Electrochimica Acta 284 (2018) 485–494

Contents lists available at ScienceDirect

Electrochimica Acta

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

Elucidating mechanisms of Li plating on Li anodes of lithium-based batteries

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ARTICLE INFO

Article history:
Received 27 February 2018
Received in revised form
14 July 2018
Accepted 22 July 2018
Available online 24 July 2018

Keywords:
Density functional theory
Lithium electrodeposition
Plating
Uneven electron distribution
Dendritic growth

ABSTRACT

Lithium metal is known as a very promising anode material for lithium-based batteries possessing a quite high theoretical capacity. But it has been kept away from practical applications due to its extreme reactivity and potential safety hazards led by serious dendrite growth. The origins of dendrite formation may be associated with the mechanisms of Li plating and with the mode of charge transfer during Li reduction or oxidation at the anode-electrolyte interface. Here, density functional theory (DFT) calculations are conducted to analyze the electron transfer between Li (100) and Li cations located in the proximity of the surface in several simulation models. The study includes two common used solvents: ethylene carbonate and dimethoxyethane (EC and DME), and a $LiPF_6$ salt, that surround the Li cation over perfect, defect-containing, and Li_2CO_3-passivated Li (100) surfaces. Our calculations demonstrate that the Li cation is easily reduced when bonding to DME rather than EC and its preferred deposition site is the hollow site on both perfect and defective Li (100). Additionally, a compact Li_2CO_3 layer inhibits the charge transfer from Li metal to Li cations, thus modifying Li plating. It is concluded that the extreme reactivity of the Li metal surface induces a strongly inhomogeneous electron distribution upon deposition of a cation on the surface. This strong charge inhomogeneity may promote uneven Li nucleation and growth, eventually resulting in dendritic behavior.

1. Introduction

Lithium metal is considered as one of the most promising anode materials with large theoretical specific capacity of 3860 $mAh \cdot g^{-1}$ and high energy density along with the most negative electrochemical potential [1–7]. The higher demands of both large-scale energy storage system and long-range electric vehicles (EV) stimulate the design and development of high-energy battery systems, including the very promising Li-sulfur and Li-air batteries having Li metal as the anode material [8–12]. But the practical usage of the Li anode is still highly problematic because of the lack of control on the formation of a stable solid electrolyte interphase (SEI) layer (formed due to side reactions at the interface between the electrolytes and Li metal) and the formation and growth of lithium dendrites. The formation of lithium dendrites is quite detrimental to the battery system, leading to serious safety issues and low Coulombic efficiency [13,14]. Also, the growth of dendrites could contribute to formation of cracks in the SEI passivation layer, accelerating the continuous electrolyte decomposition upon contact with fresh Li metal surfaces and causing the loss of active lithium materials and electrolytes.

Recently, many experiments have been conducted to detect and observe the morphology of lithium dendrites formed on lithium metal surface by ex-situ and in-situ experimental techniques [6,15–17]. Also, plenty of efforts are devoted to suppressing and mitigating the dendrite formation, such as the addition of lithium polysulfide and lithium nitrate as additives or introducing sodium as co-depositing metals with lithium [7,18]. Furthermore, the success of lithium-halide additives in suppressing lithium dendrite growth has been verified experimentally by Archer's group [19–21]. These studies were driven by earlier simulation work, which incorporates the influences of the electrolyte environment and electrode potential using joint density-functional theory (JDFT)

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https://doi.org/10.1016/j.electacta.2018.07.159

highlighting the importance of nonlinear fluid response in battery systems [22]. Moreover, pioneering work by Arias's group using density-functional calculations compared the surface properties of various SEI components and showed that the high surface stability and fast surface diffusion of the lithium-halide SEI layer are very important for the dendrite growth suppression [23]. However, the formation and growth mechanism of lithium dendrite is still being debated because the interfacial reactions and charge transfer at the electrode-electrolyte interface are quite difficult to be tracked by experimental methods. It is known that the lithium dendrite formation on anode surfaces during the charging process starts by inhomogeneous deposition of metallic lithium (Li^0) during electrochemical reduction of Li cations according to Equation (1). Once the Li cations receive electrons and plate on the Li metal surface, the best case is the formation of an even and uniform plating layer; while the worst case is that the Li^0 electrodeposits could grow and form dendritic structures that reach the positive electrode causing the battery internal short circuit [24].

$$Li^+ + e^- = Li^0 \tag{1}$$

Therefore, analyzing the electron transfer between Li^+ and Li metal surfaces is definitely essential for the development of practical applications of Li metal as anodes by alleviating or even inhibiting dendrite formation during Li plating. Here, first-principles based density functional theory (DFT) calculations are conducted to explore the interfacial charge transfer between the Li metal surface and Li cations. As far as we know, this is the first detailed theoretical investigation to explore the charge transfer between Li metal surfaces and Li cations at the anode-electrolyte interface. Our study provides a detailed and systematic analysis about electron transfer between Li (100) and Li^+ in several simulation systems, including Li^+ deposition in solvent-containing models (EC and DME), on perfect and defect-containing Li (100) surfaces, and on SEI layer coated Li metal surfaces.

2. Computational methods

Theoretical calculations of the charge transfer between the Li cations and Li metal surfaces were performed using DFT as implemented in the Vienna Ab Initio Simulation Package (VASP) code [25,26] (VASP.5.4.1 was used in our work). The electron-ion interactions were described by the projector augmented wave method (PAW) [27,28] pseudopotentials with the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) [29] functional provided in VASP database (potpaw_PBE.54). The Monkhorst–Pack [30] method with a 2 × 2 × 1 sampling was applied into the k-point grid in the Brillouin zone with a plane-wave energy cutoff of 400 eV. A Gaussian smearing with a width of 0.05 eV was used. Optimization convergence criteria were set to be 10^{-5} eV for electronic self-consistent iterations and 0.01 eV for ionic relaxation loops. A vacuum layer of 16 Å was added into the z direction to avoid the periodic interactions. The simulation model consisting of a Li (100) slab with dimensions 13.8 Å × 13.8 Å × 26.3 Å had seven Li layers and the bottom three were fixed [31]. In some cases, Bader charge analysis [32,33] was conducted to estimate the distribution of electronic charge. In this method, the total charge of each atom is approximated by the charge enclosed within the Bader volume defined by zero flux surfaces. The mesh used for charge analysis in our work was 140 x 140 x 280. However, Bader charge analysis was not used for the Li metal atoms because as discussed by Jensen [34] the results in this case are not reliable. The Atoms In Molecules (AIM) method adopted by Bader is based on the theory that the nuclei act as attractors of the electron density; however non-nuclear attractors (pseudoatoms) exist in lithium and sodium clusters [35]. The existence of these "pseudoatoms" containing electron accumulation in regions where there is no nuclei, makes the Bader charge estimate very difficult for these systems. For this reason, an alternative method has been used here for cases involving neutral Li metal atoms. Charge density difference was calculated according to the equation: $\rho_{difference=}\rho_{total}$ - ρ_{Li_slab} - ρ_{others} (ρ_{total} represented the total charge density of the whole structure; ρ_{Li_slab} was the charge density of the Li (100) slab with or without defects and SEI components; and ρ_{others} was the charge density of introduced Li^+-PF_6^- pair in the models.) The charge density distribution diagrams were visualized by the VESTA software [36]. To analyze the charges in the Li metal atoms, the electronic density difference profile $\rho(z)$ was evaluated in planes perpendicular to the slab surface (z-coordinate), and the excess (or deficit) electrons were determined by integration of $\rho(z)dz$.

To represent the Li cation, the Li^+-PF_6^- pair was introduced in the cell, since this is a very common salt in electrolyte solutions of lithium-based batteries. To separate the ions, the coordinates of the PF_6 anion were always fixed in the vacuum space of the models. This is justified because the PF_6 anions are usually located in the bulk electrolyte solutions and the concentration of PF_6 anions is very low near the anode surfaces.

3. Results and discussion

3.1. Charge transfer in the EC-based and DME-based electrolyte systems

In electrolytes currently used in lithium-based batteries, EC and DME are very common solvents. Several possible adsorption configurations for both solvents were tested, and all the adsorption energies and calculation details are provided in Fig. S1. The most stable adsorption structures for EC and DME on Li (100) are shown in Fig. 1a and b, and the corresponding adsorption energies are −0.74 eV and −0.64 eV for EC and DME, respectively. As shown in Table 1, upon adsorption EC obtained 0.19 e^- from the Li anode and DME obtained 0.27 e^-. Fig. 1c and d shows the charge density difference distribution diagrams for the two adsorption structures. Yellow represents the electron-accumulation area, while cyan is the electron-depletion area. Obviously, the minor charge obtained by the two solvents was mainly localized on the oxygen atoms, which were located in the electron-rich areas bonding to the lithium metal surfaces.

Next the Li^+-PF_6^- pair was introduced into the model to investigate the charge transfer at the electrode-electrolyte interface. Both the single Li cation and an EC-solvated Li cation were added into the EC adsorption model as shown in Fig. 2a and b. From the Bader charge analysis results (Table 1), compared to the only 0.19 e^- transfer in the adsorption model, 1.87 e^- were transferred to EC from the Li (100) surface after the addition of the Li^+-PF_6^- pair into the simulation model. The number of electrons transferred to EC was almost the same whether the Li^+ was solvated by one or two EC molecules with the transferred charge of 1.87 e^- and 1.95 e^-, respectively. This was also verified again by the very similar charge density distributions shown in Fig. 2c and d, where the only difference was the adsorbed EC decomposed by the spontaneous C–O bond cleavage after the structure optimization when the Li cation was solvated by two EC solvent molecules. Therefore, both the Li^+-PF_6^- pair and solvated-Li^+ contributed to the charge transfer to the EC solvents, enhancing the tendency for EC to be reduced on anode surfaces, while the Li^+ remained as a cation in the Li^+-PF_6^- ion pair (Table 1). However, when the Li cations were added to the DME adsorption structures (Fig. 3a and b), DME still obtained very small amount of charge from the Li metal. Instead, the Li cations received