

Understanding the anchoring effect of two-dimensional layered materials for lithium-sulfur batteries

The implementation of rechargeable lithium-sulfur battery has been impeded by multiple challenges, especially the dissolution of intermediate lithium polysulfide (Li_2S_n) species. Recently, there have been exciting developments in promoting their performances by designing nano-structured sulfur-based cathode, such as introducing carbon composites and nano-structured additives, which can efficiently trap soluble lithium polysulfide during charge or discharge processes, and at the same time, improve the conductivity.

Although widely used in many applications, current rechargeable lithium-ion batteries cannot fulfill the increasing energy demands of modern society owing to a limited theoretical specific capacity of its cathodes. As potential improvements, sulfur cathode has a specific capacity of 1673 mAh/g, giving lithium-sulfur batteries a more than five times higher specific energy than conventional lithium-ion ones. Nevertheless, successful implementation of lithium-sulfur batteries has been hindered by a series of obstacles, such as the dissolution of lithium polysulfide (Li_2S_n) species into the electrolyte, the low ionic/electronic conductivity of both sulfur and lithium sulfide, and large volumetric expansion of sulfur (~80%) upon lithiation. To address these challenges, introducing nanoscale anchoring materials (AM) is viewed as an effective method since various types of polar nano-AMs have been demonstrated to enhance the battery performance. However, due to lack of microscopic insight into the interaction features between AM and Li_2S_n species, the choice of AM to use is largely empirical in nature. Although a number of modeling simulations have been carried out using simplified Li-S molecule models, it is still far from a clear clarification of the interaction mechanism.

Recently, the anchoring effect of layered materials with reference to carbon and the mechanism behind them have been systematically investigated based on entire-lithiation-process computation by first-principles approach, with van der Waals interaction included [1]. The binding strength between Li_2S_n clusters and various layered structure materials including graphene are calculated. The simulation shows that carbon structure cannot adsorb the Li_2S_n species strongly, especially

when the cluster evolves to middle-lithiated stage (around Li_2S_4), so introducing AMs with stronger binding strength is important. As shown in Figure 1a, for unlithiated S_8 adsorption, these AMs can induce the similar binding energy (0.75–0.85 eV) as graphene. As soon as the lithiation begins, different materials induce distinct anchoring effect. According to the magnitude of binding energy (E_b), these materials can be classified into three types: oxides (V_2O_5 and MoO_3), sulfides (TiS_2 , ZrS_2 , VS_2 , NbS_2 , and MoS_2) and chlorides (TiCl_2 , ZrCl_2), which can be viewed as strong, moderate and weak AMs, with the induced binding energies in ranges of 2.0–4.2 eV, 0.8–2.0 eV, and 0.4–0.8 eV, respectively.

The computation also shows that the anchoring effect of AM mainly originates from its chemical interaction with the Li atom in Li_2S_n species, which overcomes the weak chemical adsorption by carbon substrate. For all the AM materials studied, the vdW interaction dominates the unlithiated stage with the ratios of nearly 100%, which means these AMs cannot form a chemical bond with S atom. The chemical interaction gradually grows stronger as soon as the lithiation begins, as illustrated in Figure 1b. The fundamental difference between two kinds of interaction can be visualized from the electron charge transfer analysis (see Figure 1c). For S_8 adsorption cases, there is almost no charge transfer between S_8 and AMs, while for Li_2S_4 adsorption cases, the charge migration between them indicates strongly the chemical bonding formation.

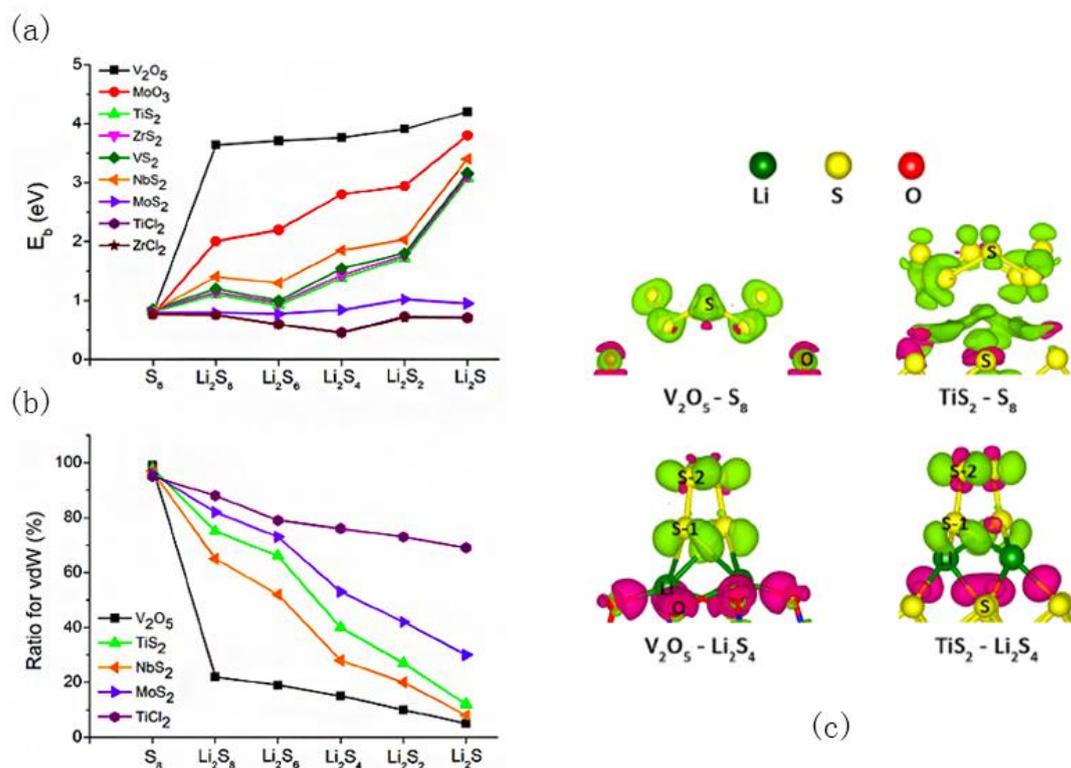


Figure 1: (a) Binding energies for Li-S composites at six different lithiation stages (S_8 , Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2 , Li_2S) on different AMs we select. (b) Ratio for vdW interaction for five kinds of extracted AMs at four different lithiation stages. (c) Charge transfers when S_8 or Li_2S_4 adsorbs on V_2O_5 or TiS_2 . The charge transfer is the charge difference after and before Li-S cluster is put on AM and can be expressed as $\Delta\rho = \rho(AM + Li_2S_4) - \rho(AM) - \rho(Li_2S_4)$, where $\rho(AM + Li_2S_4)$, $\rho(AM)$, and $\rho(Li_2S_4)$ are the charge densities for adsorption system, AM system, and Li-S cluster system, respectively. Here, pink (green) is the spatial regions gain (loss) in charge.

As lithiation goes on, more and more charge transfers from S atoms in Li_2S_n cluster into the AMs, and as a result, strong Li-AM bond is formed while the Li-S bond inside the cluster is softened. The weakening of the Li-S bond and the charge transfer into AM suggests that too strong chemical binding between Li ion and AM is not good news for the performance of Li-S battery, because it can cause decomposition of the Li_2S_n species, which means lithium prefer to stay alone instead of forming bond with sulfur and leads to separation of these two elements. Even worse, it induces Li_2S_n species to form Li^+ and S_n^{2-} ions, resulting in the dissolution of sulfur material. Therefore, too strong AMs might not be good choices. In contrast, moderate AMs can strike a balance between binding strength and intactness of the Li_2S_n species, overcoming the disadvantage of both strong and weak AMs. That is the most likely reason why moderate AMs including TiS_2 , ZrS_2 , and VS_2 have been demonstrated to induce one of the best cycling

performances until now, while many oxide materials predicted to have stronger binding strength cannot improve the performance as efficiently as these sulfides in experiments.

In conclusion, it has been demonstrated that different materials lead to distinct adsorption features with Li_2S_n species, whereas the binding strength is determined by the amount of charge transfer from S atoms in cluster into the AM, accompanied by the softening of Li–S bonds. This work explores the reason why carbon substrate, like graphene, cannot firmly adhere Li_2S_n species and reveals the mechanism for anchoring effect for different lithiated Li_2S_n species at the atomic level. On the basis of the computation, it is suggested that moderate AMs are the best choices for battery electrode.

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

Reference

- [1] **Q. F. Zhang***, Y. P. Wang, Z. W. Seh, Z. H. Fu, R. F. Zhang, Y. Cui*, “Understanding the anchoring effect of two-dimensional layered materials for lithium-sulfur batteries” *Nano Lett.* 15, 3780 (2015).