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Electron transfer through solid-electrolyte-interphase layers formed on Si anodes of Li-ion batteries



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ABSTRACT

Solid-electrolyte interphase (SEI) films are formed on the electrode surfaces due to aggregation of products of reduction or oxidation of the electrolyte. These films may grow to thicknesses in the order of 50-100 nm and contain a variety of organic and inorganic products but their structure is not well defined. Although in some cases the films exert a passivating role, this is not always the case, and these phenomena are particularly more complex on Silicon anodes due to swelling and cracking of the electrode during lithiation and delithiation. Since the driving force for SEI growth is electron transfer, it is important to understand how electron transfer may keep occurring through the heterogeneous film once the bare electron surface is covered. Here we introduce a novel approach for studying electron transfer through model films and show preliminary results for the analysis of electron transfer through model composite interfacial systems integrated by electrode/SEI layer/electrolyte. Ab initio molecular dynamics simulations are used to identify deposition of SEI components, and a density functional theory/Green's function approach is utilized for characterizing electron transfer. Three degrees of lithiation are modeled for the electrodes, the SEI film is composed by LiF or Li₂O, and the ethylene carbonate reduction is studied. An applied potential is used as driving force for the leakage current, which is evaluated as a function of the applied potential. Comparative analyses are done for LiF and Li₂O model SEI layers.

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1. Introduction

Silicon has been proposed as a promising material for negative electrode of lithium ion batteries. This is due to its much higher capacity to store Li, which is about one order of magnitude higher (4212 mAhg⁻¹)[1] than graphite (372 mAhg⁻¹) [2]. Also, Si is an abundant material that can form mixtures with up to 4.4 lithium atoms/silicon atom (Li_{4.4}Si) [2]. However, Li_{4.4}Si expands 300% in volume during lithiation leading to change in the surface area and mechanical stresses[3] [4]. Typical electrolytes consist of mixtures of alkyl carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (EMC), propylene carbonate (PC), and ethyl methyl carbonate (EMC) [2]. During discharge, lithium ions flow from the anode to the cathode through the electrolyte and the anode shrinks as the lithium ions are ejected. The opposite

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process occurs during charge where the Si electrode changes volume swelling dramatically due to lithiation.^[2] Starting during the first cycle, the electrolyte decomposes electrochemically and a solid electrolyte interphase (SEI) [5], [6] develops on the anode surface. The SEI layer is formed by a variety of products which result from several decomposition reactions. [7,8] Depending on its thickness and on the type of products the SEI film may block electron transfer between electrolyte and anode during charging, thus passivating the electrode and preventing further SEI reactions. [9] However, the film needs to be ionically conductive to avoid Li retention which leads to irreversible capacity loss that affects power cyclability.[10] Some additives have shown to be useful to develop a more stable SEI and therefore to enhancing the cycle life in silicon electrodes. [11] Fluoroethylene carbonate (FEC) is one of the most used solvents that ameliorate the capacity retention of the battery.[12]. Several characterization studies [13-16] have found that SEI layers formed on silicon electrodes is alike to those formed on carbon electrodes; however additional products may be generated on silicon by conversion of silicon oxide (SiO₂) to lithium silicon oxides (Li_nSiO_m) [10]. Most of the reported surface analyses[10,13–16] agree that the SEI layer may be formed by fluorinated species, such as lithium fluoride (LiF), Li_xPF_v and PF_v, as well as Li₂CO₃, alkyl carbonates, ethers, phosphates, and Li₂O, depending on the cycling stage, electrolyte composition, but also electrode nanostructure and morphology.[15] Additionally, multiscale modeling has been used to characterize the initial stages of SEI formation. Quantum chemical studies [7,17–19] include detailed density functional theory (DFT) analyses of solvent decomposition mechanisms in Li/solvent complexes, as well as ab initio molecular dynamics including the description of the surface chemistry[8,20,21]. However, much less information is available regarding the growth SEI stages, where issues such as aggregation, polymerization, and nucleation of the heterogeneous SEI film are critical. An important and not-yet answered question is how the electron transfer proceeds through such film that contains several insulator species. For example, both LiF and Li₂O are wide-gap electrical insulators [22], with reported bulk experimental band gaps of 14.2 eV[23] and 7.99 eV[24] respectively. Although some research has focused on ionic conduction^[22], much less is known about electronic conduction through SEI blocks containing such species, although we note that interfacial capacitances can also be obtained from first-principles calculations, and have been reported by others.[25] In this work we report a novel approach to evaluate electron transfer through composite interfacial films. The reported atomistic simulations focus on the chemistry of the SEI reactions and on the electron transfer events during SEI growth. They are not designed to investigate the swelling phenomena of Si anodes. Other coarse-grained models are much better suited to tackle that problem, and we will address that aspect in future reports

Here first we briefly review and discuss the possible formation of SEI products such as LiF and Li₂O. We then introduce our model composite films formed by electrode/SEI/solvent species and evaluate the electron currents through such systems for a number of interfacial configurations. The results of this study contribute new insights to two important problems: 1) How the SEI layer is formed on Si anodes; 2) How the SEI layer may grow based on the electronic conductivity assessed in representative SEI model compounds (LiF and Li₂O). The advantage of ab initio approaches is that they are free of fitting parameters; therefore the results are such that can provide a "theoretical microscope" additional tool to obtain insights of phenomena in most cases not accessible to experiments.



Fig. 1. The studied model represents a piece of the composite interface integrated by electrolyte/model SEI layer/model Li_xSi_y electrode. Both ends of the composite interface are connected to nano-gold contacts, which are used to apply an external applied potential (V). Such applied potential is the driving force for the leakage that would occur during charge of the battery. The extent of electron transfer through the system for various SEI layer compositions and degrees of lithiation of the electrode is measured using the same nano-gold contacts. The red arrow indicates the direction of electron flow during the SEI layer nucleation and growth.

2. Methodology

Fig. 1 illustrates the overall idea of the interfacial system we aim to investigate. A composite interfacial system is built that is composed by a model Li_xSi_y electrode covered by a multicomponent model SEI layer which is in contact with an electrolyte layer. Such electrolyte layer in principle may contain some solvents, salt and/or additives. An applied potential is imposed between two gold nanoelectrodes representing the leakage current that would occur during battery charge. The constituent SEI molecules that we discuss in this paper include LiF and Li_2O . The calculated systems are discussed below. In this section we explain the methodology used to arrive at the formulation of the employed models.

2.1. AIMD simulations

First, we determine the possible SEI layer constituents using static quantum density functional theory (DFT) calculations^[21] and ab initio molecular dynamics (AIMD) simulations [8] of Li_xSi_y surfaces covered by an electrolyte. In our previous reports we have examined the decompositions of EC and FEC on representative Li_xSi_y surfaces and clusters^[8,21]. Here we report AIMD simulations of the decomposition of the salt LiPF₆ on Li₁₃Si₄ slabs. As done in our previous work[8], optimizations were performed using the Vienna ab initio simulation package VASP, [26–30] with the Perdew-Burke-Ernzerhof functional (GGA-PBE)[31] and the projector augmented wave (PAW) pseudopotentials provided in the VASP databases describing electron-ion interactions.[32,33] The plane wave was expanded up to a cutoff energy of 400 eV. The convergence criteria for ionic relaxation loop and for electronic self-consistent iteration were set to 10^{-3} and 10^{-4} eV respectively. A Gaussian smearing with a width of 0.05 eV was employed and a $4 \times 4x1$ k-points Monkhorst-Pack[34] mesh sampling was used in the surface Brillouin zone. The AIMD simulations were carried out on the optimized LiSi surfaces in contact with liquidphase EC (density = 1.32 g/cm^3), using the NVT ensemble at 450 K and a time step of 1 femtosecond. The Nose thermostat was used to control the temperature oscillations during the simulation with a Nose-mass parameter of 0.5, which gives a frequency of oscillation corresponding to 176 time steps. A Γ -point Brillouin zone sampling was applied in this case with a planewave energy cutoff of 300 eV. In every case, EC molecules were placed randomly in the liquid phase and a molecular dynamics minimization was performed using the consistent valence force field (CVFF) as implemented in the DISCOVER simulation software.[35] CVFF is considered good for modeling small organic crystals and gas phase structures. [36] For the minimization a smart algorithm was used combining steepest descent, conjugate gradient, and Newton methods. The maximum force among all the atoms in the system required for convergence was set to 0.001 kcal mol^{-1} ${\rm \AA}^{-1}.$ Two different initial configurations were used for each of the surfaces studied. Bader charge analysis was used to perform charge calculations.[37,38] Within this method, the total electronic charge of an atom is approximated by the charge enclosed within the Bader volume defined by zero flux surfaces. The electrolyte utilized in the AIMD simulations is composed by a 1.1 M solution of LiPF₆ and EC solvent molecules at their liquid density of 1.32 g/cm^3 . Additives were not tested in these simulations. These molecules are represented by their full electronic structure, which gives the correct dipole moment, and other higher order multipoles. For this reason, although we have not calculated the electric permittivity, we expect the experimental value to be accurately reproduced.

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