

# Theoretical simulation and optimum design of lithium-sulfur battery electrode system

The research on the new lithium battery with high energy density, stable cycling performance and low cost has become the hotspot today, and the exploration of battery electrode material with excellent performance is of great significance to the research of lithium battery. Sulfur materials have a high theoretical energy density (2600Wh/kg), and the advantages of environment-friendly and low price, making the lithium-sulfur batteries more attractive among many different types of lithium batteries. Lithium-sulfur battery technology began to be studied in the 1960s, and, after several decades of development, the lithium-sulfur battery technology still has some problems (low discharge capacity and the rapid decayed capacity). Related research focuses on the optimization of the performance of the electrode material system. It is necessary to optimize the design of positive and negative electrode system of lithium-sulfur battery in theory.

## **The negative electrode system protection & modification**

Lithium metal has the highest theoretical relatively capacity ( $3860\text{mAh g}^{-1}$ ), the lowest density, the smallest electrochemical equivalent ( $0.26\text{g Ah}^{-1}$ ) and the lowest standard potential ( $-3.04\text{V}$ ) of all metal elements, which is assembled as a negative electrode metal lithium battery that has a higher capacity density and operating voltage. However, the practical application of lithium metal anode still faces many challenges, for example, charge and discharge process of lithium metal electrode changes a lot in volume; complex reaction happens on metal surface, and induces remarkable interface resistance; lithium dendrites and “dead lithium” can be caused during both charge cycle and discharge cycle, which may even induce the battery internal short circuit and cause explosion. In view of the above problems, there have been proposed various methods for modifying the surface of a lithium metal electrode and the two-dimensional layered material has been used as a protective film for a lithium metal electrode and has achieved very good results. In addition, there is a very broad space in the two-dimensional material research. One of the most promising directions is to build Vander Waals heterogeneous structure, that is, these different properties of the two-dimensional material layers stacked to form a new artificial structure. The

initial results of this type of structure have shown that rich device functionality can be achieved. In the future trend of small-scale integration of small devices, the two-dimensional material heterogeneous knot must be the next generation of electronics and optoelectronics most critical elements.

In this work, the first-principles method is used to study the feasibility the two-dimensional layered materials with different elemental composition and structural features as protective films for lithium metal or sodium metal electrode, and investigate the main factors that determine the protection effects. It is found that the defect type, the crystal structure, the bond length of the key, the size of the ring and the metal neighbor effect can have a significant effect on the protective effect. On one hand, the introduction of defects, the increase of bond length and the appearance of metal proximity can promote the diffusion of lithium ions (sodium ions) through the protective film, thereby reducing the ion transport impedance and improving the electrode ion conductivity; on the other hand, all of these factors will induce the negative impacts on the mechanical properties of the protective film, so that its Young's modulus and critical strain and stress are greatly reduced, which is not conducive to inhibition of metal lithium dendrite growth.

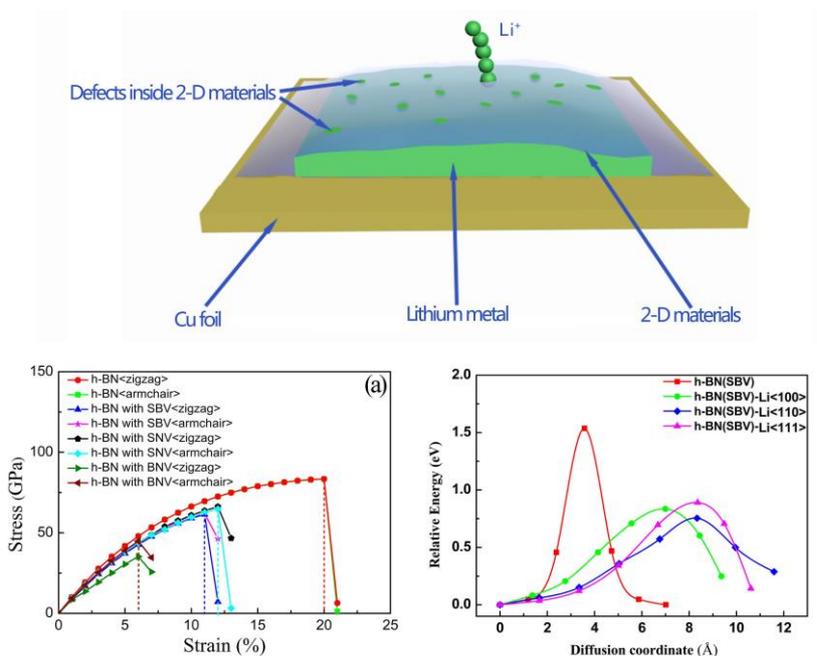


Fig 1. This picture shows the lithium metal anode diagram, from bottom to top are copper foil substrate, lithium metal and two-dimensional material protective film; the lower graph shows the strain-stress curve of hexagonal boron nitride under equivalent biaxial tensile load, indicating that the hexagonal boron nitride

**strain is the same as that of the copper foil substrate, the lithium metal and the two-dimensional material protective film, The presence of defects can significantly weaken the mechanical strength; the lower right shows the metal near-neighbor effect: the emergence of metal can greatly reduce the ion diffusion barrier, accelerate the diffusion of ions and improve the conductivity of ions.**

Based on the calculated results, the theoretical analysis shows that the influence of the electrons in the two-dimensional layered material and the distribution of the charge affect the protective effect of the protective film. For example: electron capture is a major factor in determining the diffusion barrier of  $\text{Li}^+$  ion; the lower the charge density around the defect, the smaller resistance the ion diffusion passes through; the electrons in the metal transfer to the protective film, filling in the anti-binding orbit and weakening the covalent bond in the protective film, which is the origination of the metal proximity effect<sup>[1]</sup>. Our study not only provides new insights into the interaction mechanism between lithium (sodium) ions and protective film materials at the atomic level, but also provides a basis for the study of the application of new layered materials in metal electrode systems.

### **The catalytic properties of the cathode system**

Lithium-sulfur battery cathode material system also faces great challenges, for example: large volume expansion happens on sulfur material during lithiation process; conductivity of  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  is poor; polysulfides easily solve in the electrolyte, resulting in the shuttling effect between cathode and anode, speeding up the battery capacity attenuation and reducing the battery Coulomb efficiency. In order to solve these problems, various nanostructured electrodes are used as a loading material to suppress the dissolution and loss of polysulfides, such as nanostructured C/S composite electrodes, heteroatom-doped carbon materials, metal oxides, metal sulfides (MOF), etc., the results showing that the role of polysulfides bonding and limiting field for the electrode material design is very important, which also further improves the performance of lithium-sulfur battery and provide an important theoretical guidance. However, the understanding of the interaction between anchoring materials and polysulfides and their mechanisms for improving battery performance is not clear enough. Using the theoretical simulation and experimental analysis, the adsorption of Li-S species, the catalytic oxidation and the functional transport mechanism of  $\text{Li}_2\text{S}$  by metal sulfide can be investigated, and the important parameters that determine the performance of battery can be explored at the atomic scale<sup>[3]</sup>.

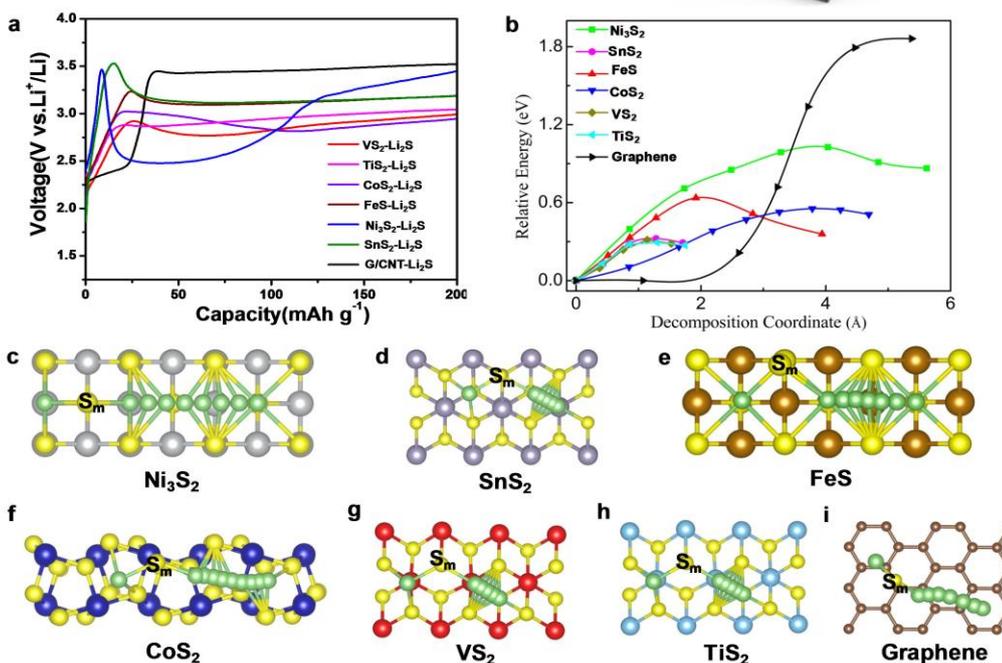
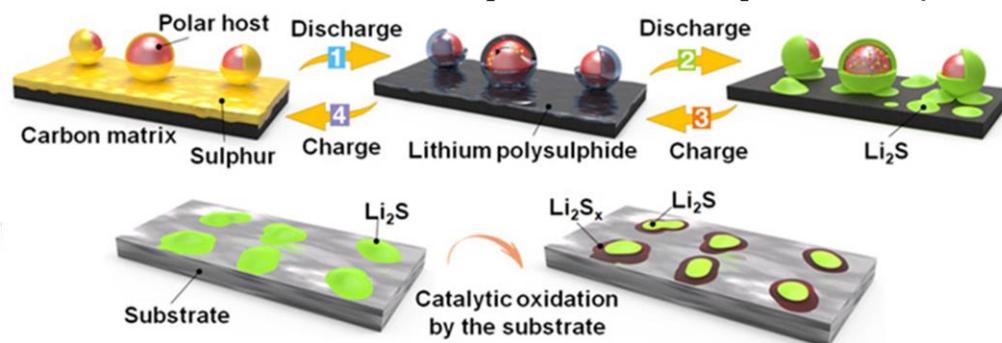


Fig 2. The top: schematic illustration of the sulfur conversion process and the Li<sub>2</sub>S catalytic oxidation on the surface of the substrate. The lower graph shows electrochemical activation and Li<sub>2</sub>S decomposition mechanism on the surface of various metal sulfides and graphene. (a) First cycle charge voltage profiles of Ni<sub>3</sub>S<sub>2</sub>-Li<sub>2</sub>S, SnS<sub>2</sub>-Li<sub>2</sub>S, FeS-Li<sub>2</sub>S, CoS<sub>2</sub>-Li<sub>2</sub>S, VS<sub>2</sub>-Li<sub>2</sub>S, TiS<sub>2</sub>-Li<sub>2</sub>S, and G/CNT-Li<sub>2</sub>S electrodes. (b) Energy profiles for the decomposition of Li<sub>2</sub>S cluster on Ni<sub>3</sub>S<sub>2</sub>, SnS<sub>2</sub>, FeS, CoS<sub>2</sub>, VS<sub>2</sub>, TiS<sub>2</sub>, and graphene. The bottom: the schematic representations of the corresponding decomposition pathways for (c) Ni<sub>3</sub>S<sub>2</sub>, (d) SnS<sub>2</sub>, (e) FeS, (f) CoS<sub>2</sub>, (g) VS<sub>2</sub>, (h) TiS<sub>2</sub>, and (i) graphene.

We have focused on the interaction between the lithium-sulfur clusters and the loading materials<sup>[2]</sup>. This time, we further investigate the key parameters that make great influence on catalytic properties and cycling performance. We explored the lithium-sulfur battery discharge products Li<sub>2</sub>S in the metal sulfide surface catalytic oxidation mechanism, made a series of metal sulfide depth study, simulated decomposing energy barrier and transport energy barrier. The

results show that the size of the catalytic oxidation-reduction ability of metal sulfide, as the main material, is very important for the transportation of lithium ions and the adsorption of polysulfide. The strong interaction between metallic conductivity and  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_x$  can reduce the energy barrier, promote the transport of lithium ions, control the surface precipitation of  $\text{Li}_2\text{S}$ , accelerate the surface-mediated redox process, and improve the Li-S battery overall performance. Experimental results show that the decomposing energy barrier and transport energy barrier have important effect on the initial over-potential and lithiation reaction rate.

Through a systematic study on various metal sulfides, especially compared with carbon materials like  $\text{Ni}_3\text{S}_2$ ,  $\text{SnS}_2$ ,  $\text{FeS}$  and other electrode load materials,  $\text{VS}_2$ ,  $\text{TiS}_2$ ,  $\text{CoS}_2$  and other materials as a positive electrode have a higher specific capacity, lower over-potential and good cycle stability. It is demonstrated that the inherent metallic conductivity, strong interaction with LiPSs, facilitated Li ion transport, controlled  $\text{Li}_2\text{S}$  precipitation, accelerated surface mediated redox reaction, and catalyzing reduction/oxidation capability of  $\text{M}_x\text{S}_y$  are critical in reducing the energy barrier and contributing to the remarkably improved battery performance. More importantly, our density functional theory simulation results are in good agreement with our experiments measuring the activation barrier, polysulfide adsorption, lithium diffusion rate, and electrochemical behavior, which allows us to identify the mechanism for how binding energy and LiPSs trapping dominate the  $\text{Li}_2\text{S}$  decomposition process and overall battery performance. The catalytic mechanism of  $\text{Li}_2\text{S}$  catalytic oxidation of metal sulfide is expounded by the first-principles calculation and experiment. It provides a practical and feasible way for designing new electrode materials and improving the performance of lithium-sulfur battery<sup>[3]</sup>.

Qianfan Zhang, associate professor, school of material science and engineering, Beihang University, E-mail: qianfan@buaa.edu.cn

Ruifeng Zhang, professor, school of material science and engineering, Beihang University, E-mail: zrf@buaa.edu.cn

## References

[1]Hongzhen Tian, ZhiWei Seh, Kai Yan, Zhongheng Fu, Peng Tang, Yingying Lu, Ruifeng Zhang, Legut, Dominik, Yi Cui(\*), **Qianfan Zhang**(\*), Theoretical Investigation of Two-Dimensional Layered Materials as Protective Films for Lithium and Sodium Metal Anodes. *Advanced Energy Materials*, 2017, 1602528.

[2]**Qianfan Zhang**(\*), Yapeng Wang, ZhiWei Seh, Zhongheng Fu, **Ruifeng Zhang**, Yi Cui(\*), Understanding the Anchoring Effect of Two-Dimensional Layered Materials for Lithium Sulfur Batteries, *Nano Letters*, 2015, 3780-3786.

[3]Guangmin Zhou(<sup>#</sup>), Hongzhen Tian(<sup>#</sup>), Yang Jin(<sup>#</sup>), Xinyong Tao, Bofei Liu, Rufan Zhang, ZhiWei She, Denys Zhuo, Yayuan Liu, Jie Sun, Jie Zhao, Chenxi Zu, David Sichen Wu, **Qianfan Zhang**(\*), Yi Cui(\*), Catalytic oxidation of Li<sub>2</sub>S on the surface of metal sulfides for Li-S batteries, *Proceedings of the National Academy of Sciences*, 2017, 840-845.