Electrochimica Acta 56 (2011) 10424–10435

Contents lists available at ScienceDirect

Electrochimica Acta

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

On the difference in cycling behaviors of lithium-ion battery cell between the ethylene carbonate- and propylene carbonate-based electrolytes

Ken Tasaki[a,*], Alexander Goldberg[b], Martin Winter[c]

[a] Mitsubishi Chemical Holdings America, 410 Palos Verdes Blvd., Redondo Beach, CA 90277, United States
[b] Accelrys Software Inc., 10188 Telesis Ct., San Diego, CA 92121, United States
[c] Institut für Physikalishe Chemie, Westfälishe Wilhelm-Universität Münster, Corrensstr., D-48149, Münster, Germany

ARTICLE INFO

Article history:
Received 12 November 2010
Received in revised form 25 May 2011
Accepted 26 May 2011
Available online 1 July 2011

Keywords:
Ethylene carbonate
Propylene carbonate
Lithium desolvation
Ternary graphite intercalation compounds

ABSTRACT

Density functional theory (DFT) calculations and classical molecular dynamics (MD) simulations have been performed to gain insight into the difference in cycling behaviors between the ethylene carbonate (EC)-based and the propylene carbonate (PC)-based electrolytes in lithium-ion battery cells. DFT calculations of the lithium solvation, $Li^+(S)_i$ (S = EC or PC; i = 1–4) with and without the presence of the counter anion showed that the desolvation energy to remove one solvent molecule from the first solvation shell of the lithium ion was significantly reduced by as much as 70 kcal mol^{-1} (293.08 kJ mol^{-1}) in the presence of the counter anion, suggesting the lithium ion is more likely to be desolvated at high salt concentrations. The thermodynamic stability of the ternary graphite intercalation compounds, $Li^+(S)_iC_{72}$, in which $Li^+(S)_i$ was inserted into a graphite cell, was also examined by DFT calculations. The results suggested that $Li^+(EC)_iC_{72}$ was more stable than $Li^+(PC)_iC_{72}$ for a given i. Furthermore, some of $Li^+(PC)_iC_{72}$ were found to be energetically unfavorable, while all of $Li^+(EC)_{i=1-4}C_{72}$ were stable, relative to their corresponding $Li^+(S)_i$ in the bulk electrolyte. In addition, the interlayer distances of $Li^+(PC)_iC_{72}$ were more than 0.1 nm longer than those of $Li^+(EC)_iC_{72}$. MD simulations were also carried out to examine the solvation structures at a high salt concentration of $LiPF_6$: 2.45 mol kg^{-1}. The results showed that the solvation structure was significantly interrupted by the counter anions, having a smaller solvation number than that at a lower salt concentration (0.83 mol kg^{-1}). We propose that at high salt concentrations, the lithium desolvation may be facilitated due to the increased contact ion pairs so as to form a stable ternary GIC with less solvent molecules without destruction of graphite particles, followed by solid–electrolyte-interface film formation reactions. The results from both DFT calculations and MD simulations are consistent with the recent experimental observations.

1. Introduction

It has long been known that a lithium-ion battery cell having graphite as the anode active material in the EC-based electrolyte can be cycled between the charged and discharged states, while charging of a similar cell in the PC-based electrolyte only results in continued decompositions of PC and exfoliation of graphite [1–3]. There have been a large number of reports discussing the electrochemical differences between the two electrolytes experimentally as well as theoretically [1–8]. Yet, there is no widely accepted single explanation for this observation. It has also been reported that while a Li-ion battery cell can be cycled in electrolytes using linear carbonates such as dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) as the solvent, cycling is difficult when diethyl carbonate (DEC) is used [9]. This is a series of reports to examine the electrochemical differences among solvents in terms of cycling behaviors [8]. Here we focus on the difference between EC- and PC-based electrolytes. The difference in cell behaviors between the two solvents is as much of scientific interest as of industrial one. For example, PC can be used for a wide range of temperatures: its melting point is −49 °C, whereas EC has the melting point of 36.4 °C. It has been reported that addition of PC to the electrolyte significantly improved the low temperature performance of Li-ion battery cells, compared to a cell without PC [10].

As for the mechanism on the difference in the cycling behavior between the two solvents, the co-intercalation model has been extensively used [1,11–15], though other models have been proposed based on the graphite surface processes [16–22]. From a theoretical point of view, exhaustive calculations on the reductive decomposition intermediates have been performed by Balbuena and co-workers, though their results were inconclusive to explain the striking difference between EC and PC [5,6]. Further, graphite

---

* Corresponding author. Tel.: +1 310 373 4196.
E-mail address: ken_tasaki@m-chem.com (K. Tasaki).

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.05.112

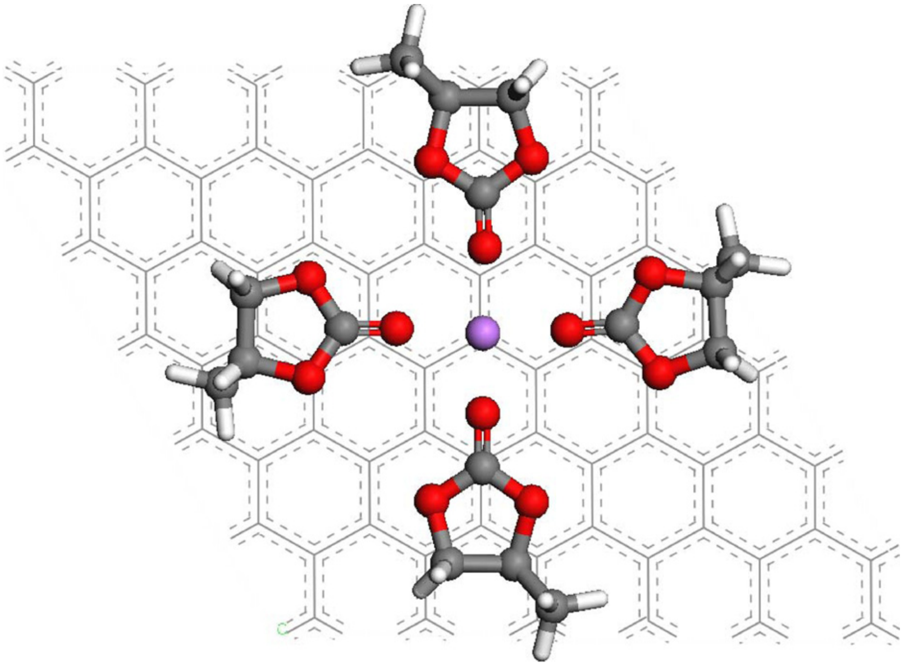

Fig. 1. A unit cell for the ternary GIC with four PC molecules used in DFT calculations. The ternary GIC was inserted between graphene layers having 72 carbon atoms.

was not included in the discussion of the reactivity of EC or PC in their calculations [5,6]. Their subsequent work concerned only the adsorption of lithium alkyldicarbonates on a graphite surface [7]. If the co-intercalation model by Besenhard et al. [12] is acceptable, the electrochemical difference between the two solvents should be discussed within the context of ternary graphite intercalation compounds (GIC), $Li^{+}(S)_{i}C_{n}$, where S is EC or PC, i is the solvation number, and n is the stoichiometric number for the graphite carbon with respect to the lithium ion.

Our earlier work focused on the physical properties of solid-electrolyte-interface (SEI) film components derived from either the EC-based or the PC-based electrolyte [8]. We found from classical molecular dynamics (MD) simulations that dilithium ethylene glycol dicarbonate had a higher density, a higher cohesive energy, and a less solubility to the solvent than dilithium propylene glycol dicarbonate. The calculations were based on the surface model proposed by Aurbach et al. [22]. In this work, we discuss the cycling characteristic difference between the two solvent-based electrolytes within the framework of the co-intercalation model.

The kinetics of lithium intercalation into graphite has been extensively investigated and the activation barrier for the process has been determined by impedance spectroscopy [2,23–26]. On the other hand, the thermodynamics for the lithium co-intercalation is difficult to measure due to spontaneous decomposition reactions of co-intercalated compounds inside graphite and also side reactions associated with SEI film formation. Reynier et al. have reported the thermodynamic parameters for lithiated graphite anode materials having different lithium concentrations by open circuit potential measurements [27]. Yet, the results are not for the lithium co-intercalation process. Computational approach may help gain insight into the thermodynamic process of lithium co-intercalation.

Lately, it has been found that a lithium-ion cell having graphite as the anode can be cycled in a PC-based electrolyte when the salt concentrations were high [28]. Here, we examine the effect of salt concentration on the lithium solvation/desolvation and also the stability of the $Li^{+}(S)_{i}C_{n}$ by means of density functional theory (DFT) calculations and classical MD simulations on the difference in cycling behavior between the two electrolytes. It is known, however, that weak interactions such as van der Waals interactions, the important force for graphite, are poorly described by DFT calculations, especially within the framework of the generalized-gradient approximation (GGA) [29]. Recently, corrections have been made to the DFT formalism in order to improve the ability to describe van der Waals interactions [30]. We have tested the new corrections against the graphite crystallographic data, then applied the DFT calculations with the new corrections to a series of ternary GIC's.

2. Computational

All the DFT calculations have been performed, using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [31,32] within the framework of GGA [33]. The numerical basis sets were used for efficient computation of wave functions [34]. Typically, integration with analytical basis set functions takes longer than numerical basis sets. The triple-numerical polarization (TNP) basis set was chosen for geometry optimization of the solvation structures and the ternary GIC's, having one atomic orbital (AO) for each occupied atomic orbital, the second and the third sets of valence AO's, d-functions for non-hydrogen atoms, and p-functions on hydrogen atoms [34]. Combining the basis set TNP with the GGA-PBE functional, we refer to the theory as GGA-PBE/TNP. The calculations of the lithium ion solvation structures, $Li^{+}(S)_{i=1-4}$ (S = EC or PC), by EC and PC were carried out in the gas phase with and without the presence of the counter anion, PF_6^{-}. For geometry optimization of the solvation structures, the initial structure for $Li^{+}(S)_4$ was first constructed, based on the crystallographic data of Li(tetrahedron $(THF))_4$ [35]; then, the geometry was optimized. Once the optimized geometry for $Li^{+}(S)_4$ was determined, the solvent molecules were removed one by one successively for the geometry optimization of $Li^{+}(S)_{i=1-3}$. The solvation number of 3.7 has been recently reported for the $LiClO_4$/PC electrolyte by Yamada et al. [36]. Similar values have been also published in the literature 4.1–4.3 in $LiClO_4$/EC [37] and 3.6–4.4 in $LiClO_4$/PC [38].

For the constructions of the ternary GIC's, $Li^{+}(S)_{i=1-4}$ was inserted into a cell consisting of graphene layers having 72 carbon atoms each. The same size of graphene layer was also used in earlier calculations of intercalated graphite by another group