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Heteroatomic Te_xS_{1-x} molecule/C nanocomposites as stable cathode materials in carbonate-based electrolytes for lithium-chalcogen batteries

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A stable cathode material in a conventional carbonate-based electrolyte for high-energy lithium-chalcogen batteries was successfully fabricated by homogeneously confining heteroatomic $Te_sS_{1:x}$ molecules into ordered mesoporous carbons CMK-3 *via* a facile melt-impregnation route. The Te-S bonds in the heteroatomic $Te_sS_{1:x}$ molecules endow them with higher intrinsic electrical conductivity and electrochemical reaction activity with Lithan the homoatomic S_8 molecules. Moreover, the Te-containing polychalcogenide intermediates could induce the formation of solid electrolyte interphase (SEI) layers on the $Te_sS_{1:x}$ /CMk-3 surfaces in the carbonate-based electrolyte, which efficiently prevent polychalcogenides from shuttle effect and side reaction with the carbonate solvent. With further assistance of mesopore confinement of CMK-3, the $Te_sS_{1:x}$ /CMk-3 composites can be reversibly charged and discharged in the carbonate-based electrolyte with long cycling stability and high rate capability. Therefore, the $Te_{0.1}S_{0.9}$ /CMK-3 composite with an optimal Te/S mole ratio of 1/9 maintains the high reversible capacities of 845 mAh g⁻¹ after 100 cycles at 250 mA g⁻¹ and 485 mAh g⁻¹ after 500 cycles at 1 A g⁻¹. These encouraging results suggest that the heteroatomic $Te_sS_{1:x}$ molecule/C composite could be a promising cathode material for the long cycle life and high power density lithium battery.

Introduction

The rapidly developing market for mobile electronics and electric vehicles (EVs) has prompted the urgent need for high energy density and long-lasting rechargeable batteries. Current Li-ion batteries using electrodes based on transition metal oxides and phosphates cannot satisfy this demand in terms of specific energy. Elemental sulfur, abundant and nontoxic, has been considered to be one of the most promising cathode materials because of its high theoretical specific capacity (1675 mAh g⁻¹).^[1, 2] However, the practical application of Li-S batteries is still restricted by their inherent problems, including the insulating nature of S and the high solubility of polysulfide intermediates into the electrolyte.^[3, 4] Many strategies, such as coupling S with porous carbons or polar hosts, surface coating S and choosing suitable electrolytes, have been employed to trap sulfur species in the cathode side. ^[5, 6] Although improvements have been achieved, the applications of sulfur cathodes are still suffered by its intrinsically low electrical conductivity (5×10⁻²⁸ S m⁻¹) and limited long term cycling performance. Therefore, it is of great importance to explore new high-energy cathode materials, beyond the present S, with improved electronic conductivity

and cycling stability for efficient Li ion storage.

From this perspective, selenium and tellurium, the other two solid nonradioactive chalcogen element, have much higher electronic conductivity (Se: 1×10^{-3} S m⁻¹; Te: 2×10^{2} S m⁻¹ ¹) than S and comparable theoretical volumetric capacity (Se: 3240 mAh cm⁻³; Te: 2621 mAh cm⁻³) to S.^[7-9] It is also reported that Se and Te have higher utilization rate, better electrochemical activity and faster electrochemical reaction with Li than S.^[10-12] Nevertheless, Se and Te have much lower theoretical gravimetric capacity (Se: 675 mAh g⁻¹; Te: 419 mAh g⁻¹) as compared with S.^[13-15] The major stream of previous studies on these chalcogen-based cathode materials has focused on the structural design of S/Se/Te hosts, but molecular modification on the S/Se/Te-containing guests could be a new way to improve the performance of the Li-chalcogen batteries. Due to the above-mentioned opposite but complementary features among these chalcogen elements, heteroatomization of chalcogen molecules has been proposed as an attractive strategy to obtain advanced comprehensive Listorage performances. However, rational integration and design of the heteroatomic chalcogen molecules for advanced lithium-chalcogen batteries is still great challenging.

In addition to S/Se/Te hosts, the molecular structures and electronic features of the different chalcogen-chalcogen bonds in heteroatomic chalcogen molecules should be also critically important on the performances of chalcogen-based cathode materials. Heterocyclic Se_xS_y molecules with Se-S covalent bonds have been reported to possess higher specific capacities

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than Se alone, and improved conductivity and cycling stability compared to S alone.^[16-19] Qian et al.^[20] reported that introducing a small amount of Se into S molecules could anchor S during cycling, and thus effectively reduce the dissolution of polysulfides and shuttle effect. Similarly, a broad class of Se_xS_y cathode materials, such as SeS_2 ,^[21] $Se_{0.7}S$,^[22] $Se_{0.4}S_{0.6}^{\ \ [23]}$ and $Se_{2}S_{5}^{\ \ [24]}$ demonstrated greatly improved electrochemical performance. Recently, our group discovered that the $\mathsf{Se}_n\mathsf{S}_{8\text{-}n}$ cathodes exhibited unique electrochemical behavior rather than a simple hybrid of Li-S and Li-Se batteries.^[25] The selenium sulfide molecules are able to recover through the highly reversible conversion of polysulfoselenide intermediates during discharge-charge cycles. Density functional theory calculations (DFT) further reveal that heteroatomic selenium sulfide molecules with higher polarizability could bind more strongly with hosts than homoatomic sulfur molecules, which provides more efficient suppression of the shuttling phenomenon and improvement of electrochemical performance.

In this sense, tellurium has higher polarizability and conductivity than selenium.^[26-28] It is therefore rational to anticipate that the Te-S bonds with higher polarizability could enable heteroatomic Te_xS_y molecules to promise better lithium-chalcogen batteries. Herein, we demonstrate the heteroatomic Te_xS_{1-x} molecule with the highly heteropolar Te-S bond as an attractive cathode material in the commerical and electrolyte for the highlow-cost carbonate-based performance lithium battery. The Te_xS_{1-x} (x=0.05, 0.1 and 0.2) molecules were homogeneously confined in the ordered mesoporous carbons CMK-3 via a facile melt-impregnation route starting from elemental Te, S and CMK-3. Due to the introduction of Te atoms with higher p orbitals, the heteroatomic Te_xS_{1-x} molecules have higher intrinsic electrical conductivity than the homoatomic S₈ molecules. The Te-S bonds could strongly anchor S in the CMK-3 frameworks, and thus effectively reduce the formation and dissolution of polysulfides, which could be also favorable for the fast formation of stable electrode interfaces. Moreover, the Tecontaining polychalcogenide intermediates could induce the formation of solid electrolyte interphase (SEI) layers on the surfaces of Te_xS_{1-x}/CMk-3 electrodes, which further pretect polychalcogenides from dissolution and side reaction with carbonate-based electrolytes. Therefore, the Te_xS_{1-x}/CMK-3 composite with an optimal Te/S mole ratio exhibits excellent long-term cycling stability and high rate capability. These encouraging results suggest that the heteroatomization of chalcogen (such as S, Se, or Te) molecules in mesostructured carbon hosts is a promising strategy in enhancing the electrochemical performances of chalcogen/carbon-based cathodes for Li batteries.

Experimental section

Preparation of CMK-3

The CMK-3 was prepared by a nanocasting method as described in Nazar's paper.^[29] Typically, 1.25 g sucrose was

dissolved in 5.0 mL water containing 0.14 g concentrated H_2SO_4 . Then, 1.0 g SBA-15 was dispersed in the solution and sonicated for 1 h. The mixture was heated at 100 °C for 12 h and at 160 °C for another 12 h, followed by repetition of impregnation process once with another 5 mL aqueous solution containing 0.8 g sucrose and 0.09 g H_2SO_4 . The obtained dark brown intermediate product was completely carbonized at 900 °C for 5 h in an Ar flow. To remove the SBA-15 template, the carbonized product was stirred in a 5% HF solution for 4 h. The as-prepared CMK-3 was collected by centrifugation, repeatedly washed by distilled water and finally dried at 80 °C.

Preparation of the Te_xS_{1-x}/CMK-3 composites

The Te_xS_{1-x}/CMK-3 nanocomposites were prepared following a facile melt-diffusion strategy. In a typical synthesis procedure, 0.97 g sulfur (30.6 mmol) and 0.43 g tellurium (3.4 mmol) were mixed homogeneously. The mixture was degassed in a vessel and then sealed under vacuum, followed by heating at 550 °C for 4 h. The obtained Te-S solid solution was homogeneously mixed with 0.60 g CMK-3. The melt infiltration was further carried out in the vacuum-sealed vessel at 550 °C for 12 h. In this work, by controlling the composition of tellurium, sulfur and carbon in the precursors, three composites with different Te/S mole ratios and a fixed Te-S solid solution content (70 wt.%) were prepared, which were denoted as Te_xS_{1-x}/CMK-3, where x/(1-x) represented the Te/S mole ratios in the composites.

Material characterization

The thermogravimetric analysis (TA Instrument Q600 Analyzer) of samples was carried out in a nitrogen flow. The samples were heated to 800 °C with a rate of 10 °C min⁻¹. The surface chemistry of the samples was analysed using an Axis Ultra DLD X-ray photoelectron spectroscopy. The X-ray source operated at 15 kV and 10 mA. The working pressure was lower than 2×10^{-8} Torr (1Torr = 133.3 Pa). The C 1s, S 2p, Te 3d and Te 4s XPS spectra were measured at 0.1 eV step size. The binding energies were calibrated taking C 1s as a standard with a measured typical value of 284.6 eV. The S 2p, Te 3d and Te 4s XPS signals were fitted with mixed Lorentzian-Gaussian curves, and a Shirley function was used to subtract the background using a XPS peak processing software. The X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max 2550 diffractometer operating at 40 KV and 20 mA using Cu K α radiation (λ = 1.5406 Å). The FTIR analysis of the samples was carried out using a BRUKER-VERTEX 70 instrument with highsensitivity detector MCT. Nitrogen adsorption/desorption isotherms were measured at 77 K with a Quadrasorb SI analyser. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. The total pore volume was calculated using a single point at relative pressure of 0.985. The pore size distributions were derived from desorption branch by using the Barrett-Joyner-Halenda (BJH) model. The morphologies of samples were observed under scanning electron microscopy (SEM, JEOL 7100F) and transmission electron microscopy (TEM, JEOL 2100F). The scanning transmission electronic microscope (STEM) was conducted on a Tecnai G2 F30.

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Electrochemical tests

The Te_xS_{1-x}/CMK-3 samples were slurry-cast onto an aluminium current collector. Typically, 80 wt. % of Te_xS_{1-x}/CMK-3 sample, 10 wt. % carbon black (Super P Conductive Carbon Black) and 10 wt. % sodium alga acid (SA) binder were mixed in water solvent. The areal mass loadings of the Te_xS_{1-x}/CMK-3 samples were all controlled to be 2.5-2.9 mg cm⁻². The slurries were coated on aluminium current collectors and dried at 80 $^{\circ}\mathrm{C}$ overnight. Electrochemical tests of these electrode materials were performed using coin cells with the Te_xS_{1-x}/CMK-3 cathodes and lithium metal as the counter electrodes. The electrolyte was electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The separator was a microporous membrane (Celgard 2400). The cell was assembled in an argon filled glove box. The galvanostatic charge-discharge tests and cyclic voltammetry measurements (CV) were conducted using an Arbin battery cycler (Arbin, BT2000, USA). Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical working station PCI4/300 (Gamry Instrument, Warminster, PA, USA). The sinusoidal excitation voltage applied to the coin cells was 5 mV, with frequency range from 100 kHz to 0.01 Hz. All the electrochemical tests were performed at room temperature.

Result and discussion



Figure 1. SEM images of (a) CMK-3 and (b) $Te_{0.1}S_{0.9}/CMK-3$. STEM elemental mapping images of (c) $Te_{0.05}S_{0.95}/CMK-3$, (d) $Te_{0.1}S_{0.9}/CMK-3$ and (e) $Te_{0.2}S_{0.8}/CMK-3$. Inset in (a) is the magnified SEM image of CMK-3.

The Te_xS_{1-x}-based composites were prepared *via* a facile meltimpregnation method, in which the melt tellurium and sulfur were miscible with each other at 550 °C in the vacuum-sealed vessel and then infiltrated into the order mesopores of CMK-3 (The order mesoporous structure of CMK-3 is shown in Figure S1) during the heating procedure. In this way, the Te_xS_{1-x}/CMK-3 composites with different x value of 0.05, 0.1 and 0.2, as well as the S/CMK-3 and Te/CMK-3 composites, were obtained by tuning the mole ratio of Te to S in the mixed precursors. The total contents of Te and S in these composites were fixed at 70 wt. %. SEM images in Figure 1a-b display that the obtained composites still retain the short rod-like morphology of CMK-3 after Te and S loading. No Te_{0.1}S_{0.9} particle agglomerations were observed on the external surfaces of CMK-3, suggesting the Te_{0.1}S_{0.9} were well penetrated into the mesoporous channels of carbon hosts. There are no distinct differences between the XRD patterns of the Te_{0.1}S_{0.9} confined in the mesopores are very small nanocrystals or in an amorphous form. The relative ratios of Te to S and uniform distribution of Te and S in the Te_xS_{1-x}/CMK-3 composites can be further evidenced by STEM elemental mapping images in Figure 1c-e.



Figure 2. (a) Pore size distribution of CMK-3 (BET surface area=1110 m² g⁻¹, pore volume=1.3 cm³ g⁻¹) and Te_{0.1}S_{0.9}/CMK-3 (BET surface area=55 m² g⁻¹, pore volume=0.1 cm³ g⁻¹). (b) TGA and DTG curves of Te_{0.1}S_{0.9}/CMK-3, S/CMK-3 and Te/CMK-3.

The porous structures of the $Te_xS_{1-x}/CMk-3$ samples were analyzed by N₂ sorption. As shown in Figure 2a and S3, in comparison with the pristine CMK-3, the specific surface area and pore volume of the $Te_{0.1}S_{0.9}/CMk-3$ sample exhibit the demonstrating the expected decrease. successful incorporation of $Te_{0.1}S_{0.9}$ into the inner surface of the ordered mesoporous channels. TGA analysis in Figure 2b shows that all samples exhibit a weight loss of approximately 70 wt. % between 150 and 650 °C in a nitrogen flow, corresponding to the evaporation of Te and S during the heating process. Moreover, the Te_{0.1}S_{0.9} in the Te_{0.1}S_{0.9}/CMK-3 sample evaporates at a intermediate temperature between that of the Te/CMK-3 and S/CMK-3 samples, suggesting the possible existence of Te-S interaction in the $Te_{0.1}S_{0.9}/CMK-3$ sample.

It is known that heteroatomic Te_xS_{1-x} molecules with covalent Te-S bonds are formed in molten mixtures of Te and S at a high temperature.^[30-34] To confirm the presence of Te-S bonds in the Te_xS_{1-x}/CMk -3 composites, the high resolution X-ray photoelectron spectroscopy (XPS) analysis was conducted. As shown in Figure 3a, the Te/CMK-3 sample presents characteristic Te $3d_{5/2}$ and $3d_{3/2}$ peaks located at ~573.6 and ~584.0 eV for the Te-Te homopolar bond, accompanied by a doublet signal at ~576.5/~586.9 eV for the Te-O bond which could be originated from the oxidized Te on the surface of the sample. However, in addition to the Te-Te and Te-O bonds, a doublet peak at a intermediate binding energy of ~574.7/~585.1 eV, which corresponds to the Te-S heteropolar bond, was deconvoluted and curve-fitted in the Te_{0.1}S_{0.9}/CMk-3 sample. The existence of tellurium sulfide compounds in the

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 $Te_{0.1}S_{0.9}/CMk$ -3 sample was also evidenced by the S 2p XPS spectras in Figure S4.

To further reveal the reaction and phase transition in the Te-S mixtures during heating process based on the sulfurtellurium binary phase diagram (Figure S5), XRD analysis was employed. As shown in Figure 3b, all the diffraction peaks of the obtained bulk $Te_{0.1}S_{0.9}$ without the addition of CMK-3 are similar to the P2/c monoclinic phase of S₈, rather than the mixed precusors of the Fddd orthorhombic S₈ phase and the P3121 hexagonal Te phase. It has been known that the monoclinic phase (S₈) usually exists only at high temperatures (> 95.3 $^{\circ}$ C), and only the orthorhombic (S₈), rhombohedral (S₆) and hexagonal (S₈) phases are stable at room temperature.^[35] Therefore, it is deduced that the Te doping into S₈ molecules endow the monoclinic phase with improved roomtemperature stability. The obtained monoclinic Te_xS_{1-x} consists of 8-membered cyclic molecules, where the Te and S atoms appear to be struggling for the atomic positions. The possible crystal structure of the P2/c monoclinic phase Te_{0.1}S_{0.9} is shown in Figure 3c. Statistically, the struggle and occupation of Te and S over the whole molecules guarantee their uniform distribution in the final amorphous $Te_xS_{1-x}/CMK-3$ sample.



Figure 3. (a) High-resolution Te 3d XPS spectras of $Te_{0.1}S_{0.9}$ /CMK-3 and Te/CMK-3. (b) XRD patterns of the bulk Te, bulk S and as-prepared bulk $Te_{0.1}S_{0.9}$ without the addition of CMK-3. (c) Possible crystal structure of the monoclinic phase $Te_{0.1}S_{0.9}$ at different view orientations. The yellow and red balls in (c) represent the S and Te atoms, respectively.



The electrochemical properties of the $Te_xS_{1-x}/CMK-3$ (x=0.05, 0.1 and 0.2) composites were evaluated in the conventional carbonate-based electrolytes. We pay special attention to the integrated advantages of the heteroatomic Te_xS_{1-x}, in comparison with the homoatomic S_8 or Te_8 , confined in CMK-3 as cathode materials. As shown in the CV curves of the S/CMK-3 sample (Figure S6), no oxidation and reduction current peaks are observed after the first cathodic scanning. It is well known that such electrochemical incompatibility of the S/CMK-3 sample in the carbonate-based electrolytes should be due to the polysulfide consumption by an undesired chemical reaction with carbonates which occurs when the polysulfides into the electrolytes to form a single-phase dissolve solution.^[36, 37] However, for the $Te_{0.1}S_{0.9}/CMK-3$ sample (Figure 4a), in addition to two reduction peaks at 2.3 and 1.6 V in the first cathodic process, one intense oxidation peak at 2.0 V is also present in the subsequent anodic process, suggesting the high electrochemical reversibility of the Te_{0.1}S_{0.9}/CMK-3 sample in the carbonate-based electrolytes. It has been reported that polytellurides can also react with carbonates, but form the solid electrolyte interface (SEI) layers on the cathode surfaces.^[38, 39] Therefore, it is deduced that the high electrochemical reversibility of the $Te_{0.1}S_{0.9}/CMK-3$ sample should be owing to the Te-induced formation of SEI layers on the $Te_{0.1}S_{0.9}/CMK-3$ surfaces.

Density functional theory calculations (DFT) were conducted to calculate the binding energy of the carbons with Te-S containing species, as shown in Figure S7. It is revealed that the Te-S bonds could strongly anchor S in the CMK-3 frameworks and effectively reduce the formation and dissolution of polysulfides, which could be also favorable for the fast formation of stable electrode interfaces, as well as the SEI layers. In the CV curves of the Te_{0.1}S_{0.9}/CMK-3 sample (Figure 4a), the reduction peak at 2.3 V in the first cathodic process is corresponding to the conversion of $Te_{0,1}S_{0,9}$ to polysulfides, polytellurides and possible new intermediates of polysulfotellurides (Li₂Te_xS_y, $4 \le x + y \le 8$) generated by the disproportionate reactions in the Te-S system; the reduction peak at 1.6 V in the first cathodic process is attributed to the conversion of polysulfides/polytellurides/polysulfotellurides to Li₂S/Li₂Te. In the second and subsequent cycles of the $Te_{0.1}S_{0.9}/CMK-3$ sample, only one pronounced reduction and oxidation peaks centered at 1.8 V and 2.0 V, respectively, are clearly observed. Such one-step reduction and oxidation process is also observed for the sulfur encapsulated in the micropores where electrolyte solvent is deficient. $^{\left[40,\ 41\right] }$ It is indicated that the conversion process between Li₂S/Li₂Te and $Te_{0.1}S_{0.9}$ after the SEI coating is dominated by the one-step "quasi-solid-state" reaction mechanism which involves the desolvation of Li ions before migrating through the SEI layer. The overlapped redox onset potential after the first cycle promises the excellent electrochemical reversibility of the Te_{0.1}S_{0.9}/CMK-3 sample under the protection of the in-situ formed SEI layer, which prevent the polychalcogenides from shuttling and irreversibly reacting with the carbonates (Figure 4b).

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The discharge and charge properties of the Te_xS_{1-x}/CMK-3 (x=0.05, 0.1 and 0.2) composites in the carbonate-based electrolytes at a current density of 250 mA g⁻¹ were further investigated. As shown in Figure 5a and S8, two discharge plateaus and one charge plateaus are clearly observed in the first cycle for the $Te_xS_{1-x}/CMK-3$ samples. The electrochemical beheviors of the Te_xS_{1-x}/CMK-3 samples are different from that of the S/CMK-3 sample which no longer work after the first discharge, as shown in Figure 5b. These two discharge plateaus in the first cycle of the $Te_xS_{1\mbox{-}x}/CMK\mbox{-}3$ composites could be attributed to the formation of polysulfides, polytellurides and polysulfotellurides at 2.3 V, and the formation of Li₂S/Li₂Te at 1.6 V, respectively. The single voltage plateau in the second and subsequent cycles of the Te_xS_{1-x}/CMK-3 composites could be corresponding to the "quasi-solid-state" reaction path, which agrees well with the CV results. The initial discharge and charge capacities of the $Te_{0.1}S_{0.9}/CMK-3$ sample are 1250 and 989 mAh g⁻¹, respectively, corresponding to a large initial irreversible capacity of 261 mAh g⁻¹. Such large initial irreversible capacity should be due to the formation of the SEI layer through the irreversible reaction of carbonates with polytellurides and polysulfotellurides in the first cycle. In the second and third cycle, the Te_{0.1}S_{0.9}/CMK-3 sample still exhibits the high discharge capacities of 995 and 960 mAh g⁻¹, respectively, with the high coulombic efficiencies of 96.0% and 99.0%. These imply that the Te_xS_{1-x} molecules confined in the CMK-3 possess high electrochemical activity and reversibility after the formation of effective SEI layers on the electrode surfaces.



Figure 5. The charge-discharge curves of (a) $Te_{0.1}S_{0.9}/CMK\text{-}3$ and (b) S/CMK-3 at 250 mA $g^{-1}.$



Figure 6. (a) The survey XPS spectras of the fresh and cycled $Te_{0.1}S_{0.9}/CMK-3$ electrode (after 1 cycle at 3.0 V). (b) EIS of the fresh and cycled $Te_{0.1}S_{0.9}/CMK-3$ electrode. (c) TEM and (d) STEM elemental mapping images of the cycled $Te_{0.1}S_{0.9}/CMK-3$ electrode.

The Te-induced formation of the SEI layer on the Te_xS₁₋ x/CMK-3 surface in the carbonate-based electrolyte, was further demonstrated by the survey XPS spectra of the $Te_{0.1}S_{0.9}$ /CMK-3 electrode after the first discharge-charge cycle at 3.0 V. As shown in Figure 6a, the Na XPS peak in both the fresh and the cycled $Te_{0.1}S_{0.9}/CMK-3$ electrodes is resulted from the sodium alginate binder. Compared with the fresh electrode, the obviously increased O content and the presence of strong F XPS peak in the cycled electrode, further prove the formation of the SEI layer with the F/O-containing components on the cycled Te_{0.1}S_{0.9}/CMK-3 surface. The chemical composition of the SEI layer on the cycled Te_{0.1}S_{0.9}/CMK-3 surface is further revealed by the FTIR spectra in Figure S9. The TEM and STEM elemental mapping images (Figure 6c-d) of the cycled Te_{0.1}S_{0.9}/CMK-3 electrode show that the amorphous SEI layer with a thickness of ~ 10 nm is coated on the $Te_{0.1}S_{0.9}$ /CMK-3 surface. Furthermore, the existence of charge transfer resistance of the SEI layer on the cycled Te_{0.1}S_{0.9}/CMK-3 electrode is confirmed by the EIS analysis, as shown in Figure 6b. Instead of the only one semicircle in the EIS spectra of the fresh electrode, two depressed semicircles were observed for the cycled Te_{0.1}S_{0.9}/CMK-3 electrode, suggesting the "two RC parallel circuits"-typed electrochemical impedance behavior of the cycled $Te_{0.1}S_{0.9}/CMK-3$ electrode. The semicircles of the high- and middle-frequency ranges in the EIS spectra of the Te_{0.1}S_{0.9}/CMK-3 electrode are corresponding to the charge transfer resistances of the SEI layer and the electrode material, respectively. The overlapped EIS spectras of the Te_{0.1}S_{0.9}/CMK-3 electrode after varied cycles further confirm the formed SEI layer is highly stable on the $Te_{0.1}S_{0.9}/CMK$ -3 surface. The stable SEI layer combined with the CMK-3 framework could effectively prevent the polysulfides/polytellurides/polysulfotellurides from dissolving and irreversibly reacting with the carbonate-based electrolyte,

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which is expected to improve the cycling stability of the Te_xS_{1-}

,/CMK-3 electrode.

Figure 7. (a) Cycling performance of $Te_xS_{1,x}/CMK-3$ (n = 0.05, 0.1 and 0.2) at 250 mA g⁻¹. (b) Rate performances of $Te_xS_{1,x}/CMK-3$ at different current densities. (c) Long-term cycling performance of $Te_xS_{1,x}/CMK-3$ at 1 and 3 A g⁻¹. Inset in (a) shows the coulombic efficiency of $Te_{0.1}S_{0.9}/CMK-3$ at 250 mA g⁻¹.

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The cycle performances of the $Te_xS_{1-x}/CMK-3$ (x=0.05, 0.1 and 0.2), S/CMK-3 and Te/CMK-3 composites in the carbonatebased electrolyte at 250 mA g⁻¹ are compared in Figure 7 and S10. The Te_{0.1}S_{0.9}/CMK-3 sample exhibits the best electrochemical performance with the highest reversible capacity of 845 mAh g⁻¹ after 100 cycles (Figure 7a). A high coulombic efficiency of 99.6% is also obtained for the $Te_{0.1}S_{0.9}/CMK-3$ sample after 100 cycles (Inset of Figure 7a), revealing the diminished shuttle effect and side reaction between polychalcogenides and carbonate-based electrolytes. The cycling of the $Te_{0.1}S_{0.9}/CMK-3$ sample is also quite stable at the higher rates of 1 and 3 A g⁻¹, with stable capacities of 485 and 387 mAh g^{-1} achieved after 500 cycles (Figure 7c). When the reversible capacity, the initial coulombic efficiency, the Te/Se/S loading and the used electrolyte are all considered, the electrochemical performance of the Te_{0.1}S_{0.9}/CMK-3 sample is among the best series of chalcogen-based cathode materials in the commerical and low cost carbonate-based electrolyte (as listed in Table S1). In addition, the expected decline in the specific capacity is found by increasing the Te/S mole ratio from 1/9 to 2/8 in the Te_xS_{1-x}/CMK -3 composites, undoubtedly due to the limitation of the theoretical capacity, as shown in Figure S11. The Te_{0.1}S_{0.9}/CMK-3 sample also presents excellent cycling response to continuously varying current densities from 0.25 to 5 A g^{-1} , as shown in Figure 7b. Even at the maximum current density of 5 A g^{-1} , the highest rate capacity of 590 mAh g^{-1} is obtained for the Te_{0.1}S_{0.9}/CMK-3 sample after 70 cycles. The outstanding kinetic behavior should be attributed to the improved electronic transport characteristics of the $Te_{0.1}S_{0.9}/CMK-3$ sample, which could be further supported by their relatively low charge transfer resistances from the EIS results (Figure S12). Such high electrochemical activity and reversibility of the Te_{0.1}S_{0.9}/CMK-3 sample further confirm the synergistic effects of the protection of SEI layers, the confinement of mesopores and the heteroatomization of Te_xS_y molecules.

Conclusions

In conclusion, we sucessfully fabricate a mixed Te-S cathode materials for high-energy lithium batteries by homogeneously confining heteroatomic Te_xS_{1-x} molecules into CMK-3 via a facile melt-impregnation route starting from elemental Te, S and CMK-3. The highly heteropolar Te-S bonds existing in the Te_xS_{1-x} compounds and its possible impact on electrochemical behaviors of the Te_xS_{1-x} cathodes in the conversional carbonate-based electrolytes were revealed by ex-situ characterization and electrochemical tests. The obtained Te_{0.1}S_{0.9}/CMK-3 composite exhibits excellent overall electrochemical performance, which could be due to: (1) the great capacity contribution by S component; (2) the improved conductivity and reaction kinetics by introducing Te component; (3) the mesopore confinement of CMK-3; (4) the enhanced immobilization of S by the Te-S bonds, which effectively reduce the formation of polysulfides and stabilize the electrode interfaces, and (5) the Te-induced formation of SEI layers on the electrode surfaces, which further prevents

polychalcogenides from dissolution and irreversible reaction with carbonates. As Te and S are infinitely miscible, with many readily available solid solutions, the heteroatomic Te_xS_y -based cathodes represent a broad class of battery electrodes, which could pave the way for promising opportunities to enable high energy batteries for transportation and grid applications.

Conflicts of interest

There are no conflicts to declare.

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References

- H. Pan, J. Chen, R. Cao, V. Murugesan, N. N. Rajput, K. S. Han, K. Persson, L. Estevez, M. H. Engelhard, J. Zhang, K. T. Mueller, Y. Cui, Y. Shao and J. Liu, *Nat. Energy*, 2017, 2, 813.
- 2 M. J. Klein, G. M. Veith and A. Manthiram, J. Am. Chem. Soc., 2017, **139**, 9229.
- 3 H. Peng, J. Huang, X. Cheng and Q. Zhang, Adv. Energy Mater., 2017, 7, 1700260.
- 4 J. H. Kim, G. Y. Jung, Y. H. Lee, J. H. Kim, S. Y. Lee, S. K. Kwak and S. Y. Lee, *Nano Lett.*, 2017, **17**, 2220.
- 5 H. Peng, J. Huang and Q. Zhang, *Chem. Soc. Rev.*, 2017, **46**, 5237.
- 6 T. Lei, W. Chen, J. Huang, C. Yan, H. Sun, C. Wang, W. Zhang, Y. Li and J. Xiong, *Adv. Energy Mater.*, 2017, **7**, 1601843.
- 7 J. Zhang, Y. Yin, Y. You, Y. Yan and Y. Guo. *Energy Technol.*, 2014, **2**, 757.
- 8 J. U. Seo, G. K. Seong and C. M. Park, Sci. Rep., 2015, 5, 7969.
- 9 K. Eom, J. T. Lee, M. Oschatz, F. Wu, S. Kaskel, G. Yushin and T. F. Fuller, *Nat. Commun.*, 2017, 8, 13888.
- 10 J.He, Y. Chen, W. Lv, K. Wen, Z. Wang, W. Zhang, Y. Li, W. Qin and W. He, ACS Nano, 2016, **10**, 8837.
- 11 C. P. Yang, S. Xin, Y. X. Yin, H. Ye, J. Zhang and Y. G. Guo, *Angew. Chem. Int. Ed.*, 2013, **52**, 8363.
- 12 S. Xin, L. Yu, Y. You, H. Cong, Y. Yin, X. Du, Y. Guo, S. Yu, Y. Cui and J. B. Goodenough, *Nano Lett.*, 2016, **16**, 4560.
- 13 J. Xu, S. Xin, J. W. Liu, J. L. Wang, Y. Lei and S. H. Yu, *Adv. Funct. Mater.*, 2016, **26**, 3580.
- 14 Q. Li, H. Liu, Z. Yao, J. Cheng, T. Li, Y. Li, C. Wolverton, J. Wu and V. P. Dravid, *ACS Nano*, 2016, **10**, 8788.
- 15 Y. Zhou, Z. Li and Y. Lu, Nano Energy, 2017, 39, 554.
- 16 Z. Li, J. Zhang, H. Wu and X. W. Lou, Adv. Energy Mater., 2017, 7, 1700281.
- 17 G. Xu, J. Liu, R. Amine, Z. Chen and K. Amine, ACS Energy Lett., 2017, 2, 605.
- 18 J. Zhou, T. Qian, N. Xu, M. Wang, X. Ni, X. Liu, X. Shen and C. Yan, Adv. Mater., 2017, 29, 1701294.
- 19 A. Abouimrane, D. Dambournet, K. W. Chapman, P. J. Chupas, W. Weng and K. Amine, J. Am. Chem. Soc., 2012, 134, 4505.
- 20 X. Li, J. Liang, K. Zhang, Z. Hou, W. Zhang, Y. Zhu and Y. Qian, *Energy Environ. Sci.*, 2015, **8**, 3181.
- 21 J. Zhang, Z. Li and X. W. Lou, Angew. Chem. Int. Ed., 2017, 56, 14107.

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- 22 C. Luo, Y. Zhu, Y. Wen, J. Wang and C. Wang, Adv. Funct. Mater., 2014, 24, 4082.
- 23 Y. Yao, L. Zeng, S. Hu, Y. Jiang, B. Yuan and Y. Yu, *small*, 2017, **13**, 1603513.
- 24 G. Xu, T. Ma, C. Sun, C. Luo, L. Cheng, Y. Ren, S. M. Heald, C. Wang, L. Curtiss, J. Wen, D. J. Miller, T. Li, X. Zuo, V. Petkov, Z. Chen and K. Amine, *Nano Lett.*, 2016, **16**, 2663.
- 25 F. Sun, H. Cheng, J. Chen, N. Zheng, Y. Li and J. Shi, ACS Nano, 2016, **10**, 8289.
- 26 N. Ding, S. Chen, D. S. Geng, S. W. Chien, T. An, T. S. A. Hor, Z. Liu , S. Yu and Y. Zong, *Adv. Energy Mater.*, 2015, 5, 1401999.
- 27 L. L. Hawes, *Nature*, 1963, **198**, 1267.
- 28 X. Ji, K. T. Lee and L. F. Nazar, Nat. Mater., 2009, 8, 500.
- 29 K. Xu, X. Liu, J. Liang, J. Cai, K. Zhang, Y. Lu, X. Wu, M. Zhu, Y. Liu, Y. Zhu, G. Wang, and Y. Qian, ACS Energy Lett., 2018, 3, 420.
- 30 R. S. Laitinen and P. Pekonen, *Coordin. Chem. Rev.*, 1994, **130**, 1.
- 31 J. Taavitsainen and R. Laitinen, *Main Group Chem.*, 1999, **3**, 59.
- 32 T. Chivers, R. S. Laitinen, K. J. Schmidt and J. Taavitsainen, Inorg. Chem., 1993, **32**, 337.
- 33 M. V. Coul et, R. Bellissent and C. Bichara, J. Phys.: Condens. Matter., 2006, 18, 11471.
- 34 C. H. W. Jones and M. Mauguin, J. Chem. Phys., 1977, 67, 1587.
- 35 S. Moon, Y. H. Jung, W. K. Jung, D. S. Jung, J. W. Choi and D. K. Kim, Adv. Mater., 2013, 25, 6547.
- 36 J. Gao, M. A. Lowe, Y. Kiya and H. D. Abruna, J. Phys. Chem. C, 2011, 115, 25132.
- 37 T.Yim, M.S.Park, J.S.Yu, K. J. Kim, K. Yung. Im, J. H. Kim, G. Jeong, Y. Nam Jo, Sang. G. Woo, K. S. Kang, I. Lee and Y. J. Kim, *Electrochim. Acta.*, 2013, **107**, 454.
- 38 Y. Liu, J. Wang, Y. Xu, Y. Zhu, D. Bigiob and C. Wang, *J. Mater. Chem. A*, 2014, **2**, 12201.
- 39 T. Koketsu, B. Paul, C. Wu, R. Kraehnert, Y. Huang and P. Strasser, J. Appl. Electrochem., 2016, 46, 627.
- 40 E. Markevich, G. Salitra, Y. Talyosef, F. Chesneau and D. Aurbacha, J. Electrochem. Soc., 2017, **164**, A6244.
- 41 Z.Li, L.Yuan, Z. Yi, Y. Sun, Y. Liu, Y. Jiang, Y. Shen, Y. Xin, Z. Zhang and Y. Huang, *Adv. Energy Mater.*, 2014, **4**, 1301473.

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A stable cathode material in a conventional carbonate-based electrolyte was successfully fabricated by homogeneously confining heteroatomic Te_xS_{1-x} molecules into CMK-3.