In-situ Fabrication of a Freestanding Acrylate-based Hierarchical Electrolyte for Lithium-sulfur Batteries

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\textbf{A B S T R A C T}

A number of methods have been attempted to suppress the shuttle effect in lithium-sulfur (Li-S) batteries to improve battery performance. Conventional methods, however, reduce the ionic conductivity, sacrifice the overall energy density and increase the cost of production. Here, we report a facile synthesis of an acrylate-based hierarchical electrolyte (AHE). This quasi-solid electrolyte is assembled by in-situ gelation of a pentaerythritol tetraacrylate (PETEA)-based gel polymer electrolyte (GPE) into a polymethyl methacrylate (PMMA)-based electrospun network. The structural similarity and synergetic compatibility between the electrospun network and GPE provide the AHE an ester-rich robust structure with a high ionic conductivity of $1.02 \times 10^{-3} \text{ S cm}^{-1}$ due to the strong uptake ability and the elimination of commercial separator. The S/AHE/Li polymer battery also renders a high rate capability of 645 mAh g$^{-1}$ at 3C, while maintaining excellent retention at both high and low current densities (80.3% after 500 cycles at 0.3C and 91.9% after 500 cycles at 3C). First-principle calculations reveal that the reduced shuttle effect can be attributed to a strong polysulfide anchoring ability of ester functional groups, while cell modeling shows that the geometric design effectively suppresses polysulfide flux. This in-situ integrated method opens up an avenue for the future development of solid-state and polysulfide redox flow sulfur-based batteries.

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1. Introduction

The lithium-sulfur (Li-S) battery has received increasing attention owing to its potential in revolutionizing energy storage systems to be able to meet the energy demands of applications such as electrical vehicles (EVs) \cite{1,2}. The reduction of sulfur, in the form of lithium polysulfides and lithium sulfide, can theoretically boost the battery to reach an energy density of 2600 W h kg$^{-1}$, but this involves a multistep process of complex equilibrium states between long- and short-chain polysulfides. To complicate matters, the intermediate liquid product polysulfides are highly soluble in ether-based liquid electrolyte (LE), creating a shuttle effect to the lithium metal anode \cite{3,4}. Coupled with low electronic conductivity and large structural/volumetric changes (79%) during the cathodic reaction (from S to Li$_2$S), the conventional Li-S battery suffers from poor cycle life, low specific capacity and low energy efficiency \cite{5}.

To overcome the abovementioned problems, carbon materials with special porous structures have been extensively studied to accommodate sulfur by forming carbon/sulfur composites \cite{6-8}. Among these materials, ordered mesoporous carbons, such as CMK-3, have been particularly studied due to it being able to effectively improve the electronic conductivity of sulfur and simultaneously suppress the dissolution of polysulfides during charge/discharge of Li-S batteries \cite{9}. Despite these advantages, existing sulfur uptake techniques (such as mechanical mixing \cite{10}, melting-diffusion \cite{9} or chemical-deposition \cite{11}) are unable to guarantee that the sulfur content is entirely maintained within pores during phase transition from solid to liquid, especially when the loading mass reaches a relative high level. Residual sulfur outside pores will be rapidly lost in the form of liquid polysulfides \cite{12}. Thus, novel structural configurations, including conductive and porous carbon interlayers \cite{13}, functional modified separators \cite{14} and solid electrolytes \cite{15} are presented to further block the diffusion of polysulfides. Among these configurations, solid
electrolytes have attracted special attention since the additional benefits such as lithium dendrite suppression and enhanced safety [16]. Recently, various solid electrolytes, including all-solid-state polymer electrolytes [17–19], gel polymer electrolytes (GPEs; prepared by hot-press [20], phase inversion [21,22], or electrospinning [23] approaches), glass–ceramic electrolytes [24,25] and fast ionic conductors [26,27] have been employed in Li-S batteries. On the one hand, unfortunately, these solid electrolytes generally suffer from limited ionic conductivities and large electrode/solid electrolyte interfacial resistances, which leads to rapid capacity decay and large polarization for the solid Li-S batteries. Therefore, developing solid electrolytes that simultaneously possess high ionic conductivity, low interfacial resistance and also can be synthesized in a facile manner, remains a challenge for the next-generation Li-S battery technology.

On the other hand, the functional groups also fill an essential role for the blockage of the polysulfides in the solid electrolytes. Innovatively, Y. Cui et al. proposed that Li2S exhibits strong interaction with oxygen donor atoms in ester (R-COO-R') groups, an observation which has been experimentally testified by other research groups [28,29]. In a recent study, we proposed a novel poly pentaerythritol tetraacrylate (PPETA) gel polymer electrolyte (GPE) rich in acrylate on its polymer matrix, demonstrating compatibility with a bare sulfur cathode and a robust integrated electrolyte/electrode interface [30]. Further mechanical enhancement of the GPE so as to elimination of commercial separator and continually optimizing the ionic pathways in a porous medium are crucial factors for blocking polysulfide diffusion [30,31]. Herein, we present an acrylate-based hierarchical electrolyte (AHE) for Li-S batteries to realize the controllable polymer channels and maximize polysulfide trapping with the minor sacrifice of electrolyte conductivity. The freestanding AHE was assembled by integrating a PPETA GPE with a polymethyl methacrylate (PMMA)-based electrospun fiber network. The in-situ prepared S/AHE/Li batteries exhibit electrochemical performances, which can be attributed to the dual polysulfides immobilization effect, chemical interaction and physical diffusion barrier. Ester (R-COO-R') was shown to be a strong polysulfide capturer from first-principle calculations. A macroscopic cell model is used to evaluate the battery performance with a physical barrier and the correlation between the diffusion flux of the polysulfides and geometric parameters of the porous medium is proposed. The hierarchical electrolyte opens up a facile, low-cost and effective way to enhance the performance of current Li-S batteries, and takes a key step toward capitalizing on high-performance Li-S batteries.

2. Experimental section

2.1. Preparation of PMMA-based electrospun fiber network

PMMA-based electrospun fiber network was prepared by using a SS-2535 electrospun equipment (Beijing Ucalery Co., Ltd.). 3 wt% PAN (Mw = 150,000, J&K Scientific LTD.) and 7 wt% PMMA (Mw = 350,000, J&K Scientific LTD.) was dissolved in N,N-dimethylformamide (DMF) with continuous stirring at 70 °C for 5 h. After that, the solution was sequentially electrospun onto the target rotating collector with a flow rate of 1.0 mL h−1 for 5, 6 and 7 h. The voltage applied to the needle tip and the distance from needle to the collector were set as 22 kV and 15 cm, respectively. The obtained PMMA-based electrospun fiber network was removed from the collector and dried at 60 °C for 12 h under vacuum before further use.

2.2. Electrochemical performance measurements

CR2032-type Li-S coin cells were assembled in an Ar-filled glove box. The coin cells were fabricated in-situ by direct polymerization. Cells were comprised of S@CMK/3 as the cathode, a freestanding quasi-solid electrolyte, and lithium foil as the anode. The S@CMK-3 nanocomposite was prepared following a melt-diffusion strategy. 0.25 g CMK-3 (XF Nano, Nanjing) and 0.75 g nano sulfur powder (Dk Nano technology, Beijing) were ground and heated to 155 °C for 10 h. The S@CMK-3 electrode was prepared by mixing 80 wt.% S@CMK-3 powder, 10 wt.% Super P and 10 wt.% PVDF in a NMP solvent disperse, coated with slurry on carbon-coated aluminum foil and dried at 60 °C for 24 h. The mass loading of the sulfur active material on the electrode is 1.5–1.8 mg cm−2. The precursor solution (containing 1.5 wt% PETEAl and 0.1 wt% AIBN dissolved in 1M LiTFSI/DOL: DME (1:1 by volume) with 1 wt% LiNO3 electrolyte) was injected into a PMMA-based electrospun fiber network and entirely covered the lithium anode. To ensure the accuracy of the experiment, the precursor solution in each cell is uniformly set as 0.02 ml. Then the cathode was placed on the top of wetted PMMA-based electrospun fiber network and sealed the coin cell with pressure of 75 Mpa. Subsequently, the assembled cells were aged for 2 h to ensure that the precursor solution was fully-wetted the electrospun network. The cells were then heated at 70 °C for 2 h in a vacuum oven to ensure complete polymerization of monomers. During heating process, there may exist gas generation. LiNO3 in the electrolyte could potentially suppress the gas generation and enhance the cycle life of lithium metal [32,33].

The electrochemical performance of polymer battery without LiNO3 additive was shown in the supporting information. The assembled Li-S cells were cycled at various charge/discharge rates between 1.7 – 2.8 V on a Land 2001A battery testing system at 25 °C. Cyclic voltammograms (CVs) of the assembled polymer Li-S cells were tested using a VMP3 electrochemical working station (Bio Logic Science Instruments, France) at a scanning rate of 0.1mV s−1 with sulfur electrode as the working electrode and lithium coin as both reference and counter electrodes. An electrochemical impedance spectrum (EIS) of Li-S cells at a half discharge state was examined using the VMP3 multichannel electrochemical station in the frequency range of 10−2 to 106 Hz by applying a 5mV-ac oscillation.

The Li-S coin cells were transferred into the glove box and disassembled for further examination after cyclic tests. Their AHEs were repeatedly rinsed with DME and vacuum dried at 50 °C for 6 h to remove any residual solvent. The air-sensitive samples were rapidly transferred into the vacuum chamber of SEM/FTIR/XPS under the protection of vacuum box before the following test. Fourier transform infrared (FTIR) spectra of the AHEs were recorded with a Bruker Vertex70 instrument at ambient temperature. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Physical Electronics PHI5802 instrument using an X-ray magnesium anode (monochromatic Ka X-rays at 1253.6 eV) as the source. C 1s region was used as references and set at 284.8 eV.

2.3. Computational methods of first-principle study

All calculations were performed by density functional theory (DFT) based first-principle study using an ABINIT [34,35] code. The electron-ion interactions were described by the projector augmented wave (PAW) method [36], and the electronic exchange–correlation effect was implemented within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) type [37]. A cubic box sized 20 × 20 × 20 Å, which was large enough to avoid the interaction caused by periodicity, was prepared as the periodic cell. The plane-wave energy cutoff was set to be 22 Ha and k-space sampling was restricted to the Γ-point. Atomic positions were fully relaxed during structural optimization. To maintain a reasonable computational cost, the illustrative monomers were
extracted from saturated polymeric species. The adsorption energy ($E_{\text{ads}}$) was calculated to evaluate the relative stability of polysulfides on pristine acceptors and defined as:

$$E_{\text{ads}} = E_a + E_{\text{LiS}} - E_{\text{tot}}$$  \(1\)

where $E_a$, $E_{\text{LiS}}$, and $E_{\text{tot}}$ were the DFT energies of pristine acceptors, polysulfides and polysulfides-adsorbed systems, respectively.

2.4. Computational methods of macroscopic cell simulation

A dynamic one-dimensional lithium-sulfur battery model was established using a finite volume method (FVM) [38–40]. Simulations of discharge behaviors of batteries with and without the porous medium, including spatial and temporal analysis, were performed to evaluate non-uniform species distribution. The computational domain of the Li-S battery is composed of an interface representing lithium foil anode, a porous medium ($L_{\text{PM}} = 30 \mu m$), which insulates electron transfer and blocks shuttle effects, and a sulfur/carbon cathode ($L_c = 90 \mu m$). Details about the simulation methods are shown in the supporting information.

3. Results and Discussion

3.1. Characterization of fabricated AHE

To immobilize the diffusion of polysulfides and simultaneously provide lithium ion pathways, PETEA monomer was in-situ polymerized in a PMMA-based electrospun fiber network to form a freestanding AHE. It should be noted that the PPETEA-based GPE and PMMA-based fiber network are both rich in ester functional group, which synergistically capture polysulfides to significantly thwart diffusivity. The field emission scanning electron microscopy (FE-SEM) images in Fig. 1a and b show that the microstructure of the PMMA-based electrospun network is composed of randomly

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**Fig. 1.** Synthesis and structure characterization of AHE: FE-SEM images of the PMMA-based electrospun fiber network (the optical images is shown in inset) (a, b); uptake ability of the PMMA-based electrospun fiber network for the PPETEA GPE precursor (c); the optical images of AHE (d); Schematical architectures and atomic configurations of AHE (e, f).
oriented smooth fibers with an average diameter of approximately 300 nm. The overlapping nanofiber structure possesses high porosity and superior wettability, both of which contribute to a much higher uptake ability (933.5% for the GPE precursor) than a commercial separator (83.9%), which allows for a fully permeabilized pathway for lithium ions. Infiltration of the precursor solution and vacuum heating to fully polymerize the PETEA contribute to excellent strength and robustness as shown in Fig. 1d. The specific architecture and atomic configuration of AHE are schematically illustrated in Fig. 1e and f. The PPETEA GPE has a jelly-like consistency and possesses a symmetrical star structure with high density ester groups, which enwraps the PMMA-based electrospun fiber and sufficiently fills the overlap pores. The similarity in the chemical composition ensures a superior miscibility between two polymers for a freestanding polymeric blend. Fig. S1 presents the temperature dependence of ionic conductivities for the AHE at a temperature range from −10 to 80 °C. For the AHE, the plots of log σ versus T−1 exhibit a non-linear relationship, which can be adequately described by the Vogel–Tamman–Fulcher (VTF) empirical equation below [41]:

\[ \sigma = \sigma_0 T^{-1/2} \exp\left(\frac{E_a}{RT - T_0}\right) \]

where \( E_a \) is the activation energy, \( \sigma_0 \) is the pre-exponential factor, \( T_0 \) is a parameter correlated to the glass transition temperature, and \( R \) is the ideal gas constant. Due to the high uptake ability of PMMA-based electrospun fiber network and the elimination of commercial separator, the conductivity of AHE is able to reach a high value of \( 1.02 \times 10^{-2} \text{ S cm}^{-1} \) at 25 °C, a value at which is much higher than that of LE with a commercial separator \( (2.16 \times 10^{-3} \text{ S cm}^{-1}) \). A high ionic conductance is expected to reduce the ohmic polarization and therefore enhance the rate performance of Li-S batteries.

### 3.2. Electrochemical performance of S/AHE/Li battery

The thickness of a porous medium affects the transportation of polysulfides, which determines the performance of the Li-S battery [42]. A thick intermediate layer increases the ohmic polarization and deteriorates the electrochemical performance of polymer batteries [43]. In-situ synthesis would ideally reduce the thickness of the AHE to match the thickness of the PMMA-based fiber network, which is controlled by the duration of electrospinning (PMMA-based fiber networks with a thickness of 25, 30 and 35 μm were fabricated, respectively). S/AHE/Li cells containing CMK-3/S cathodes, AHEs and lithium metal anodes were fabricated via in-situ formation of the PPETEA GPEs in the PMMA-based fiber network. First of all, different thickness (including 25, 30 and 35 μm) PMMA-based electrospun nanofibers were fabricated through controlling the electrospun time. For the in-situ polymerization of PETEA-based GPE in PMMA-based electrospun nanofiber, the thickness of AHE is equal to the electrospun nanofiber. It is easy to predict that with the thicker of the AHE, the polysulfides immobilization function increases meantime the resistance increase that damages the electrochemical performance. To obtain the most balanced thickness between immobilization function and polarization, we have carried out the thickness experiment. Figure

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**Fig. 2.** Electrochemical performances of Li-S batteries by capitalizing on AHE: rate performances and the corresponding Coulombic efficiencies of the S/LE/Li and S/AHE/Li cell from 0.1 to 5C (the current density of 1C is 1675 mA g−1) (a); typical charge/discharge voltage curves of S/AHE/Li cell at various C-rates (b); cycling performances of S/LE/Li and S/AHE/Li cell at 0.3C (c) and 3C (d); cyclic voltammograms (CVs) of S/AHE/Li at a scan rate of 0.1 mV s−1 (e); electrochemical impedance spectroscopy (EIS) plots of S/AHE/Li cell after 100 cycles at 0.1C (f). Impedances are measured at fully charged state (2.8 V); Specific capacity values were calculated based on the mass of sulfur.
R1 shows the 0.3C cycling performance of Li-S cell with varying AHE thicknesses. In the end, the optimal network thickness is determined to be 30 μm, which is an optimized empirical value in our experiment.

Fig. 2a compares the rate performances of the S/LE/Li cell and S/AHE/Li cell at various rates from 0.1 to 5C (the current density of 1C is 1675 mAg⁻¹). It is apparent that the S/AHE/Li cell performs a much better rate performance than the S/LE/Li cell. The specific discharge capacities of the S/AHE/Li at 0.1, 0.3, 0.5, 1, 3 and 5C are 1107, 988, 898, 792, 645 and 486 mAh g⁻¹, respectively, whereas the corresponding capacities of the S/LE/Li are 1047, 717, 602, 501, 437 and 372 mAh g⁻¹, respectively. When the C-rate was switched from 5 to 0.1C (Fig. 2a), the initial capacity of S/AHE/Li was largely recovered, reflecting that the S/AHE/Li cell is robust and highly stable. The corresponding S/AHE/Li charge/discharge curves are shown in Fig. 2b. For the S/LE/Li cell, the initial discharge capacity of 1370 mAh g⁻¹ is not completely reversed during the following charge process, mainly due to the initial dissolution of the polysulfides; the corresponding Coulombic efficiency is 93.8% (defined as the discharge capacity per the charge capacity). The S/AHE/Li shows a first cycle Coulombic efficiency of 97.1%, higher than that of S/LE/Li, mainly due to the inhibition of dissolution of polysulfides. Generally, during the following cycles, an overall higher coulombic efficiency (~100%) is achieved for the S/AHE/Li. Such electrochemical performance can further prove the polysulfide immobilization function of AHE. The cycling performances of the S/LE/Li cell and S/AHE/Li cell under low and high current densities are presented in Fig. 2c and d. The S/AHE/Li cell is able to deliver a discharge capacity of 792 mAh g⁻¹ after 500 cycles at 0.3C with a capacity retention of 80.3% (Fig. 2c). In sharp contrast, the corresponding retention for the S/LE/Li cell is only 38.1%. The S/AHE/Li cell also exhibits an obvious enhanced cycling performance at a high current density. It can be seen from Fig. 2d that the S/AHE/Li cell achieves a discharge capacity of 574 mAh g⁻¹ (a capacity retention of 91.9%) after 500 cycles at 3C. In contrast, the S/LE/Li cell delivers a low discharge capacity of only 321 mAh g⁻¹ after 500 cycles. In the experiment, the weight of PMMA-based electrospun nanofiber (2.3 mg) is nearly double lighter than the commercial separator (3.98 mg). Furthermore, to ensure the accuracy of the experiment, the precursor solution in Li/AHE/S cell is uniformly set as 0.02 ml, which is equal to the amount of LE in Li/LE/S. After polymerization, the weight of AHE maintains nearly unchanged compared with before. The increase of specific capacity during cycling is identical to the promotion of energy density for Li-S batteries. More importantly, with the development of higher sulfur mass loading cathode, the shuttle effect becomes much more...

Fig. 3. Chemical interaction property characterization of AHE: the most stable adsorption cases between polysulfides and PPETEA (a), PP/PE (b) and PMMA (c); the adsorption binding energies Ea between polysulfides and PP/PE, PMMA and PPETEA respectively (d); the adsorption binding energies Ea between polysulfides and different sites of PPETEA (e); O 1s XPS spectra of pristine AHE and cycled AHE (f); FTIR spectra of pristine AHE and cycled AHE (g).
severe, the advantages of GPE would be of great potential for future application.

Fig. 2e shows the cyclic voltammograms (CVs) of the S/AHE/Li cell obtained at a scanning rate of 0.1 mV s⁻¹. For the S/AHE/Li cell, the cathodic peaks appear at approximately 2.28 V and 2.03 V and the corresponding overlapping anodic peaks are located at approximately 2.39 V, which are the characteristic peaks of Li-S batteries [13]. The cathodic and anodic peak current densities and locations exhibit stability with an increase in CV cycles, reflecting that the AHE is able to efficiently block the diffusion of the liquid intermediate product, which would otherwise be an undesirable effect that causes active material loss and unstable curves. Electrochemical impedance spectroscopy (EIS) is used to evaluate the interfacial resistance and reversibility of Li-S batteries. The high-frequency and medium-frequency semicircles are attributed to the SEI film resistance ($R_{SEI}$) and charge transfer resistance ($R_{ct}$), respectively. The incline at low frequency corresponds to the lithium-diffusion process within the electrode [15,16]. After 100 cycles, the impedance of S/LE/Li cell increases significantly compared with the initial state (Fig. S3). In sharp contrast, the resistance of the S/AHE/Li battery shows no evidential change, which further demonstrates that the AHE is able to protect the electrode, leading to a more stable electrode/electrolyte interface (Fig. 2f).

3.3. Mechanism study for chemical interaction and porous physical barrier of polysulfides by AHE

The mechanism of the AHE on the Li-S battery can be described as the chemical adsorption between the functional groups and polysulfides as well as the function of the porous physical barrier. A first-principle study is performed to clarify the adsorption energies between the AHE and Li₂Sn₈ species. The optimized structures of Li₂Sn₈ (n = 6 and 8) are in three-dimensional cluster shapes instead of chains (Fig. S4), which is consistent with previous investigations [44,45]. The most stable structures of Li₂Sn₈ adsorbed on poly pentaerythritol tetraacrylate (PPETEA), poly propylene (PP)/poly ethylene (PE) and PMMA are shown in Fig. 3a, b and c, respectively. In Fig. 3a, the PPETEA saturated monomer has a symmetrical star structure with one ester functional group in each single strand, hence, one strand is extracted to keep a reasonable computational cost. The corresponding adsorption energies on these three structures are summarized in Fig. 3d. It is found that the Li₂Sn₈ adsorption energies on PPETEA and PMMA are −0.79 eV, which is about five times that of on PP/PE. The much stronger Li₂Sn₈ adsorption of the AHE than on traditional separators effectively limits polysulfide crossover. The adsorption of Li₂Sn₈ showed nearly the same tendency with Li₂Sn₆, whose mechanism is essentially identical. To further clarify the adsorption sites of polysulfides on
the AHE, adsorption between Li$_2$S$_x$ and the various functional groups of PPTEA are calculated and presented in Fig. 3e. It is apparent that the Li$_2$S$_x$ adsorption energies decrease in the order of C=O $>$ C–O $>$ C–C, suggesting that C=O plays the most important role in Li$_2$S$_x$ adsorption. From an electronic properties perspective, the adsorption energy is determined by the amount of electron transfer from sulfur atoms in the cluster into the target substrate [44]. Therefore, it is intuitive that the Li$_2$S$_x$ clusters prefer to adsorb through O atoms instead of C atoms on the substrate due to a larger electronegativity of O (3.44) in comparison with that of C (2.55). In addition, the more exposed nature of O atom in C–O than in C–O–C leads to more readily transmissible electrons from Li$_2$S$_x$ to O. Based on these calculated results, the AHE is acts as the chemical adsorption medium to inhibit diffusion of polysulfides due to the role of the ester functional group.

In order to verify the proposed mechanism of the chemical interaction between polysulfides and the AHE, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) were used. As shown in Fig. 3f, XPS was used to identify the surface constituent of an original AHE and an AHE after dissembling from S/AHE/Li cell, respectively. The O 1 s spectrum of the original AHE shows two peaks at 531.9 and 530.7 eV assigned to C–O–C and C–O, respectively, which is the typical composition of ester functional group [46]. After 100 cycles, the peak of C–O in the AHE virtually disappears, suggesting that the polysulfides have been adsorbed on the ester functional group and cover most surface signal, which also indicates that C=O plays an important role in the chemical interaction. Furthermore, Fig. 3g compares the FTIR spectra of the AHE before and after 100 cycles. It is clear that the appearance of peaks at 986 cm$^{-1}$ (C–O–C, symmetrical stretching), 1120 cm$^{-1}$ (C–O–C, symmetrical stretching), 1453 cm$^{-1}$ (CH$_2$ bending), 1407 cm$^{-1}$ (CH$_2$ bending) and 1738 cm$^{-1}$ (C=O stretching) are in line with previously reported results in the literature [47]. After cycling, the adsorption peak at approximately 1738 cm$^{-1}$ assigned to the stretching vibration of C=O bonds, whose peak location and width shows a right shift and broader trend, indicates that the C=O to polysulfides. These results further confirm that the intermediate product, polysulfides, have been strongly anchored by ester functional group on the AHE, slowing down the polysulfide diffusion rate.

In addition to the chemical interaction, a porous physical barrier is another important function of the AHE, which could be achieved by building a porous medium (PM) between the electrodes to physically inhibit the diffusion of byproduct. To simplify the transport of polysulfides species through the porous medium, the formula regarding the diffusion flux can be expressed as follows, which has been mentioned in our previous research on mass transport in fuel cells [48]. In general, the polysulfide shuttle effect through the porous medium is due to the diffusion of polysulfides caused by a concentration gradient (1st term) and electric migration (2nd term). The flux of polysulfides crossover can therefore be expressed as:

$$N_{S_n^{\text{pm}}} = D_{S_n^{\text{pm}}} \nabla C_{S_n^{\text{pm}}} + \frac{2}{RT} D_{S_n^{\text{pm}}} C_{S_n^{\text{pm}}}^\text{an} F \nabla \phi$$  \hspace{1cm} (3)

where $D_{S_n^{\text{pm}}}$ is the effective diffusivity of polysulfides species across the porous medium. The diffusion flux, can be approximated $C_{S_n^{\text{an}}}/L_n$, where $L_n$ is the thickness of the porous medium; $C_{S_n^{\text{an}}}$ and $C_{S_n^{\text{pm}}}$ represent the polysulfide anion concentration at the anode/porous medium and the cathode/porous medium interfaces, respectively. Similarly, the electric migration term is dependent on the diffusivity and moreover is proportional with the anion concentration and the gradient of electrolyte potential. As can be estimated, the thickness of the porous medium and the diffusivity across the porous medium fill crucial roles. Consequently, the rate of polysulfide shuttle crossover can be reduced by decreasing the diffusivity, which can be achieved by increasing the thickness of the porous medium or reducing the polysulfide concentration gradient.

Fig. 4a shows the simulated discharge curves of S/LE/Li and S/PM/Li using COMSOL Multiphysics based on Eq. (3), where the variable is the insertion of a porous medium between the electrodes. The S/PM/Li shows an obvious higher capacity due to the blockage of continuous diffusion of the polysulfide anions, whilst accommodating the active material at the side of the cathode. In the S/LE/Li cell, the polysulfide anion concentration gradually evolves during the discharge process (Fig. 4b). Polysulfides migrate across the conventional separator and react with the metallic lithium anode, causing parasitic reactions and decreasing the overall performance (Fig. 4b). Comparably, the shuttle rate would be ideally reduced in the S/PM/Li, protecting the anode from unsustainable consumption (Fig. 4c). A similar logic can be extended to other advanced porous medium systems, including interlayers, solid-state electrolytes and modified separators. For intuitive way to represent the dual effect, the visible durability measurement was carried out in an H-type glass cell (one side with 0.5 m polysulfide dissolved in LE, and the other side with pure LE) to present the stability of the AHE in extreme working conditions (Fig. 4d and e). A commercial PP/PE separator and the AHE (30 μm) were set in the glass cell, and the test was conducted in a glove box to exclude the influence of water and oxygen. As shown in Fig. 4d, polysulfides readily diffused across the PP/PE separator and the opposite LE turned red-brown in color, suggesting that the S/LE/Li cell suffers from significant shuttle effect. In contrast, no apparent color change was observed in the AHE-set H-cell during the 2h-aging test, which proves that prevention of polysulfide anion diffusion to the LE was successful (Fig. 4e). The stability test presents a potential application of the AHE in the Li-S battery and even polysulfide redox flow batteries.

4. Conclusions

In summary, an in-situ fabricated acrylic-based hierarchical electrolyte (AHE) was crafted for the Li-S battery. This quasi-solid electrolyte is fabricated by integrating a pentaerythritol tetraacrylate (PETEA)-based gel polymer electrolyte (GPE) with a polymethyl methacrylate (PMMA)-based electrospun network. The AHE dramatically enhances the overall electrochemical performance of Li-S batteries (80.3% after 500 cycles at 0.3C and 91.9% after 500 cycles at 3C). The superior performance can be attributed to (i) the synergetic compatibility of each electrolyte components, (ii) the elimination of commercial separator, and (iii) the dual effects of strong chemical interaction and porous physical blockade for polysulfide diffusion. Dominated ester (R-COO-R') groups on the AHE were shown to be strong polysulfide traps from first-principle calculations. Moreover, the geometrical parameter of the porous medium setting between the electrodes is essential for the polysulfide diffusion flux. Hence, this electrolyte configuration opens up an avenue for the future development of Li-S batteries. The proposed solution is simple, cost-effective and is easily synthesized, possessing untapped potential for accelerating the commercialization of solid-state and redox flow sulfur-based power devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.08.015.

References