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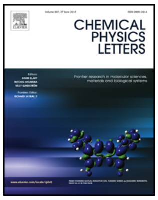

Electrochemical reduction of an anion for ionic-liquid molecules on a lithium electrode studied by first-principles calculations

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ABSTRACT

We report *ab initio* molecular dynamics studies with electric field that reveal chemical stability of room temperature ionic liquid for charge transfer from lithium and nickel electrodes. Bis(trifluoromethanesulfonyl)imide (TFSI) is oxidized on the nickel electrode under a high positive bias condition as expected. However, TFSI is reduced on the lithium electrode under both positive and negative bias conditions, because the lithium electrode acts as a strong reductant. The decomposition of TFSI anion might induce the formation of LiF as a solid electrolyte interphase, which could restrain the TFSI reduction. The stability of an cation under reductant conditions is presented.

Lithium secondary batteries have recently become one of the most important energy devices for numerous applications ranging from mobile phones to vehicles and planes. Particularly, Li-air batteries have attracted enormous interest as potential devices for future electric vehicles [1]. Compared with conventional lithium-ion batteries, Li-air batteries have a huge energy density since they use oxygen gas in the air as their cathode material. Rechargeable Li-air batteries with a nonaqueous electrolyte solution were first proposed in 1996 [2]. Various systems have been tested since then. A new type of battery with a hybrid electrolyte including both organic and aqueous electrolytes separated by a lithium superionic conductor glass (LISICON) was developed by Zhou's group [3], who confirmed that it had a very large capacity. Batteries using several kinds of electrolyte (e.g., solids and gels) have recently been proposed [4,5].

The safety of Li-air batteries poses an important issue for practical applications. Owing to the high reactivity of water with lithium, organic liquids are typically used as a solvent for the electrolyte. However, organic liquids are unfavorable from the perspective of safety because they are flammable. In place of organic solutions, room-temperature ionic liquids (RTILs) have become attractive candidates for electrolytes because of their nonflammability and nonvolatility. Although RTILs have been studied vigorously to resolve the problems in applying them to batteries [6,7], many problems remain.

The electrochemical stability of RTIL is one of the remaining problems. *Ab initio* calculations have been applied to reveal the stability and electronic structure of RTILs on electrodes. Ong discussed the electrochemical window of typical RTILs by considering the HOMO-LUMO gap estimated through the use of density functional theory (DFT) and classical molecular dynamics [8], identifying the reductive instability of bis(trifluoromethanesulfonyl)imide (TFSI) in N-propyl,N-methylpyrrolidinium–TFSI RTIL. Valencia examined the atomic and electronic structures of the interface between 1-ethyl,3-methyl-imidazolium tetrafluoroborate and the Li(1 1 0) surface [9]. Although these works clarify the basic properties of RTILs in lithium batteries, research of the reaction path on electrodes has thus far been insufficient.

Cyclic voltammetry for RTILs has revealed complex reactions on Li electrodes [6]. There are still many unsolved reactions and phenomena occurring at the interface between RTIL and the lithium electrode. The formation of a solid electrolyte interphase (SEI) is one of them. The SEI is expected to protect the electrode surface from chemical reactions. Howlett characterized the SEI formed on a lithium electrode in an N-methyl,N-alkylpyrrolidinium–TFSI RTIL by using X-ray photoelectron spectroscopy (XPS) [10]. They suggested that the SEI in the vicinity of the lithium surface is composed mainly of LiF, which is the reduction product of TFSI. Other experiments have also indicated the cleavage of C–F bonds in TFSI and fluorinated amides [11,12]. Understanding the SEI formation process will require a detailed analysis of these electrochemical reactions on lithium and other electrodes.

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To understand the electrochemical reactions at RTIL–electrode interfaces under bias conditions, we study them with *ab initio* molecular dynamics (AIMD) based on DFT [13,14]. An electric field at the interface is applied by using the effective screening medium (ESM) method [15,16]. Through the use of the ESM method, we can simulate the chemical reactions induced by various charged conditions. AIMD simulations of water decomposition on biased platinum electrodes were successfully performed [17,18]. We impose the ESM boundary condition of ideal metal and vacuum on the top and the bottom sides of the calculation cells, respectively. When the excess charge is added to the cell, the counter charge is introduced into the ideal metal side of ESM boundary in order to keep charge neutrality. This boundary condition is called as a boundary condition (iii) in Ref. [16].

We focus on the reactions of N-methyl,N-propylpiperidinium (PP13) and TFSI in this letter. Lithium and nickel are adopted as electrodes because nickel is typically used in current collectors and battery cases. We find that on a nickel electrode the oxidization reaction of TFSI occurs on the positively biased electrode as expected, whereas the reduction of the TFSI anion takes place with the charge transfer to the lithium electrodes under the same bias conditions. This process involves the breaking of C–F bonds and the movement of fluorine atoms onto the lithium electrode, which leads to the formation of LiF on the lithium electrode surface as SEI. The LiF formation observed here supports the experimental results reported previously [10].

AIMD simulation is performed within the Born–Oppenheimer (BO) approximation [19] using the code ‘STATE’ [20] to obtain both atomic configurations and the electronic structures. The exchange-correlation functional is treated within the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) [21]. The AIMD scheme does not include van der Waals force. But, it will give reasonable chemical reaction, since main molecular interaction between ions and charged electrodes is Coulombic and during the chemical reaction van der Waals force will not give the large influence.

About the spin polarization, we analyzed the electronic structure of the RTIL–electrode system with and without it. Both cases gave the similar DOS and the HOMO-LUMO levels relative to the Fermi level. Therefore, only the spin unpolarized electronic structure is considered in the whole calculations for saving the computational costs. Our simulation will capture nature of reactions also reasonably. The detail of the electronic structure is carried on supporting information.

The ultrasoft-pseudopotential scheme combined with plane-wave basis sets imposing cutoff energies of 25 and 225 Ry is used to describe the Kohn–Sham orbitals and the electron density, respectively [22]. The Brillouin-zone summation is evaluated by using a $2 \times 2 \times 1$ k-point grid. The time interval in the AIMD calculations is set to be 1.2 fs. We replace the H atoms in the system with deuterium atoms to increase the time interval in AIMD. Each simulation is carried out at a temperature of 353 K, which is controlled by the velocity scaling method. The charge amounts of ionic molecules and electrode are estimated by using Bader analysis [23–26]. To discern the nature of the electrochemical reactions from a simple model and to reduce computational cost, we model the interfaces as follows: a molecular pair of PP13 and TFSI as the RTIL are placed on Ni and Li electrodes as shown in Fig. 1 after the pair structure has been optimized in vacuum. The Ni(1 1 1) electrode includes three atomic layers in the z direction with a $5 \times 2\sqrt{3}$ lateral periodicity of 12.50Å × 12.99 Å; the Li(1 1 0) electrode includes four atomic layers in the z direction with a 4×4 lateral periodicity of 13.96Å × 13.96 Å. The positions of atoms at the bottom layer of the electrodes are fixed for all molecular dynamics calculations. The electrostatic field induced by charge on the electrode is taken into account by using the ESM method. We change the electron number in the RTIL–electrode system to control the electrode charge. The additional charge introduced into the system (*i.e.*, excess charge, Q_{ex}) is $-1e$ to $+1e$. In the case of the nickel electrode, we additionally simulate a system with an excess charge $Q_{ex} = +2e$ to encourage chemical reactions. Adding negative or positive charge into the system by using the ESM method corresponds to imposing a negative or positive bias condition at the interfaces, respectively. A counter charge of the excess charge is induced onto the boundary conditions of the ESM method unlike the uniform-background-charge approach.

Table 1
Time evolution of the charges[a] of a TFSI anion, a PP13 cation and a nickel electrode under excess charges Q_{ex}.

$Q_{ex} = -1e$			
Time [ps]	0.00	0.12	0.24
TFSI	−0.87	−0.91	−0.77
PP13	0.31	0.40	0.12
Ni electrode	−0.44	−0.49	−0.35
$Q_{ex} = 0$			
Time [ps]	0.00	0.12	0.24
TFSI	−0.98	−0.95	−1.03
PP13	0.75	0.73	0.75
Ni electrode	0.23	0.22	0.28
$Q_{ex} = +1e$			
Time [ps]	0.00	0.12	0.24
TFSI	−0.40	−0.42	−0.58
PP13	0.70	0.91	1.07
Ni electrode	0.70	0.51	0.51
$Q_{ex} = +2e$			
Time [ps]	0.00	0.12	0.18
TFSI	0.00	0.72	0.91
PP13	1.28	0.92	0.93
Ni electrode	0.72	0.36	0.16

[a] ‘Charge’ is determined by summing the Bader charges for each atom.

When an excess charge $Q_{ex} = -1e$ is introduced into the nickel electrode system, the ionic pair of TFSI and PP13 does not react during the 1 ps simulation time. Electrons are mainly introduced on the electrode surface under such a negative bias condition, causing a cation of PP13 to be attracted by the nickel electrode and an anion of TFSI to be repelled from the surface. Increasing Q_{ex} from $-1e$ to $+2e$ causes TFSI to decompose within the 1 ps simulation time. A nitrogen atom in the TFSI anion is at ~4.6 Å from the nickel electrode when the TFSI decomposes. The time evolution of S–C and C–F bond lengths is shown in Fig. 2a. The C–F bond length is kept around 1.35 Å during the simulation. But, an S–C bond in TFSI is split within 0.1 ps after the excess charge $Q_{ex} = +2e$ is introduced, as shown by a broken line in Fig. 2b, and a unit of CF_3 is finally separated from TFSI.

To analyze the decomposition reaction of TFSI from the standpoint of charge transfer, we calculate the charge amount of the TFSI anion, the PP13 cation, and the nickel electrode as listed in Table 1. When an excess charge $Q_{ex} = +2e$ is introduced, the charge of TFSI is neutral, which means that it is oxidized. During the reactions from 0 to 0.12 ps, charge transfer takes place from the electrode as well as from the cation to the anion. Most of the charge on the electrode surface transfers to TFSI within 0.18 ps, indicating that the decomposition reaction on the nickel electrodes is oxidation of TFSI by the positively charged electrode. This kind of reaction is expected under such a high positive bias condition.

The charge transfer is understood from the DOS analysis. DOS of cation, anion, and electrode are separately determined by