Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information

Ultrathin Tunable Ion Conducting Nano Membranes for Encapsulation of Sulfur Cathodes

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Poly(diallyldimethylammonium chloride) (PDAD, Polysciences), Mw=8,500; poly(4-styrene sulfonic acid), Mw=75,000 (PSS, Sigma Aldrich); polyethyleneimine, branched, Mw=10,000 (bPEI, Alfa Aesar) and lithium chloride, >=99.0% (Sigma Aldrich) were used as received for PEML assembly.SuperPLi from TIMCAL and polyvinylidene fluoride/n-Methyl-2-pyrrolidone (PVDF/NMP) mix were used for cathode slurry preparation. Slurry dilutions were performed with the addition of cyclopentanone, ReagentPlus, >=99% (Sigma Aldrich). The carbon hosts for sulfur (purum p.a. >=99.5%, Sigma Aldrich) infusion were obtained from Synthonix.Inc (TEMC) and from TDA.Inc (TDA). TEMC had a total surface area of 790 m^2 g^{-1} and a total pore volume of 0.1 cm^3 g^{-1}. TDA had a total surface area of 2100 m^2 g^{-1} and a total pore volume of 1.35 cm^3 g^{-1}. The electrolyte used in electrochemical cells was composed of 1M LiTFSI salt (purchased from 3M) in a 1:1 mixture of anhydrous 1,3-dioxolane (Sigma Aldrich) and 1,2-dimethoxyethane (Sigma Aldrich).

Sulfur infusion was accomplished by a melt-infusion strategy. The porous carbon support and elemental sulfur were ground together, and heated to 150 C for 4 hours. The weight ratio of carbon/sulfur was adjusted based on the density of elemental sulfur and the porous carbon volume in pores less than 3 nm as measured by BET to allow for expansion of the pore content on full reduction to Li_2S. This method provided a 8% sulfur content by weight in the TEMC sample and a 57% sulfur content by weight in the TDA samples.

X-ray photoelectron spectroscopy (XPS) spectra were taken on a Phi 5100 ESCA spectrometer with a Al Kα X-ray source (1486.6 eV) using a hemispherical analyzer in an ultrahigh vacuum (~10^{-9}Torr) system equipped with an Ion Beam Sputter Etching Gun for surface elemental analysis and for rendering compositional depth-profiles. C(1s) at 285.0 eV was used as a reference for all binding energies. Sputtering was done by an etching gun operated at 1

kV and 0.5 mA with an Ar^+ ion beam. All S(2p) binding energy refer to the S(2p3/2) component. A Shirley type background was used for background subtraction.

Transmission electron microscopy (TEM). The samples $TEMC_8PEML_5$ and $TEMC_8$ were dispersed on minimal volume of methanol and suspended on the TEM grid (C/Cu 200 mesh) which was later dried in air for 10 min. Immediately after, images were collected in an aberration-corrected TEM instrument (FEI Titan Krios 80-300 TEM).

BET. Surface area and porosity of carbon supports were measured by nitrogen adsorption following the DFT method using a BET instrument (Micromeritics ASAP 2020).

Fluorescence spectroscopy. Fluorescence images were acquired using a Nikon Eclipse Ti inverted microscope running Nikon Elements software and equipped with an electronic programmable stage and Perfect Focus. This microscope used a mercury lamp as the excitation source passed through a 470 nm band pass and 20X, 40X oil immersion objectives. Fluorescence images were collected on the green channel through a 535 nm band pass filter on a Coolsnap HQ CCD camera. Sample $TEMC_8PEML_3$ was placed between two microscope quartz cover slips.

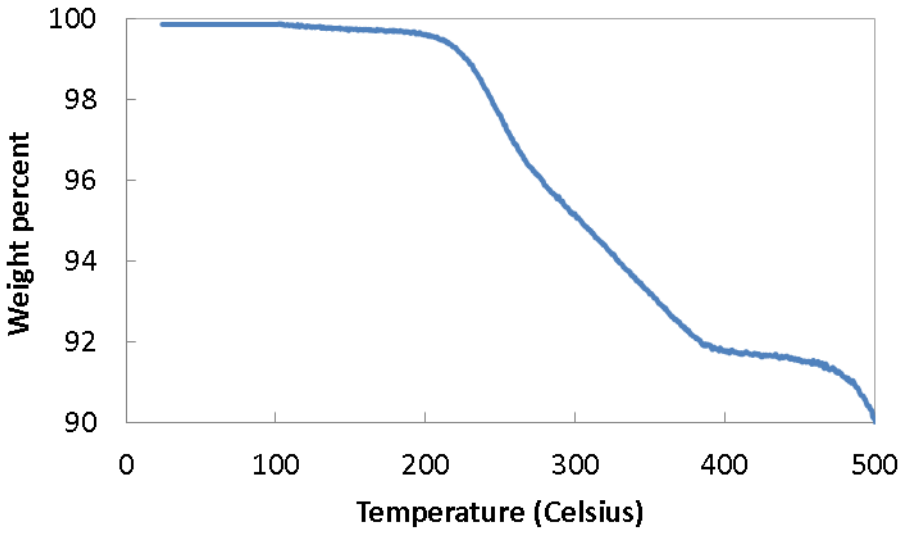

Figure S1: TGA of $TEMC_8$ obtained by melt infusion of 8% sulfur into porous carbon.

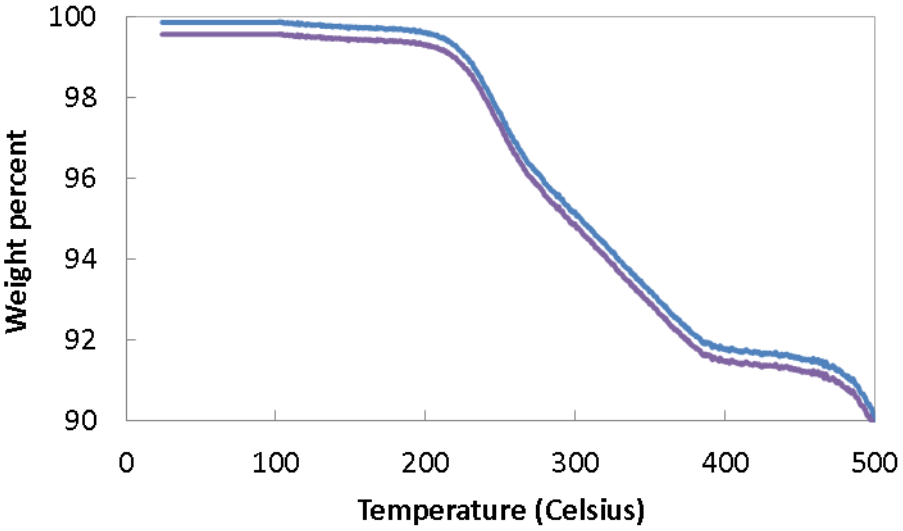

Figure S2: Validation that no sulfur is lost during encapsulation of $TEMC_8$. Blue line represents the weight loss due to sulfur by TGA of a $TEMC_8$ sample before encapsulation and the purple line displays the weight loss by TGA after encapsulation.

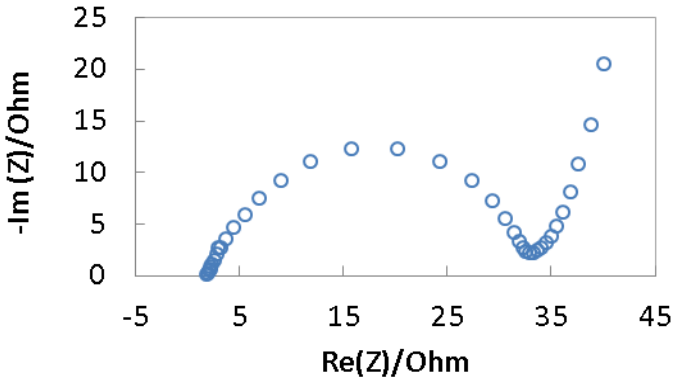

Figure S3: Impedance spectrum of a coin cell with cathodes containing $TEMC_8PEML_5$.

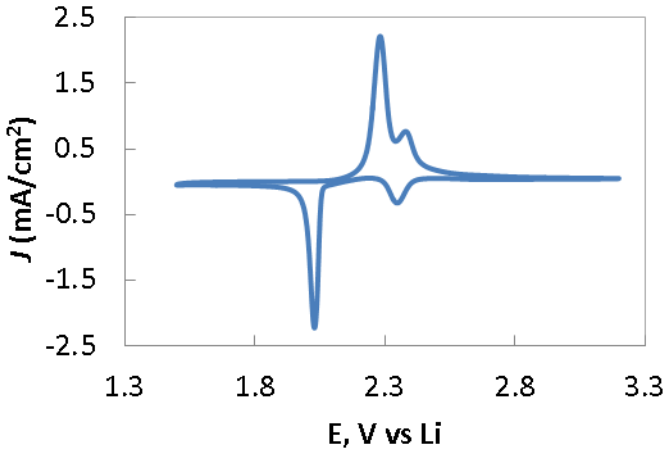

Figure S4: Cyclic voltammogram of a coin cell containing $TEMC_8PEML_3$. The first reduction wave at 2.3V corresponds to the reductive formation of lithium polysulfides. The second wave at 2.0V represents further reduction of the polysulfides to Li_2S. Two oxidation waves are observed during oxidation right below and above 2.3V. The scanning rate was 0.2 mV s^{-1}.

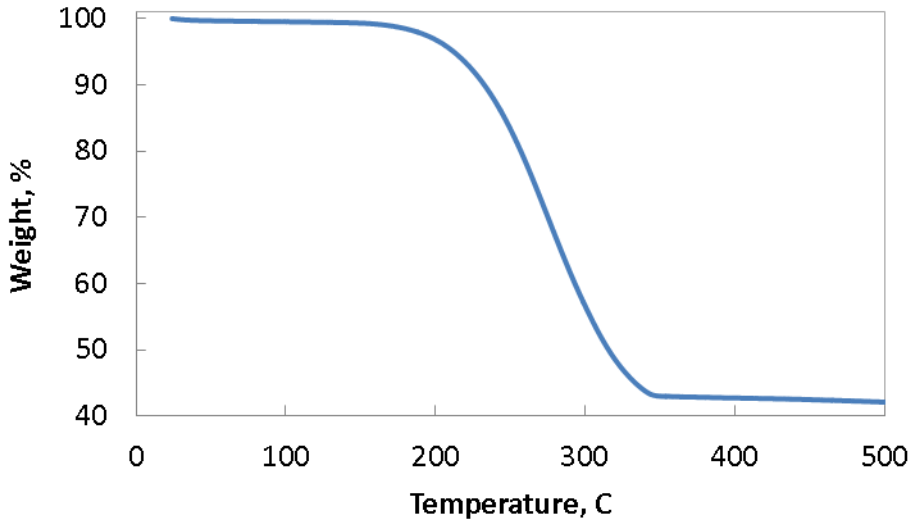

Figure S5: TGA of TDA_{57} obtained by melt infusion of 57% sulfur into TDA porous carbon.

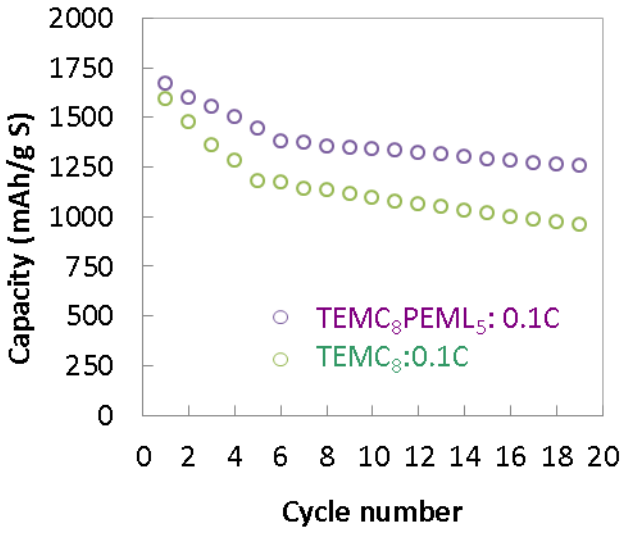

Figure S6: Discharge capacities for $TEMC_8PEML_5$ and $TEMC_{8\ at}$ a slow rate of 0.1C.

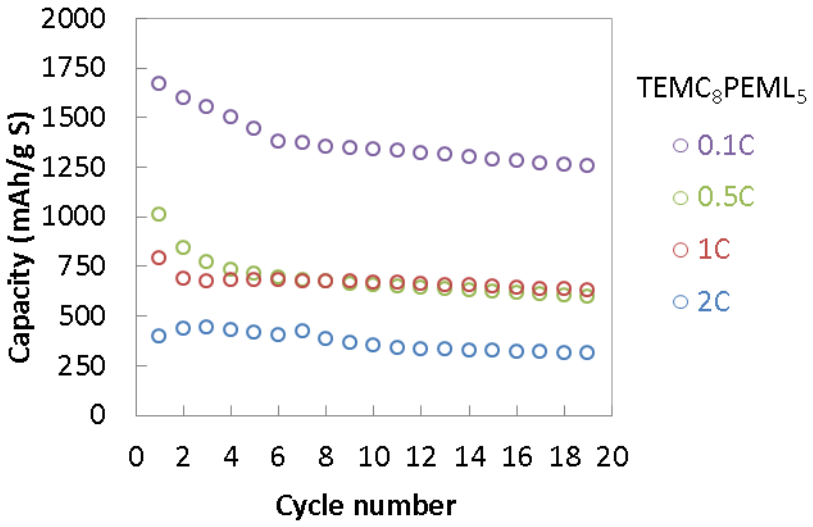

Figure S7: Discharge capacities for $TEMC_8PEML_5$ at rates varying from 0.1C to 2C.