**Single-atom tailoring of Li2S to Form Li2S2 for building better lithium-sulfur batteries**

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**Abstract**

The Li2S-based cathodes to couple with Li-free anodes are regarded as a commercially available approach to overcome the safety risk of lithium metal anodes. However, the passivated Li2S instinct leads to a high activation potential in the initial charging process, and the notorious shuttle effect of polysulfide is inevitable upon cell cycling. Here we create a single atom tailoring strategy by comproportionation reactions (Li2S + S = Li2S2) to from the liquid Li2S2 catholyte, where the Li2S2 cell enables a lower potential barrier and allows for the 3.0 V activation voltage without any other material modification. Meanwhile, the polar conducting material TaB2 is introduced to restrain the migration of polysulfides and provide fast redox reaction kinetics. With those ingenious tailoring of cell designs, the Li2S2-TaB2 cell (Li2S2 content of 91 wt%) exhibits stable capacity (initial capacity of 597 mAh/g at 4 mg/cm2 Li2S2 loading), excellent cycling stability (500 cycles at 2.4 mA/cm2).

**Introduction**

Lithium sulfide (Li2S) is a promising candidate to use as the Li-containing cathode in lithium-sulfur (Li-S) batteries, which can couple with Li-free anode with more practical safety performances to evade the problematic pure Li metal anode. Meanwhile, the Li2S has the advantages of higher melting point (938 oC) and lower density (1.66 g/cm3) which is better than those of S8 (115 oC and 2.07 g/cm3, respectively). The better thermal ability (up to 800 °C) of Li2S are favored with the application fields of Li-S battery, including firefighting robots, space exploration and high temperature sensor…which are however impossible in the S8-based Li-S cells. Unfortunately, the application of the Li2S cathode suffers from several issues which are an enormous overpotential barrier, poor utilization of material, and shuttle effect of polysulfide and so on. Studies have revealed that particle size tailoring may greatly help to improve the above problems, for example, mechanical milling, structural designing and solvated strategy of Li2S, hyperthermal reduction of Li2SO4, and redox mediator of additive, further to low the overpotential of Li2S, optimize reaction kinetics, and restrain migration of polysulfide. However, these modified strategies either increase the additional assembly processes of batteries, or add non-commercial additives, or require materials which is sensitive for H2O/O2. Accordingly, a novel strategy is attractive to develop a facile method powering the performance of commercially available Li2S particles with micron size.

Ionic crystal Li2S has a highly stable instinct of antifluorite structure which is consists of stronger bond energy with the higher standard enthalpy of formation, causing it is far from the cyclic molecular structure of elemental S8. In the first charge stage, the micron-sized Li2S cathode has nearly 0 mAh/g capacity in the 1.7-2.8 V, which is the normal voltage range of Li-S cells. After a higher working potential activating (up 4.0 V vs Li+/Li), the surface small particles of bulk Li2S are delithiated to form the solvated polysulfides (Li2S2), and those polysulfides generate more nucleation sites by the comproportionation reactions, and finally to complete the bulk Li2S activation process. The activation potential of Li-S cell does charge up to 4.0 V (even over 3.0 V) which can cause electrolyte decomposition, poor cycle performance, and low Coulombic efficiency. Therefore, the synthesis of Li2S2, replacing the Li2S, is supposed to completely solve the poor ionic/electronic conductivity of Li2S. According to density-functional theory, Li2S2 is a semiconductor with an energy gap of 1.8 eV, which is much smaller than 3.5 eV of Li2S, indicating the available intrinsic charge carriers of Li2S2 are more than that of Li2S in an order of magnitude difference. Unfortunately, the Li2S2 has been isolated from Li-S batteries due to the high difficulty and challenge in synthesis.

Herein, we create a single atom tailoring approach that offers an effective strategy to reconstitute the molecular structure of commercial Li2Sand to form high activity of Li2S2 without high temperature, complex/sensitive additions. The liquid Li2S2 catholyte is prepared via comproportionation reactions which is a simple mixed method of commercially available solutions (ethanol/carbon disulfide) and particles (Li2S/S8). By taking advantage of the high electrochemical activity of Li2S2, Li-S cell shows a little potential barrier after only 3.0 V charging voltage. For the shuttle effect of polysulfide, the polar conducting material TaB2 promotes the anchoring effect and enhances the conversion of polysulfides, rendering accelerated redox reaction in the cell cycling. Attributed to these features, the Li2S2-TaB2 cathodes exhibit stable capacity (about 500 mAh/g at 2.4 mA/cm2), excellent cycling stability (500 cycles), remarkable sulfur loading (4.0 mg/cm2), high-rate capability up to 5.0 mA/cm2.

**Results and discussion**

The host material of polysulfide is analyzed, and X-ray diffraction (XRD) pattern in Fig. 1a verifies the successful formation of TaB2. The sharp Bragg’s peaks imply its high crystallinity and indicate hexagonal phase of TaB2 (JCPDS No. 38-1462, P6/mmm, standard a = b = 0.3098 nm, c = 0.3227 nm). Furthermore, X-ray photoelectron spectroscopy (XPS) illustrates the surface state of the TaB2, and the spectrums of Ta 4*f* and B 1*s* are shown in Fig. 1b and 1c, respectively. Among the four deconvolution peaks show in Fig. 1b, four peaks are corresponding to Ta4+ and Ta5+ states, and come from the intrinsic structure of TaB2. The deconvoluting peaks of B 1*s* spectrums are matched with the results of Ta 4*f* spectrums. Those multi-chemical bonds (Ta4+/Ta5+) can offer more interfacial multi-actives for guiding powered the nucleation and growth of Li2S2/Li2S, and then to enhance the complicated 16-electron transfer/nontransfer-based multiphase evolution processes (solid S8/liquid polysulfides/solid Li2S). In the following, the scanning electron microscopy (SEM) images (Fig. 1d with inset) and transmission electron microscopy (TEM) image (Fig. 1e) show morphology of TaB2 materials, which is consisted of hexagonal sheets. The selected area electron diffraction (SAED) of TaB2 (inset of Fig. 1e) shows a highly crystalized structure which can enhance redox reaction kinetics via overcoming trap/defect in the electrode transfer processes. Next, high-resolution transmission electron microscopy (HRTEM) image (Fig. 1f) shows 0.206 nm of lattice distance, corresponding to the XRD analysis of TaB2 (JCPDS No. 38-1462). The high-angle annular dark-field imaging (HADDF-TEM) image (Fig. S1a) focus on one individual TaB2 material and illustrates the spatial correlation between Ta and B atoms (Fig. S1b-c). The density of state (DOS) of density-functional theory (DFT) describes TaB2 electron orbital states with spin polarization (spin up/down), containing Ta/B orbits (Fig. 1g). The continuous DOS emerging at the Fermi level indicates that TaB2 exhibits metallic behavior, which is dominated by a strong hybridization of B and Ta orbitals. The Fermi surface comes from an ionic bond or from the covalent hybridization in which interactions between Ta and B states near the Fermi level give rise to the high electrical conductivity in TaB2. Meanwhile, the electron location function (ELF) is applied to analyze states of electron cloud distribution at (101) planes of Ta/B atoms (Fig. 1h). The perfect electron localization (lone-pair/covalent electrons), uniform electron density, and electron-deficient state represent 1.0, 0.5 and 0, respectively. When electron transfers between Ta/B atoms of (101) planes (Fig. 1i), most of the area of ELF is around by 0.5, which is beneficial for electrons transfer through such a uniform electron cloud state. Also, the crystal structure and electron location function of TaB2 at (001) and (100) planes are given in Fig. S2.

To demonstrate chemical conversion of liquid Li2S2, those different dissolved strategies are compared with each other for visual inspection. To achieve so, the solid reactants are added in different solutions with 1 min shaking, and then observe for visual inspection. It can be seen in the Fig. 2a, the solid Li2S (46 mg) and S8 (32 mg) are not dissolved in CS2 (1.56 ml), and partially dissolved in C2H5OH (1.56 ml), respectively. In the mixed solution of CS2 (0.16 ml) and C2H5OH (1.40 ml), the Li2S (46 mg) and S8 (32 mg) can completely dissolve in them where the comproportionation reaction of chemical equation is 8Li2S + S8 = 8Li2S2. Furthermore, the electrochemical performances of TaB2-based Li2S2 cells are investigated. Fig. 2b depicts the cyclic voltammetry (CV) profiles of TaB2-based Li2S2 cell in the potential range of 1.5-3.0 V versus Li+/Li at a scan rate of 0.2 mV/s. The CV curve shows a pronounced cathodic peak centered at 2.4 V, and the broad anodic peaks between 1.8 and 2.8 V. Interestingly, the Li2S2 cells own lower cathodic peak comparing with bulk Li2S cells, revealing the Li2S2 cells have better reaction kinetics to low energy barrier of conversion by the reconstruction of molecular structure. Next, the cycling performances of TaB2-based Li2S2 cells are shown in Fig. 2c. When the cells are activated to 3.0 or 4.0 V with the current density of 2.4 mA/cm2, those cells (S loading: 2.0 mg/cm2) exhibit a stable capacity of 598 or 572 mAh/g, maintain 445 or 439 mAh/g after 500 cycles with Coulombic efficiency of over 99 %, respectively (Fig. 2c). The electrochemical behavior of Li2S2 on the galvanostatic first-charge voltage profile is shown in Fig. 2d. During the 3.0 or 4.0 V activating, those Li2S2 cells both have little initial overpotential peaks in which Li2S2 is a semiconductor, and *p*-orbits coming from the S22- ions optimize electronic properties to maintain a high concentration of polysulfides, and further enhance themselves comproportionation reaction. Also, the corresponding discharge curve reveals two-stage electrochemical reactions (Fig. 2e), where the first discharge plateau shows the high-order polysulfide conversion (∆C1: S8 to Li2S4), and the second plateau represents low-order polysulfide conversion (∆C2: Li2S4 to Li2S2/Li2S). After 3.0 V of first charge voltage (Fig. 2f), those ratios of (ΔC2)/(ΔC1+ΔC2) shows 65, 68 and 66 %, the ratios of ΔC2/ΔC1 display 1.9, 2.0 and 1.9 which are corresponding to the 10, 250 and 500 cycling with 2.4 mA/cm2, respectively. When the first charge voltage rises to 4.0 V, the ratios of (ΔC2)/(ΔC1+ΔC2) are 66, 67 and 65 %, and the ratios of ΔC2/ΔC1 reveal 1.9, 2.0 and 1.9 which belongs to the 10, 250 and 500 cycling with 2.4 mA/cm2, respectively. In the ΔC2 processes of liquid-solid redox reaction (Li2S4 to Li2S2/Li2S), sluggish two-phase evolution and solid-state diffusion barrier both cause the migration of polysulfides cannot be avoided. In the TaB2-based Li2S2 cells, these values of (ΔC2)/(ΔC1+ΔC2) are around by 2.0 after 3.0/4.0 V activation, which shows an effective contribution to the ΔC2 capacity, and a stable utilization of Li2S4 in the Li-S cell cycling. To demonstrate the application potential of the TaB2-based Li2S2 cell, the high sulfur loading cell are prepared (Fig. 2g). Under the 4.0 mg/cm2 sulfur and 2.4 mA/cm2 (3.0 V charging), TaB2-based Li2S2 cell exerts 597 mAh/g, maintains 328 mAh/g after 500 cycles with 99 % Coulombic efficiency. The performances of similar Li-S cells in the literatures are outlined in Table S1. Those TaB2-based Li2S2 cells shows a better performance than other reported other electrodes in the Li-S cells in which TaB2 materials offer efficient electron conduction and strong chemical/physical confinement to optimize reaction kinetics and suppress shuttle effect of polysulfides. The rate performances and corresponding charge-discharge profiles are displayed in Fig. 2h-i. With further cycling at 1.0, 2.0, 3.0, 4.0 and 5.0 mA/cm2, the TaB2-based Li2S2 cells presents reversible capacities of 640, 580, 480, 430 and 408 mAh/g, respectively. Fig. 2i shows charge/discharge voltage curves in the Li-S cell cycling. Two clear plateaus are corresponded to S8 to polysulfides and to Li2S2/Li2S in the discharging curve, and the one plateau of charging stage exhibits the oxidation process from Li2S2/Li2S to S8.

Furthermore, the redox reaction behaviors of TaB2-based Li2S2 cells are investigated by cyclic voltammetry (CV). Two reduction peaks come from the reduction of sulfur (S8) into polysulfides and subsequent transition into Li2S2/Li2S. The corresponding one oxidation peak demonstrates one-step oxidation of Li2S2/Li2S (Fig. 3a). By the rated scanning from 0.2 to 1.0 mV/s, the increased redox peak positions are ordered polarization, where the corresponding peak currents with the square root of the scan rate reveals a linear relationship (Fig. 3b). In addition, Randles-Sevcik equation (*I*p = 2.69 x 105*n*1/2 *A* *D*Li1/2 *V*Li1/2 *C*Li) is carried out to analyze the diffusion coefficient of lithium ions (*D*Li+), where *I*p is the current maximum, *A* is the electrode area, *N* is the number of transferred electrons, *D* is the diffusion coefficient, *C* is the concentration, and *V* is the scan rate. The diffusion coefficient of *D*Li+ shows a linear relationship with *I*p to further indicate the stable redox reactions between S8 and Li2S2/Li2S in the TaB2-based Li2S2 cells. Next, electrochemical impedance spectroscopy (EIS) of Nyquist plots can accurately explain the internal electrochemical characteristics of TaB2-based Li2S2 cells (Fig. 3c). The first semicircles are the resistance (RSEI) of solid electrolyte interface (SEI) layer in the high frequency area and generated by the decomposition of the electrolyte. The second semicircles (Rct) of Nyquist reflect electrochemical reaction kinetics which involves the interface change, phase evolution/transition, material structure/size transition. The Warburg impedance (Zw) is directly linked to the diffusion of lithium ions in the low-frequency area. Those slightly shifts of RSEI/Rct/Zw values suggest better electrolyte infiltration with fast charge transport in the TaB2-based Li2S2 cells after 250 and 500 cycles. To analyze the interrelation between the cathode interface and polysulfides, the XPS is applied to further analyze the factors which can power the electrochemical properties of TaB2-based Li2S2 electrodes. The XPS spectra (Fig. 3d-f) demonstrate major elements in the electrodes where one run 1 time (1st) and another run 500 times (500th) after aged time. Fig. 3d shows six characteristic peaks of S 2*p* around by 172-160 eV. Those Ta-Sx peaks exist in the 1st and 500th cycling, which indicates a stable anchoring for the efficient electron transport and enhanced redox reactions on the TaB2 surface. The peaks of LiTFSI salt (bis-trifluoromethane sulfonimide lithium salt) and polysulfides could be from the S=O/S–N bonds and residual sulfur molecules during the Li-S cell working. The peaks of XPS Ta 4*f* are nearby 20-40 eV (Fig. 3e), where the obtained Ta5+-S and Ta4+-S peaks are resulting from the interfacial interactions between Ta sites and polysulfides, while the Ta5+ and Ta4+ peaks are assigned to the intrinsic TaB2 in agreement with the standard XPS data. Fig. 3f shows four characteristic peaks of B 1*s* approximately 180-196 eV, the Ta5+-B-Li, Ta4+-B-Li, Ta5+-B, and Ta4+-B bindings also matched with the S 2*p* and Ta 4*f* results.

In order to better understand the interplay between polysulfides and TaB2, first principle calculations are carried out using the Vienna *ab Initio* Simulation Package (VASP). Those adsorption behaviors of polysulfides, including Li2S8, Li2S6, Li2S4, Li2S2, and Li2S, are explored on the most stable configuration of the TaB2 (101) and (001) surface, which are more commonly obtained. The adsorption energy (*E*ads) is calculated by *E*ads = *E*total - *E*sub - *E*Li-S, where *E*total are the total energies of the whole system, *E*sub are the total energies of the substrate, and *E*Li-S are the total energies of molecular clusters of Li2S8, Li2S6, Li2S4, Li2S2 or Li2S, respectively. Electronic structure methods allow directly studying the chemical transformations in molecular systems involving breaking and making of chemical bonds and the associated changes in the electronic structure. Under the circumstances, negative *E*ads suggests stronger adsorption capability in which polysulfides can be adsorbed on the substrate steadily (Fig. 4a). Those *E*ads of those polysulfides on the TaB2 (101) surface are extraordinarily negative (-7.57 eV for Li2S8, -6.31 eV for Li2S6, -9.92 eV for Li2S4, -5.85 eV for Li2S2 and -5.31 eV for Li2S, respectively). For comparison, those *E*ads of Li2S8, Li2S6, Li2S4, Li2S2, and Li2S cluster on the TaB2 (001) surface are calculated to be -1.59, -4.53, -5.11, -5.38 and -6.37 eV, respectively, where the charge density difference for the most stable adsorption configurations of Li2S8, Li2S6, Li2S4, Li2S2 and Li2S molecules on TaB2 (101) and (001) facets are shown in the Fig. S3 and Fig. S4, respectively. Those results of the *E*ads ensure an effectively reversible polysulfides adsorption-conversion process, to further restrain migration and accelerate conversion kinetics of polysulfides in Li-S cell running. Furthermore, the interactional relationship between the electronic state and chemical bonding can be analyzed by the crystal orbital Hamilton population (COHP) analysis, which can offer the quantifying the bond strength by computing Hamilton-weighted populations of localized atomic orbitals. The high soluble Li2S4 molecule is regarded as a challenging candidate of polysulfides, and the TaB2 (101) and (001) surfaces also are taken as an adsorbed substrate (Fig. 4d-e). When Li2S4 on the (101) surface, the areas of anti-bonding states (orange) and bonding states (blue) are 0.24 and 0.25, respectively. When Li2S4 on the (001) surface, the areas of anti-bonding states and bonding states are 2.83 and 2.59, respectively. Integrating the COHP (ICOHP) of Li2S4 adsorbed (101) surface (-8.08 eV) has a more negative value than (001) surface (-6.36 eV), which indicates a stronger covalent interaction between Li2S4 and TaB2, and further benefits the adsorption of intermediate Li2S4 and decreases of the potential barrier of redox reactions. Moreover, the density of states (DOS) is employed to confirm and visualize different types of bonding in the Li2S4 adsorbs on the TaB2 (101) and (001) surface. For the intrinsic Li2S4, the gap of Fermi level is about 2 eV (Fig. 4d) where S(Li2S4) 2*p* orbital have dominantly contributed to the highest occupied molecular orbital (HOMO), and Li(Li2S4) 1*s* orbital constitutes the lowest unoccupied molecular orbital (LUMO). When Li2S4 adsorbs on the TaB2 (101) surface (Li2S4-TaB2), Ta/B atoms have strong interaction with Li/S atoms nearby 3.5, -3 and -5 eV which is overlapping of 3*d*(Ta), 2*p*(B), 1*s*(Li) and 2*p*(S) orbitals (Fig. 4d). Around the 3.5, -3 and -5 eV, Ta/B atoms also have strong interaction with Li/S atoms by the overlapping of 2*p*(B), 1*s*(Li) and 2*p*(S) orbitals in the Li2S4 adsorbs on the TaB2 (001) surface (Fig. 4e). Above DFT calculations strongly support experimental observations, and polar conducting material TaB2 can efficiently restrain shuttle effect of polysulfides.

**Conclusion**

In summary, liquid Li2S2 is proposed to activate redox reaction without the potential barrier of intrinsic Li2S. Benefit from carbon disulfide/ethanol cosolvent strategy, the liquid Li2S2 directly drips into the electrode without any complex manufacturing process and/or non-commercial additives where this facile preparation is suitable for the currently commercially available. The TaB2-based Li2S2 cathode exhibits large specific capacity, impressive rate capability, and excellent cycling stability even at high sulfur loading. More importantly, our results present tailored engineering of molecular formula that can offer a new viewpoint to prepare high performance and commercialized Li-S batteries.

**Supplementary material**

Supplementary data associated with this article can be found in the online version at DOI…

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Authorship contribution statements**

Chang Liu and Yuwei Zhao conceived the project supervised by Chenyang Zha. Shuo Wang conducted theoretical calculation supervised by Kwun Nam Hui. Chongguang Lyu carried out SEM characterizations. Rong Wu, Jianglu Xiang, Kwan San Hui and Junfeng Li assisted in data analysis. All authors participated in the discussion of the manuscript.

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**Figure**

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**Fig. 1.** XRD pattern (a) of TaB2. XPS spectra of Ta 4*p* (b) and B 1*s* (c) of TaB2. SEM image (d) with an inset of high magnification of TaB2. HRTEM image (e) with an inset of SAED pattern, and a high-magnification HRTEM image (f) of TaB2. PDOS (g) of TaB2, and crystal structure (h) and ELF (i) for TaB2 (101) planes.

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**Fig. 2.** Optical images (a) of the various solvents. First-cycle CV curves (b) of liquid Li2S2-based TaB2 cells. The cycling performance (c), first charge profiles (d), first discharge profiles (e), and ratio image of ΔC2/ΔC1 (f) under different activated potential from 3.0 to 4.0 V in the liquid Li2S2-based cells.The cycling performance (g) with high sulfur loading. Rate performances (h) with the corresponding charge and discharge profiles (i).

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**Fig. 3.** Rated CV curves from 0.2 to 1.0 mV/s (a) with the corresponding cathodic and anodic peak currents from the square root of the scan rate showing a linear correlation (b). Nyquist plots of cell cycling at the 100th, 250th and 500th cycles (c). S 2*p* (d), Ta 4*f* (e), and B 1*s* (f) spectra of the XPS from Li2S2-based TaB2 cells after 1st and 500th cycles. The measured curves are in black, and the fitted ones are in red.

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**Fig. 4.** Binding energy values (a) of Li2S8, Li2S6, Li2S4, Li2S2 and Li2S adsorbed on the TaB2 (101) and (001) surfaces. COHP curves (b-c) and PDOS (d-e) of Li2S4 adsorbed on the TaB2 (101) and (001) surfaces, respectively.