Effect of the adsorption of ethylene carbonate on Si surfaces on the Li insertion behavior

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ARTICLE INFO

ABSTRACT

Effects of the ethylene carbonate (EC) solvent on Li insertion and diffusion in Si anodes are studied using density functional theory. On both (100) and (111) reconstructed surfaces of Si, a semi-dissociated (SD) configuration of EC is stable and most favorable for Li insertion, lowering its barrier by up to 0.2 eV vs a clean surface. The less stable molecular adsorption has little effect on Li insertion and diffusion, while the surface ketone formed by dissociating the SD configuration at a cost of 0.6 eV has a strong detrimental effect on Li insertion, increasing its barrier by up to 0.4 eV.

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1. Introduction

Metal ion batteries are a key technology for powering portable electronics and for achieving sustainability. Li ion batteries provide today the highest energy density at about 160–180 Wh/kg, which is still only about one tenth of that of gasoline [1]. Further increases in capacity, energy density, and rate capability are required to enable a wide use of all-electric vehicles [1] and bulk electrochemical storage [2].

This can be achieved by designing new electrode materials and nanostructures. For the longest time, carbon-based anodes have been used in commercial batteries, with the capacity of about 370 mAh/g, still exceeding that of common cathodes (about 150 mAh/g for LiCoO₂ [3]). However, as the capacity of cathodes continues to increase, reaching about 500 mAh/g in experimental cathodes [4,5], more benefit can be obtained by increasing the specific capacity of the anode. One of the most promising anode materials is Si, with a theoretical capacity of about 4200 mAh/g. It has been suggested that the issues of cyclability of Si anodes due to a large volume expansion (more than 300%) upon lithiation and pulverization with a loss of connectivity can be solved via nanostructuring [6–10]. Si and other group IV elements can today be considered as *practical* anode materials for Li ion batteries and are also actively studied as potential anode materials for other metal ion batteries [11–13]. It should be noted, however, that good cyclability has been achieved at specific capacities significantly lower than the theoretical capacity [6–10]. The rate capability, which is determined by insertion barriers and diffusivity of Li, is also lower than that of carbon-based anodes. This is confirmed by multiple experiments and by theoretical calculations of the barriers in bulk c-Si [14–18] and at different surface facets of Si [19,20]. Barriers to insertion into the (100)/(111) surfaces and for subsurface diffusion were computed to be about 0.84–0.88/ 0.51 eV and 0.48–0.63/0.53–0.74 eV respectively, and the barrier for single-atom diffusion in the bulk was found to be 0.55– 0.60 eV. These numbers compare very unfavorably with barriers to insertion and diffusion in graphite, as low as 0.2 eV [21,22] as well as with barriers in new high-capacity cathode materials [23]. The barriers computed so far are also very approximate in the sense that they ignore the presence of other atomic and molecular species. In real batteries, the interaction with the electrolyte and with Li leads to surface modification, eventually leading to the formation of an oxide or silicate layer [24]. These are expected to change drastically the barrier to insertion and diffusion. For Si specifically, the influence of Li–Li interactions has already been confirmed by density functional theory and MD studies [14,25,26]. Adsorbed species have also been shown to modify the insertion dynamics of other dopants [27]. The presence of molecules at the anode surface is also expected to influence significantly insertion dynamics, yet is much less studied. The surface of the anode is in contact with electrolyte species, and specifically with solvent molecules. Further, common electrolytes are reduced at low voltages, and the reduction products depend on the kind of lithium salt used. Although surface complexes might be formed, these are often ignored in computational models. Continuum solvent models would not be appropriate to analyze the effects due to the solvent, especially, as shown in this letter, if solvent molecules form strong

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bonds with or dissociate at the surface. The interaction of solvent molecules with the anode has to be studied explicitly at the atomic level, which is done here.

It has been computed that ethylene carbonate (EC) – a common solvent species used in batteries [28,29] – decomposes on the surface of some cathode materials, with implications for cathode cycling properties [30]. Chemical reactions at the graphite anode involving EC have been the subject of several density functional theory and molecular dynamics studies [31–33]. Recently, the interaction of (molecularly adsorbed) and fluorinated EC with graphene – a common component of experimental anodes [34–36] – was considered at the atomistic level [37]. However, atomistic studies of the formation of adsorbate complexes at the Si anode surface, possibly following solvent dissociation, and their effect on the rate, are still lacking.

In the present work, we consider the EC–Si interface and address the following questions: (i) what surface complexes are formed by EC adsorption at the Si(100) and (111) surfaces? (ii) how do these surface complexes affect the insertion of Li? and (iii) is it in principle possible to use adsorbed molecules to lower the insertion and/or diffusion barrier. We use density functional theory, which has been successfully used to model diffusion in Li batteries [14,25,26] and other electrochemical devices (see for example Ref. [38]) The article is organized as follows. In Section 2, we describe the details of the modeling method. In Section 3, we consider the results for the Si(100) surface, followed by those for the Si(111) surface. Section 4 concludes.

2. Method

The simulations were carried out within the framework of density functional theory, as implemented in the AIMPRO code [39,40]. The core electrons were accounted for by using the dual space separable pseudopotentials of Hartwigsen et al. [41]. All three electrons of Li were explicitly included in the calculation.

The basis set consists of Cartesian s, p and d-type Gaussian functions centered on each atom with four different exponents optimized for each species [42]. The basis sets used on Si, Li, O, C sites were, respectively, of type *ddpp* (28 functions per atom), *pppp* (16 functions per atom), *dddd* (40 functions per atom), and *pddd* (34 functions per atom). For hydrogen, a contracted basis set (C44G*) with 13 functions per atom, including a polarization function, was used. The exchange and correlation energy functional was approximated by the gradient approximation of Perdew, Burke and Ernzerhof (PBE) [43].

The Si(100) and Si(111) surfaces were represented by slabs, with periodic boundary conditions along the three dimensions. The slabs consisted of six or ten layers of silicon atoms. Unless otherwise stated, the results of the six-layer calculation will be given. The slabs were separated by at least 1.7 nm from the image slabs, and identical points in the slabs were separated by more than 1.3 nm from their images in the neighboring supercells. The reciprocal space was sampled at $2 \times 2 \times 1$ special **k**-points [44].

Each slab had one reconstructed surface to be used for modeling. We considered the (4×2) reconstruction for the Si(100) surface (Figure 1a)), which is its lowest energy configuration [45]. For the Si(111), we considered a (4×2) reconstruction, since it is locally very similar to the most stable (7×7) surface reconstruction[46], but can be simulated at a lower computational cost. A similar strategy has been employed in previous studies of molecular adsorption and Li in-diffusion [47,20].

The back surface of the slabs was passivated with hydrogen, and both the passivizing hydrogen atoms and the closest layers of Si atoms (two in the case of the 6-layer slab, or four in the case of the 10-layer slab) were kept fixed during the structural optimiza-

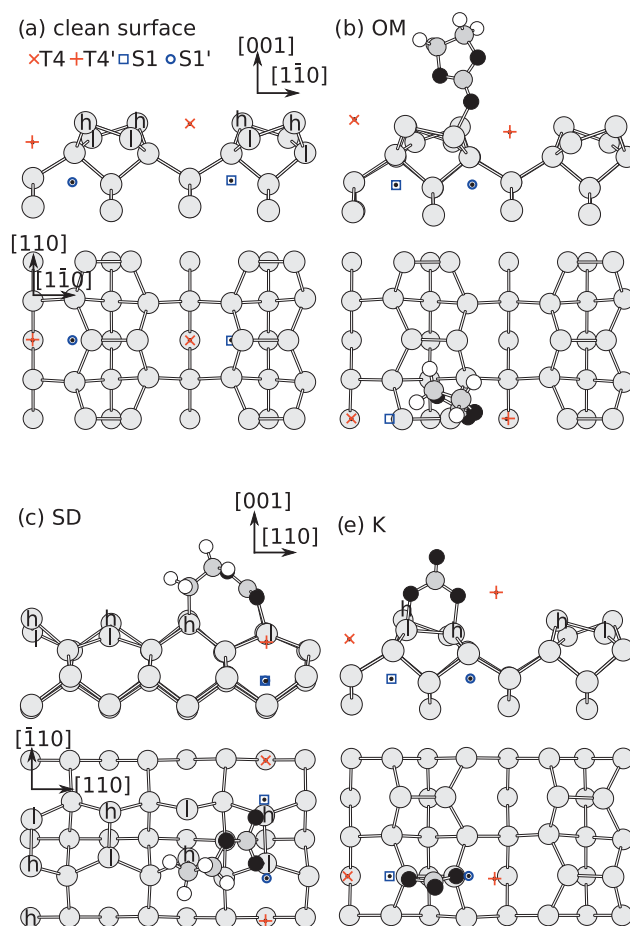**Fig. 1.** Si(100) (4×2) surface: (a) clean surface, (b) surface with an adsorbed EC molecule in the OM configuration (c) or in the SD configuration, and (d) with an adsorbed ketone group. Si, C, O and H atoms are represented by light gray, dark gray, black and white spheres, respectively. Points represent the positions considered for the Li atoms. The orientation of figures (b) and (e) is the same as (a). Higher and lower-lying atoms of the reconstructed dimer rows are indicated by 'h' and 'l'.

Table 1
Relative energies of molecularly adsorbed (OM), semidissociated chemisorbed (SD) and dissociated (K) EC on (001) and (111)-surfaces. E_{ad} is the enthalpy of adsorption, whereas E_b is the energy barrier. All values are in eV.

Adsorption mode	E_{ad} (100)	E_b (100)	E_{ad} (111)	E_b (111)
OM	−1.1		−0.4	
SD	−3.2	1.63	−1.9	3.20
K	−2.5	1.88	−1.7	4.34

tion. The lattice parameters were also kept constant, and identical to the bulk value (5.50 Å) along the directions parallel to the surface.

The minimum energy paths for diffusion and the respective saddle points were determined using the climbing image nudged elastic band method (NEB) [48] with five images. The highest energy image was allowed to move along the direction of the band (climb) after five iterations of the regular NEB method.

3. Results

3.1. Si(100) surface

We first consider the adsorption modes of the EC molecule on the Si(100) surface. The oxygen forming the C=O bond in the isolated molecule can form an additional bond to a surface Si atom, as