated. To graft IL to MSNs, a simple water-based chemistry was used. In a typical reaction, MSNs were dispersed in deionized water to create a 1 wt% aqueous suspension. Then 1.5 times excess IL precursor was added dropwise to the aqueous suspension and the mixture was heated at 80 °C for 12 h with continuous stirring. Subsequently, water in the mixture was evaporated, and the resultant MSN-IL-TFSI was washed with ethanol and acetone by centrifugation. The sample was freeze-dried to remove the final trace of solvent.

A ion exchange reaction was used in room temperature to substitute the chloride ion with bis(trifluoromethanesulfone imide) (TFSI) anion. In a typical reaction, 4 g MSN-IL-TFSI and 8 g LiTFSI salt were dissolved in 50 ml water separately, and LiTFSI solution was added to MSN-IL-TFSI solution with continuous stirring. Due to the hydrophobic nature of the TFSI anion, the MSN-IL-TFSI immediately separates from the water phase and settle to the bottom of vessel. The resultant MSN-IL-TFSI was

harvested from solution by repeated washing with deionized water and centrifugation, and finally dried. The product was re-dispersed in acetone to remove the partially exchanged MSN-IL-Cl composition, and then dried to remove the final traces of water.

(iii) Preparation of MSN-IL-TFSI/LiTFSI mixtures: Both MSN-ILTFSI and LiTFSI salt were dissolved separately in acetone. The desired amount of MSN-IL-TFSI solution was added to the LiTFSI solution, and the mixtures were sonicated to form a uniform phase. The samples were subsequently dried at 50 °C for 2 days and the final trace of water removed by drying for another 2 days in a vacuum oven at 45 °C.[2]

B. Characterization

The photomicrographs of MSNs and MSN-IL-TFSI samples were taken by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) with a JEM 100CXII (JEOL, US) and a JEM 2010 (JEOL, US) transmission electron microscopes, respectively. Thermogravimetric (TGA) analysis of various mixtures with different content of MSN-IL-TFSI was performed under nitrogen atmosphere at a rate of 10 °C/min with a Perkin Elmer UNIX/TGA7 system. Fourier transform infrared spectrophotometer (FTS6000, Bio-Rad, US) was used to confirm the successful tethering of IL on MSNs. The particle size distribution was measured by a Brookhaven 90Plus/BI-MAS Multi Angle Particle Size Analyzer. Surface area and pore size distribution of MSNs were tested by nitrogen adsorption-desorption isotherms using a Beckman Coulter SA3100 Surface Area Analyzer.

The electrochemical stability window was examined using an Autolab PGSTAT100 electrochemical workstation at a scan rate of 1 mV s^{-1}. Temperature dependence ionic conductivity was determined by impedance spectroscopy measurements, using a same electrochemical workstation, carried out from 20 °C to 90 °C with an incubator. A 10 mV amplitude signal was applied to two blocking stainless-steel electrode cells (loaded with the MSN-IL-TFSI/LiTFSI samples) with frequency range from 100 kHz to 10 Hz. The lithium ion transference number was also performed on a same electrochemical workstation in the frequency range from 10^{-2} to 10^{6} Hz at room temperature.[3] A fixed protocol was used in the galvanostatic cycling test wherein cell was periodically charged and discharged at a constant current density of 0.1 mA cm^{-2} and 2 mA cm^{-2} by a Neware CT-4008 battery tester.

C. Experimental results

Table S1: Particle size distribution, pore size distribution and surface area of silica nanoparticles and hybrid materials.

Sample	PSD[a] (nm)	D_{BJH}[b] (nm)	S_{BET}[c] (m^2/g)
SiO_2	15.9	\	121
SiO_2-IL-Cl	6.4	\	\
SiO_2-IL-TFSI	4.8	\	\
MSN_1	215.4	2.5	1046
MSN_1-IL-Cl	147.0	\	\
MSN_1-IL-TFSI	128.7	\	\
MSN_2	71.1	2.9	837
MSN_2-IL-Cl	62.1	\	\
MSN_2-IL-TFSI	45.9	\	\

Particle size distribution ([a]PSD) was determined by a particle size analyzer with a concentration of 1 g/L. [b]D_{BJH} is the pore diameter calculated from the BJH theoretical model. [c]S_{BET} is the specific surface area measured from N_2 physisorption.

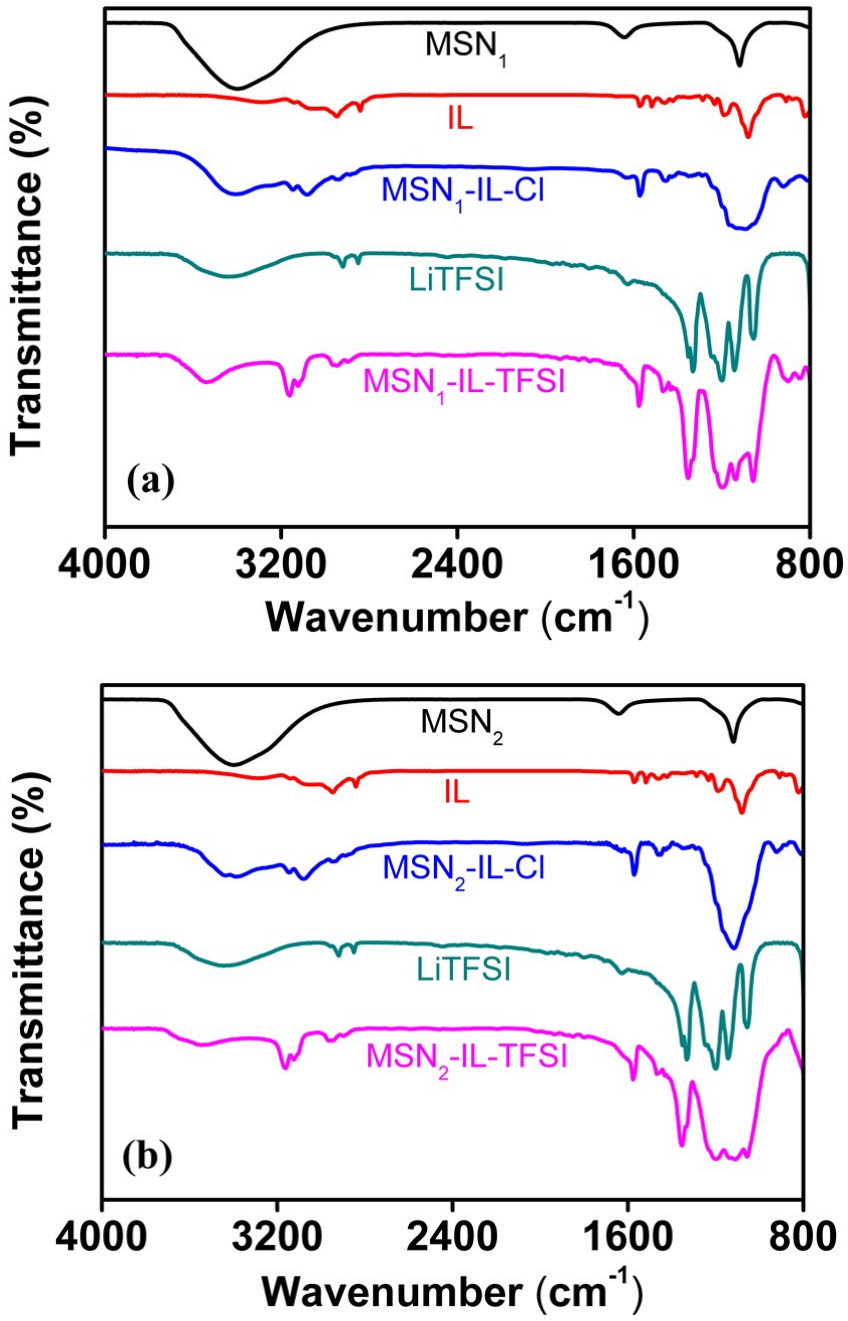

Fig. S1: FT-IR spectra for (a) MSN_1-IL-Cl, MSN_1-IL-TFSI and (b) MSN_2-IL-Cl, MSN_2-IL-TFSI. MSN_1, MSN_2, IL precursor and LiTFSI are provided as reference.

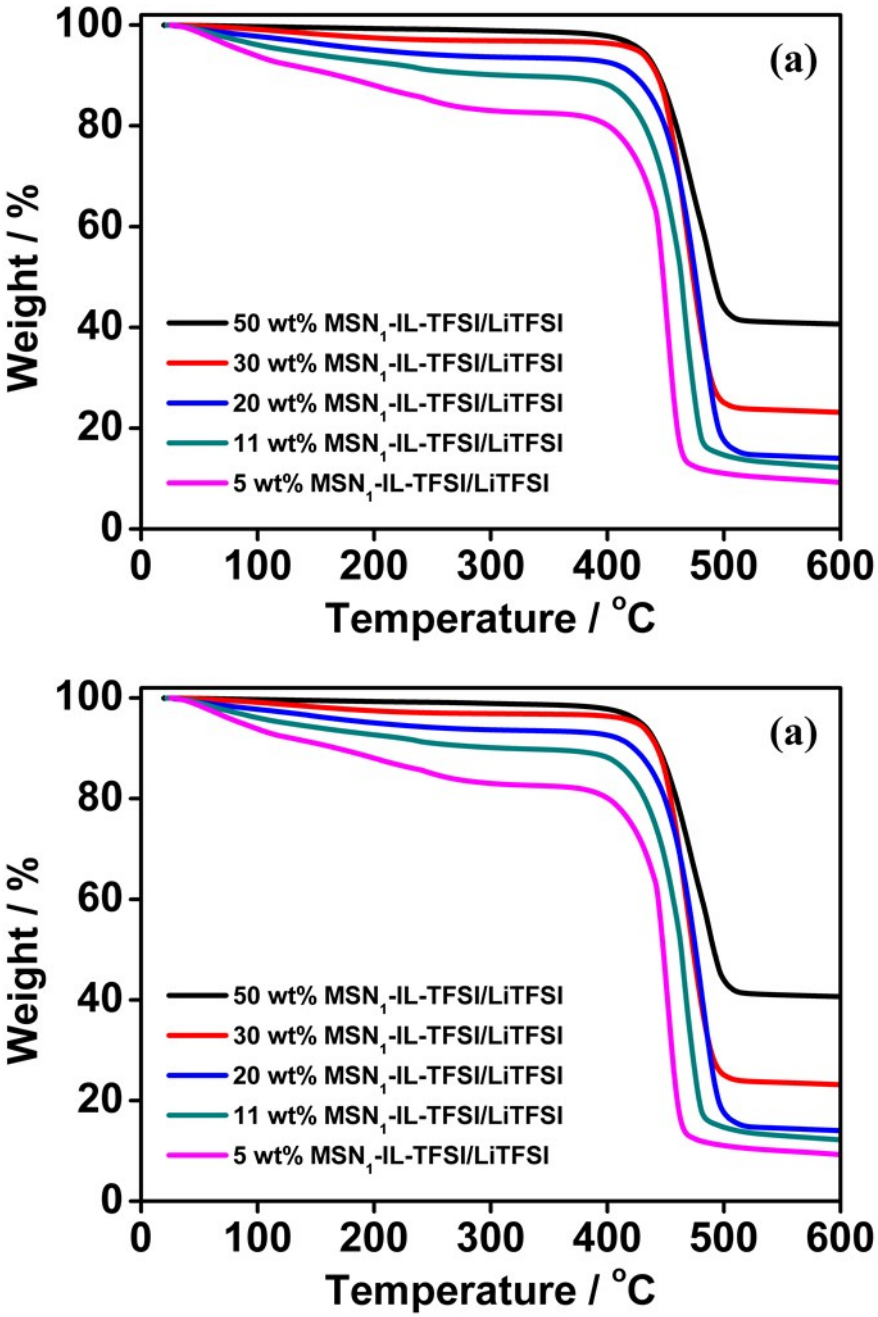

Fig. S2: TGA curves for various (a) MSN_1-IL-TFSI/LiTFSI and (b) MSN_2-IL-TFSI/LiTFSI systems under N_2 atmosphere at a rate of 10 °C/min from room temperature to 600 °C.

As shown in both TGA, residual acetone and absorbed water gradually evaporated upon heating. While some solvent or water molecules are tightly trapped within mesopores, higher temperature (up to >200 ºC) should be required to drive them all completely. Afterwards, the ionic liquid 1-methyl-3-propylimidazolium bis (trifluoro-methylsulfonyl)imide grafted decomposed at around 450 ºC, leaving behind MSNs.

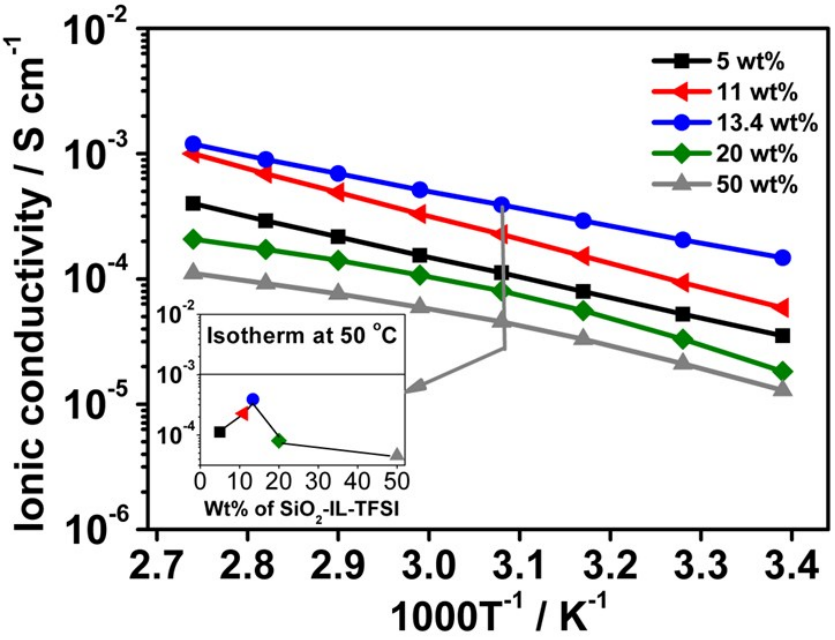

Fig. S3: Ionic conductivities of various weight fractions of SiO_2-IL-TFSI in SiO_2-IL-TFSI/LiTFSI blends as a function of temperature. Inset: isothermal ionic conductivities of SiO_2-IL-TFSI/LiTFSI systems as a function of SiO_2-IL-TFSI weight fraction at 50 °C.

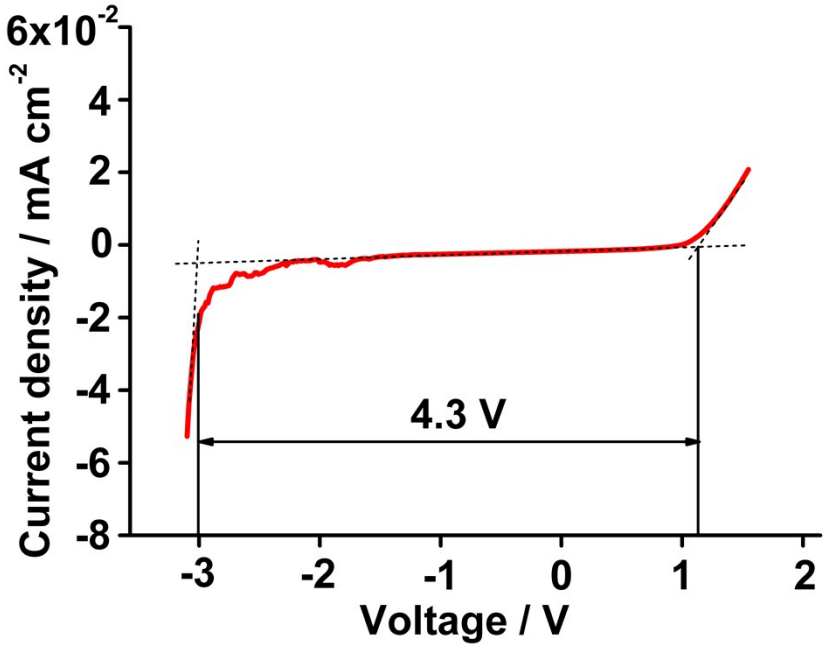

Fig. S4: I–V diagram obtained from linear-sweep voltammetry of 13.4 wt% SiO_2-IL-TFSI/LiTFSI in a symmetric lithium metal cell. The measurement was performed at a scan rate of 1 mV s^{-1} at room temperature.

Table S2: VFT fitting parameters of ionic conductivities and lithium ion transference number (t_{Li^+}) for SiO_2-IL-TFSI/LiTFSI, MSN_1-IL-TFSI/LiTFSI, MSN_2-IL-TFSI/LiTFSI.

Weight fraction (wt%)	VFT Fitting Parameters			t_{Li^+}
	A (S cm^{-1})	B (K)	T_0 (K)	
SiO_2-IL-TFSI/LiTFSI				
5	0.0078	303	245	0.31
11	0.011	288	241	0.49
13.4	0.2	1435	82	0.56
20	0.0057	445	211	0.20
50	0.0012	371	201	-
MSN_1-IL-TFSI/LiTFSI				
5	0.018	316	245	0.46
11	1.15	876	197	0.80
13.4	0.15	487	228	0.71
20	0.0084	191	271	0.31
50	0.0069	146	295	-
MSN_2-IL-TFSI/LiTFSI				
5	0.081	553	208	0.51
11	1.28	954	180	0.82
13.4	0.23	560	215	0.75
20	0.069	605	202	0.38
50	0.0036	102	292	-

References

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