Applied Surface Science 463 (2019) 331–338

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Adsorption of lithium polysulfides on an anatase (1 0 1) and an α-Al_2O_3 (0 0 0 1) surface under external electric field with first principles calculations

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ARTICLE INFO

Keywords:
Li—S batteries
Electric field
Adsorption energy
Anatase
α-Al_2O_3
First-principle calculations

ABSTRACT

The “shuttle effect” induced by the dissolution and diffusion of the Li_2S_x ($4 \leqslant x \leqslant 8$) into the electrolyte is a crucial problem of a Li—S battery. Anatase or Al_2O_3 can be used as an additive to suppress the “shuttle effect”. First-principles approach coupled with van der Waals (vdW) interaction is used to calculate the adsorption energies of Li_2S_x ($x = 4, 6, 8$) molecules on an anatase (1 0 1) or an α-Al_2O_3 (0 0 0 1) surface. The results show that the adsorption of the molecules on an α-Al_2O_3 (0 0 0 1) is stronger than that on an anatase (1 0 1) surface. Furthermore, owing to the existence of an electric field inside the battery during the charge-discharge process, the external electric field effects on the adsorption are investigated. As a result, the adsorption energy (absolute value) almost linearly increases with the increase of electric field intensity in the range from –0. 16 to 0.16 V/Å. In addition, the responses of different Li_2S_x molecules on an anatase (1 0 1) surface or an α-Al_2O_3 (0 0 0 1) surface to the external electric fields are different.

1. Introduction

Li—S battery is regarded as a promising high-power device in extensive applications, from small mobile devices to large-scale grid energy storage [1,2]. Compared with lithium-ion batteries (LIBs), Li—S batteries exhibit advantages of high theoretical energy density of 2600 W h kg^{-1} (five to seven times higher than that of LIBs) [3–5]. In addition, due to the natural abundance, eco-friendliness, and low cost, sulfur is considered as an ideal cathode material in Li—S batteries [6,7]. All these features make Li—S battery becomes one of the most attractive candidates for next-generation energy storage devices [8].

Despite these advantages of Li—S batteries, difficulties still exist on the practical application. The major challenge for the commercial application of Li—S battery is the dramatic capacity decay [9]. During a Li—S battery discharging process, elemental S is initially reduced to form soluble long chain Li_2S_x ($4 \leqslant X \leqslant 8$) species. These Li_2S_x molecules dissolve into the electrolyte and migrate through the separator, which results “shuttle effect” [10]. In addition, the insulating nature of sulfur (conductivity ~10^{-30} S cm^{-1}) and a large volume expansion by up to ~ 80% upon full lithiation are serious concerns in the sulfur electrode design [11].

Recently, extensive efforts have been devoted to addressing the shortcomings, including preparation of novel composite electrodes [12,13], decoration the separators [14], and anode protection [15,16]. Due to the long-chain lithium polysulfides are highly polar, therefore polar materials (metal oxides) or polar groups should be used to inhibit the shuttling of lithium polysulfides [17]. Some metal oxides with polar surfaces, including $Mg_{0.6}Ni_{0.4}O$, Al_2O_3, MnO_2, V_2O_5, TiS_2, TiO_2 and Co_9S_8 [18–24] have been used as additives or absorbents to inhibit the “shuttle effect”. For example, TiO_2 and Al_2O_3 are promising additives due to their strong interaction with lithium polysulfides. Furthermore, TiO_2 is one of important environmental purification photocatalysts because its excellent air pollution control and its ability to fully disintegrate harmful pollutants [25–29]. Gao et al. [30] reported hierarchical TiO_2 sphere-sulfur frameworks assisted with graphene as a cathode material can trap the polysulfides via chemisorption. The interactions between Li_2S_x species and TiO_2 have been studied with experimental and theoretical methods and the results show that TiO_2 and Li_2S_x species can form strong chemical bonds [31]. Yushin et al. [32] reported that Al_2O_3 coated electrodes can improve the cycling

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https://doi.org/10.1016/j.apsusc.2018.08.184
Received 30 January 2018; Received in revised form 18 July 2018; Accepted 21 August 2018

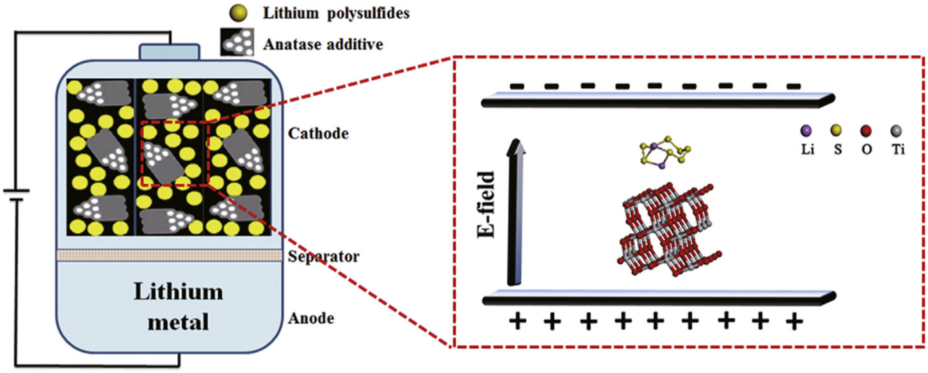

Fig. 1. Schematic illustration of a Li_2S_8 molecule is adsorbed on an anatase (1 0 1) surface. The electric field is perpendicular to the anatase (1 0 1) surface.

performance of Li—S batteries, owing to the inhibited deposition of Li_2S on electrodes by Al_2O_3 coating. Chen et al. [33] reported a free-standing Al_2O_3—Li_2S-graphene oxide sponge (GS) composite cathode, in which ultrathin Al_2O_3 films are preferentially coated on Li_2S by an atomic layer deposition (ALD) technique. The results show that the ultra-thin Al_2O_3 film not only acts as a physical barrier to Li_2S nanoparticles, but also provides a strong binding interaction to suppress lithium polysulfides dissolution.

Therefore, it is meaningful to investigate the adsorption between TiO_2/Al_2O_3 and lithium polysulfides. Furthermore, owing to the existence of electric field inside the battery during the process of charging and discharging, it is crucial to investigate the electrical field effects on the adsorption [34,35].

In this paper, first-principles approach coupled with vdW interaction is used to investigate the adsorption of Li_2S_x ($x = 4, 6, 8$) molecules on an anatase (1 0 1) and an α-Al_2O_3 (0 0 0 1) surface. The results show that the adsorption of the molecules on the α-Al_2O_3 (0 0 0 1) is stronger than that on the anatase (1 0 1) surface. In addition, the external electric field effects on the adsorption of Li_2S_x ($x = 4, 6, 8$) on an anatase (1 0 1) and an α-Al_2O_3 (0 0 0 1) surface are studied using density functional theory (DFT) calculations. The responses of different Li_2S_x molecules on an anatase (1 0 1) surface or an α-Al_2O_3 (0 0 0 1) surface to the external electric fields are different.

2. Computational details and models

2.1. Calculation details

The adsorption energies of Li_2S_x ($x = 4, 6, 8$) on an anatase (1 0 1) surface and an α-Al_2O_3 (0 0 0 1) surface are studied with DFT [36,37] calculations, which are performed using Vienna ab initio simulation package (VASP) code [38]. The exchange correlation functional within the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Enzerof (PBE) [39] is applied in the calculations. The projected augmented wave (PAW) method [40] is used to deal with the wave functions near the core region. The smooth part of the wave function is expanded in plane waves with a kinetic energy cutoff of 400 eV. In order to avoid the periodic interactions between neighbor anatase/α-Al_2O_3 slabs, a vacuum layer with the thickness of 20 Å is on the top the slabs. A grid of $2 \times 2 \times 1$ k-point mesh is used for adsorption calculations. The energy convergence criterion of the self-consistent functional (scf) calculation is 10^{-4} eV. The conjugate gradient method is used to relax the Hellmann-Feynman force in the ionic relaxation with the force stopping criterion of values of 0.05 eV/Å. In order to evaluate the long range effects, some adsorption energies are calculated using the DFT-D3 method with Becke Jonson damping [41], in which the vdW interaction is considered.

DFT calculations underestimate the band gaps of semi-conductor materials. To overcome this problem, on-site Coulomb interactions (DFT + U) [42] are used in the calculations. The U value of 4 eV is applied for the 3d orbital electrons, which enlarges the band gap from 1.1 eV to 2.0 eV. Although we can get gap value which is close to the experimental data with a larger U value, the lattice constants of anatase are not reasonable with this U value [43].

The adsorption energy of a Li_2S_x ($x = 4, 6, 8$) molecule on an anatase (1 0 1) or an α-Al_2O_3 (0 0 0 1) surface ΔE_{ad} is defined as:

$$\Delta E_{ad} = E_{surf+Li_2S_x} - E_{surf} - E_{Li_2S_x} \tag{1}$$

here $E_{surf+Li_2S_x}$ and E_{surf} are the total energies of an anatase or an α-Al_2O_3 slab with or without adsorbed Li_2S_x molecules, respectively. $E_{Li_2S_x}$ is the energy of an isolated molecule. For the structural optimization of the molecules, the molecules are inside a cubic box of $10 \times 10 \times 10$ Å^3.

Because of the physical vdW interaction, the Li_2S_8 and Li_2S_6 molecules deform seriously after adsorbed on two dimensional layered materials [44]. It is suggested that the lying-in-plane Li_2S_x is energetic favorable on surfaces. In addition, Li ions prefer to stay on the O sites and S ions prefer to stay on the Ti or Al sites to form strong chemical bonds. Therefore, Li_2S_x ($x = 4, 6, 8$) molecules with lying-in-plane configurations on an anatase (1 0 1) or an α-Al_2O_3 (0 0 0 1) surface are used to calculate the adsorption energies. Totally, more than ten initial adsorption configurations of each molecular on an anatase (1 0 1) or an α-Al_2O_3 (0 0 0 1) surface are chosen and then the systems are relaxed (see Tables S1 and S2 in Supporting Information for detail). The system with the lowest system energy is used to study the electric field effects on the adsorption.

The adsorption behaviors are investigated under an external electric field, which is applied in the direction perpendicular to the anatase (1 0 1) surface or the α-Al_2O_3 (0 0 0 1). The schematic of a Li_2S_8 molecule adsorbed on an anatase (1 0 1) surface is shown in Fig. 1. The electric field is perpendicular to the anatase (1 0 1) surface. In our calculations, the adsorption energies are calculated under the electric field intensity of the range from −0. 16 to 0.16 V/Å with a increment of 0.04 V/Å. In addition, external electric field effects on the system energy of the Li_2S_x ($x = 4, 6, 8$) molecules are evaluated with Gaussian package [45]. The results show that the electric field has little effect on the system energies of the Li_2S_x ($x = 4, 6, 8$) molecules. As a result, when we calculate the external electric field effects on the adsorption energies of the Li_2S_x ($x = 4, 6, 8$) molecules on an anatase (1 0 1) or an α-Al_2O_3 (0 0 0 1) surface, the ground state energies of the molecules are used.

In order to evaluate vdW interactions, the vdW interactions effect ratio is defined as:

$$R = \frac{E_{ad}^{vdW} - E_{ad}^{no-vdW}}{E_{ad}^{vdW}} \tag{2}$$

where E_{ad}^{vdW} and E_{ad}^{no-vdW} represent the adsorption energies calculated with and without vdW functional, respectively.