Supporting information

A gel-ceramic multi-layer electrolyte for long-life lithium sulfur batteries

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Experimental

Preparation of gel-ceramic multi-layer electrolyte

Preparation of lithium ionic conductor LAGP has been previously reported[1]. The LAGP ceramic pellet (diameter 17.5 mm and thickness 0.6 mm) with a density of 3.2 g cm^{-3} was used as the solid electrolyte. The as-prepared LAGP powder was sieved through 200-mesh prior to use. Tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich) and anhydrous acetonitrile (AN, Aladdin Industrial Inc.) were dried for a week over 4Å molecular sieves, and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, Sigma-Aldrich) was dried at 110°C under vacuum for 12 h. Linear poly(ethylene oxide) (Aldrich), having a molecular mass of 6×10^5, was dried under vacuum at 50 °C for 24 h before use.

GPE slurry, which consist of poly (ethylene oxide) (PEO), the LiTFSI lithium salt with the O/Li ratio of 18/1 and 10 wt% of the ceramic filler LAGP powder in AN, was subjected to vigorous mixing via magnetic stirring to yield a uniform dispersion of LAGP particles. In order to further improve liquid uptake of the final GPE, commercial available porous carbon paper and porous glassy fiber soaked with GPE slurry were stuck to the LAGP sides facing to cathode and anode, respectively. After evaporation of the solvent and further dried for 12 h under vacuum, 30 uL of a solution of 1M LiTFSI dissolved in TEGDME was added as the gel-forming electrolyte.

Sulfur cathode preparation

Carbon/Sulfur (C/S) composite was first prepared by heating the ground mixture of Ketjen black and Sulfur powder at 155°C for 12 h under vacuum, with a sulfur loading of 80 wt%. The active material slurry was prepared by mixing 80 wt% C/S composite, 10 wt% Super P conductive carbon black, 5 wt% Carboxy Methylated Cellulose and 5wt% Styrene Butadiene Rubber binder in distilled water for 6 h. Then the homogeneous slurry was tape-casted onto an aluminum foil (thickness of 12 μm) current collector. After evaporation of the solvent water, the as-prepared cathode film sheet was roll-pressed and cut into circular disks with 12 mm in diameter and dried at 60 °C for 12 h under vacuum. The total material loading density was 1mg cm^{-2}.

Characterization

Morphology observation was carried out with a HITACHI S-3400 scanning electron microscope (SEM).

Electrochemical Measurements

To assemble the Li-S batteries, the gel-ceramic multi-layer electrolyte was directly used as the separator and Li metal was used as the anode. Finally, all the components were sealed using a plastic film in an argon-filled glove box. The cells were charged and discharged at various current densities in the voltage range of 1.5-3.0 V vs Li/Li$^+$ on a LAND CT2001A battery test system (Wuhan, China). The electrochemical impedance spectroscopy (EIS) measurements were performed on an Autolab PGSTAT302N Electrochemical Workstation (ECO CHEMIE B.V, Netherlands). The frequency range was varied from 1 MHz to 0.1 Hz with a small perturbation voltage of 10 mV. All electrochemical tests were conducted at room temperature. The value of coulombic efficiency is determined by taking the ratio of discharge capacity and charge capacity of each cycle.

Ionic conductivity and Transference number Measurements

The ionic conductivities of the electrolyte were measured by means of impedance spectroscopy. For the conductivity measurement of the GPE and the layered gel-ceramic electrolyte as well as the LAGP pellet, symmetrical stainless steel electrodes were used and gold films were sputtered on the both sides of the LAGP sample, respectively. Meanwhile, as a comparison, ionic conductivity of the glass fiber (GF) mat separator soaked by the liquid electrolyte was also measured by the impedance spectroscopy with two symmetrical stainless steel electrodes. The ionic conductivities(σ) are calculated from their total resistance, and $\sigma = h/(R*S)$ is used. Here, h is the thickness of the electrolyte; R is the total resistance of the electrolyte measured by the EIS; S is the active surface area of the electrolyte.

LAGP, an inorganic solid state electrolyte, is lithium single ion conductor that have a lithium transference number (t_+) of unity. The Nyquist plot of the LAGP pellet is composed of a high-frequency depressed semicircle and a low-frequency tail, which is an indication of the ionic nature of the NASICON-type material.[2] The total resistance of the LAGP pellet is obtained from the right intercept of the semicircle with the real axis in the plot, and the bulk resistance is obtained from the left intercept of the semicircle with the real axis. The value of the difference between the total resistance and the bulk resistance is the grain boundary resistance. While, the conductivity of an liquid electrolyte depends on the number and mobility of charge ionic carriers that compose of both the cations and anions. The transference numbers were evaluated by using a technique that combines both the direct current (DC) polarization and impedance spectroscopy technique. For the electrical measurements, the GF mat soaked with liquid electrolyte and the GPE were sandwiched between two non-blocking electrodes made of lithium disk. In the DC polarization technique, the current was monitored as a function of time on the application of a fixed DC voltage (ΔV) across the symmetrical cell. During the application of the electric field, the current is observed to fall with time and a steady-state current (I_s) is achieved eventually. In the impedance spectroscopy technique, a small perturbation voltage of 10 mV was applied to the symmetrical cell in the frequency range from 1 MHz to 0.1 Hz. The resulted impedance plots were fitted to obtain the bulk electrolyte resistances (R^b) and the passivating layer resistances (R^P). The high-frequency end of the semicircle (left-hand side) and the low- frequency end (right-hand side) represent the R^b and R^P, respectively. The lithium ion transference number was calculated by using the formula $t_+= Rb/(\Delta V/I_s-R^P)$.[3, 4] All the measurements were performed in an argon filled glove box at room temperature.

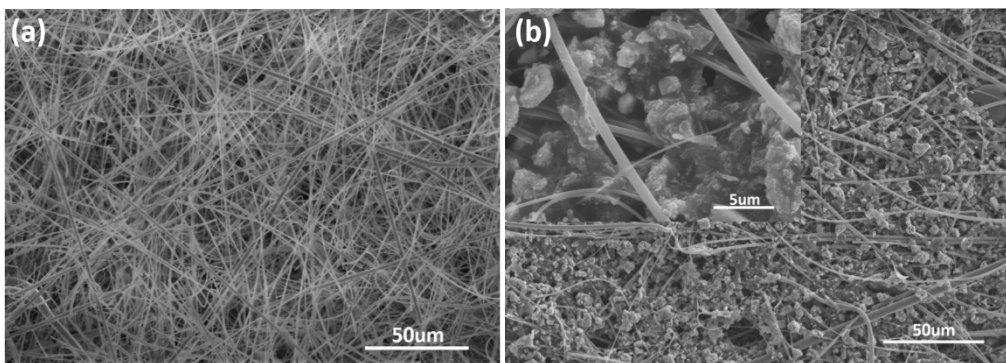**Fig. S1** An experimental demonstration of the gel-ceramic multi-layer Li-S cell.

Fig. S2 SEM images of (a) the pristine porous glass fiber mat; (b) the porous glass fiber mat soaked with GPE
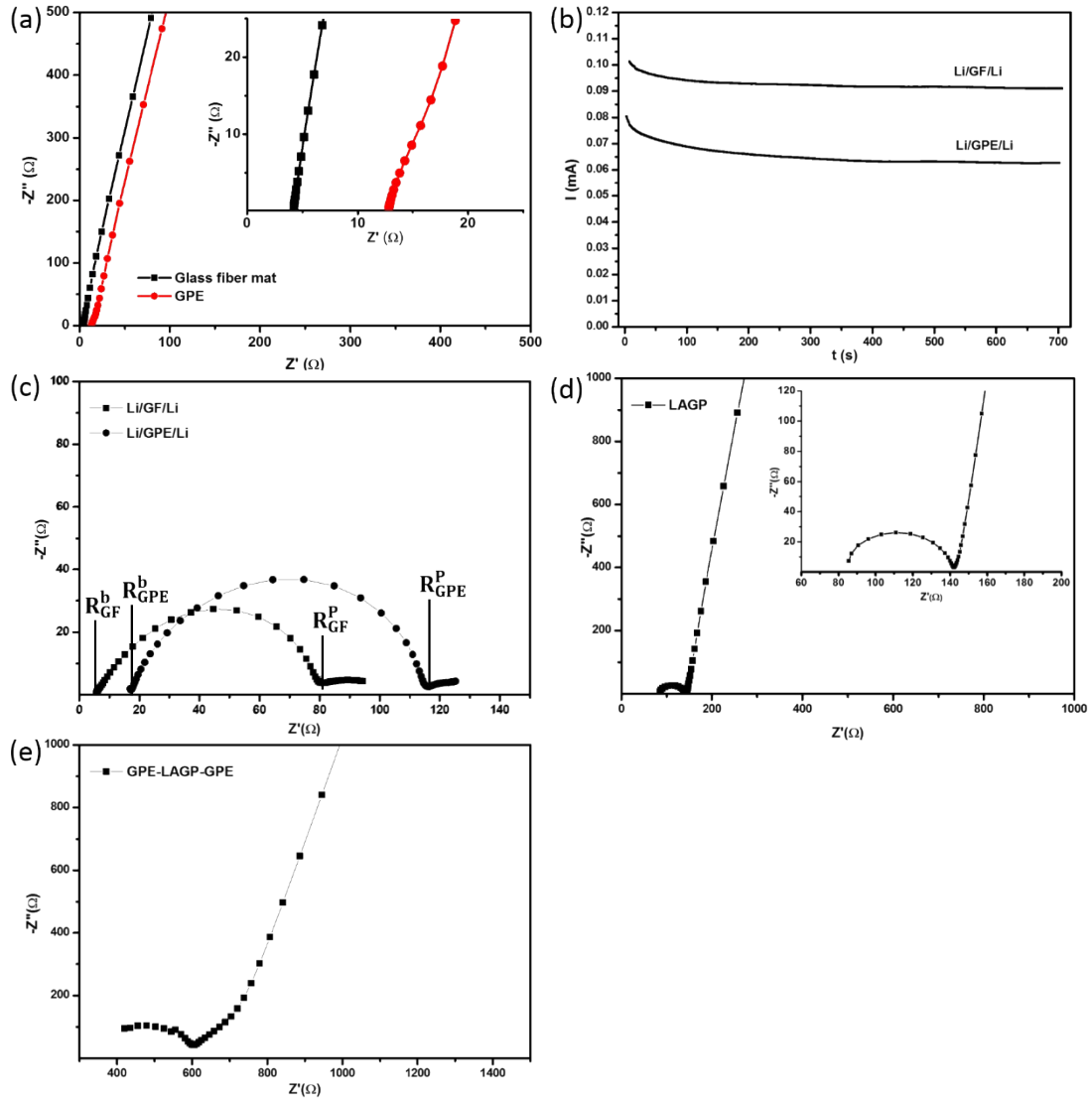
Fig. S3 (a) Nyquist plots of the symmetrical cells comprising the liquid electrolyte soaked GF mat and the GPE with stainless steel electrodes; (b) Current-time profiles of the symmetrical cells comprising the liquid electrolyte soaked GF mat and the GPE with lithium metal electrodes, with the DC voltage of 10 mV; (C) Nyquist plots of the symmetrical cells comprising the liquid electrolyte soaked GF mat and the GPE with lithium metal electrodes; (d) Nyquist plots of the LAGP pellet with gold films as the blocking electrodes; (e) Nyquist plot of the symmetrical cell comprising the gel-ceramic multi-layer electrolyte with stainless steel electrodes.

Table S1 Parameters and ionic conductivities of the electrolyte.

Sample	h/mm	d/mm	R/Ω	σ/S cm^{-1}
GF	0.3	16	4	37.3×10^{-4}
GPE	0.3	16	13	11.5×10^{-4}
LAGP	0.6	17.4	142.1	1.78×10^{-4}
GPE-LAGP-GPE	1.2	12.0	620.7	1.71×10^{-4}

Table S2 Parameters and lithium ion transference number of the electrolytes.

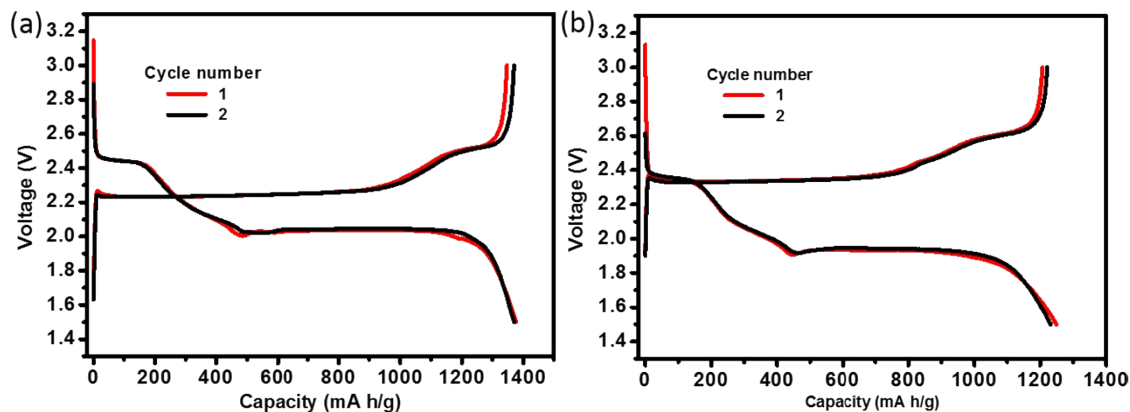| Sample	ΔV/mV	I_s/mA	R^b/Ω	R^p/Ω	t_+
GF	10	0.0910	5.6	75.5	0.16
GPE	10	0.0626	16.8	99.3	0.28

Fig. S4 The first two discharge/charge cycle profiles of the Li-S cells. (a) 1/20 C. (b) 1/10 C.

Table S3 Comparison of the initial capacity loss at different rates.

Rate(C)	1th discharge (mAh/g)	2nd discharge (mA h/g)	loss (%)
1/20 (present)	1376	1370	0.4
1/10 (present)	1249	1232	1.4
1/5 (present)	1058	1024	3.2
1/2 (present)	725	605	16.6
1/4 (ref. [5])	1265	905	28.5
1/10 (ref. [6])	1856	1081	41.8

Here is the example for calculating the loss (%) at 1/20 C, (1376-1370) / 1376 = 0.4%. In ref. 2 and ref. 3, Li-S cells are based on the liquid electrolyte.
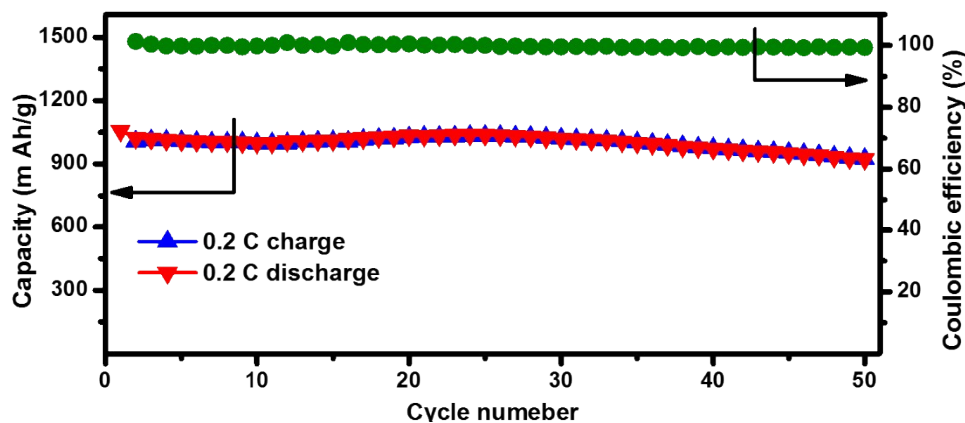

Fig. S5 Cell performance of the gel-ceramic multi-layer Li-S cell cycling at 1/5 C
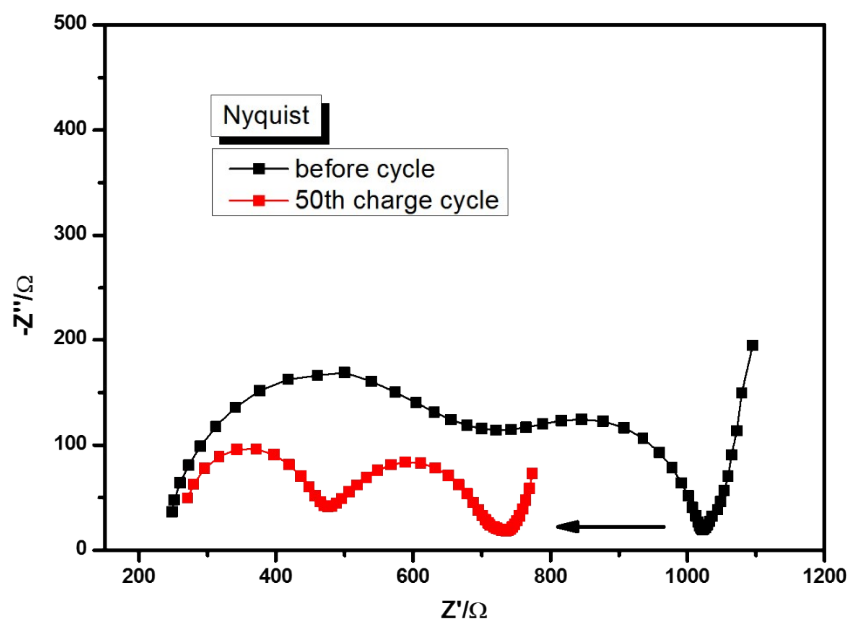
Fig. S6 Nyquist plots of the Li-S cell at fully charge state: before cycle (black) and at the 50th charge cycle (red).
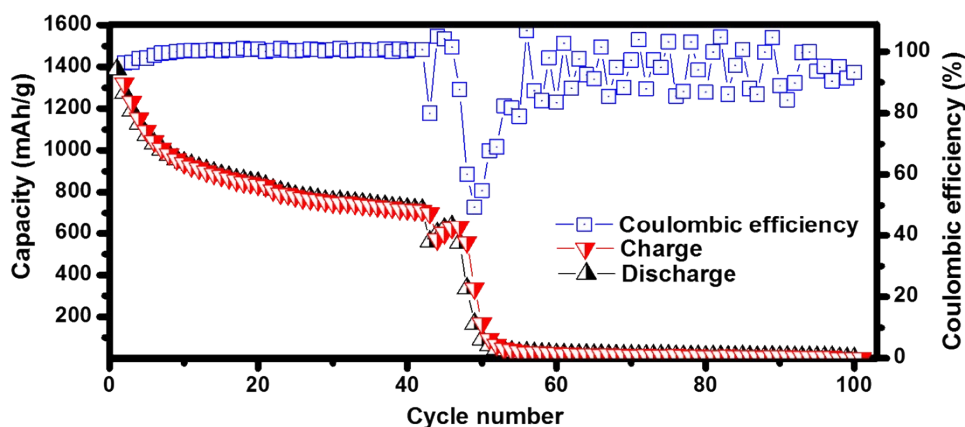

Fig. S7 Cell performance of the hybrid liquid-LAGP-liquid Li-S cell cycling at 1/5 C.

References:

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