



# Theoretical evaluation of ethylene carbonate anion transport and its impact on solid electrolyte interphase formation



Mathew J. Boyer, Gyeong S. Hwang\*

McKetta Department of Chemical Engineering, University of Texas, Austin, TX 78712, USA

## ARTICLE INFO

### Article history:

Received 5 August 2017

Received in revised form

26 January 2018

Accepted 7 February 2018

Available online 8 February 2018

### Keywords:

Solid electrolyte interphase

Lithium ion battery

Metadynamics simulation

Free energy profile

Intermediate diffusion behavior

## ABSTRACT

Despite its critical role in determining the performance of lithium ion batteries (LIBs), evolution of the chemical composition and morphology of the solid electrolyte interphase (SEI) formed on graphite negative electrodes remains poorly described even for a conventional electrolyte consisting of 1 M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC), which is considered here. The EC<sup>-</sup> radical anion produced from one-electron reduction of EC is known to be a key intermediate responsible for the formation of two commonly found products in the SEI, carbonate (CO<sub>3</sub><sup>2-</sup>) and ethylene dicarbonate (EDC<sup>2-</sup>). We evaluate the diffusion behavior of EC<sup>-</sup> associated with solvent reorganization near the graphite electrode using molecular dynamics (MD) and metadynamics simulations. The predicted free energy profiles of EC<sup>-</sup> transport at the onset of SEI formation show two distinct minima, depending on the EC:DMC ratio of the solvent and the voltage applied to the electrode. EC<sup>-</sup> radical intermediates trapped in the free energy well located at  $z = 0.65$  nm (or  $z = 1.5$  nm) from the electrode surface may favorably undergo further reduction to CO<sub>3</sub><sup>2-</sup> (or a combination reaction with another EC<sup>-</sup> to form EDC<sup>2-</sup>). Moreover, suppressed EC<sup>-</sup> migration could contribute to the formation of a thin, compact SEI layer. This study highlights that in addition to the kinetics and thermodynamics of solvent reduction, the near-electrode transport of reaction intermediates/products should be considered in modeling of SEI structure and growth.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Over the past few decades, lithium ion batteries (LIBs) have fueled a technological revolution due to their high energy density, light weight, low self-discharge rate, and long cycle life. The superior properties have allowed for advancements in portable electronic devices, but further improvement of these properties is required for a transition to widespread use in electric vehicles, particularly expansion of energy density, power density, and cycle life while maintaining safe operability. This challenge has prompted a need for further understanding of the properties of electrode and electrolyte materials and their interfaces [1–7].

For a LIB to operate safely, the electrolyte must be stable under the oxidative and reductive conditions of both the cathode and anode, respectively, or the electrolyte must be able to form a very thin, electrically insulating but ionic conducting solid-like layer upon cycling. The interfacial layer has been termed the solid

electrolyte interphase (SEI) [8–13]. Dahn and coworkers first showed that stable SEI could be formed on a graphite anode using an electrolyte based on ethylene carbonate (EC) [14]. Tarascon and Guymard added dimethyl carbonate (DMC), which can form a homogenous mixture with EC at any ratio, to reduce the electrolyte viscosity [15,16]. Aurbach et al. have since studied in great detail the SEI formed at the interface between a graphite anode and electrolytes based on these solvent mixtures [10]. It has been widely reported that when present, EC acts as the primary SEI-forming agent [17–20]. Upon single-electron reduction, EC may favorably undergo a ring-opening reaction to form a stable radical anion (EC<sup>-</sup>) [21]. This radical anion can then either be further reduced to produce carbonate (CO<sub>3</sub><sup>2-</sup>) and ethylene (C<sub>2</sub>H<sub>4</sub>) or combine with another EC<sup>-</sup> to form ethylene dicarbonate (EDC<sup>2-</sup>) and C<sub>2</sub>H<sub>4</sub> [22–24]. The reductive decomposition reactions of EC have also been extensively studied using first-principles calculations, in the gas phase [25,26], in solution [27,28], and at interfaces [29,30]. However, evolution of composition and morphology of the SEI layers formed on graphite electrodes from EC-based electrolytes still remains poorly described. This can be largely attributed to the

\* Corresponding author.

E-mail address: [gshwang@che.utexas.edu](mailto:gshwang@che.utexas.edu) (G.S. Hwang).

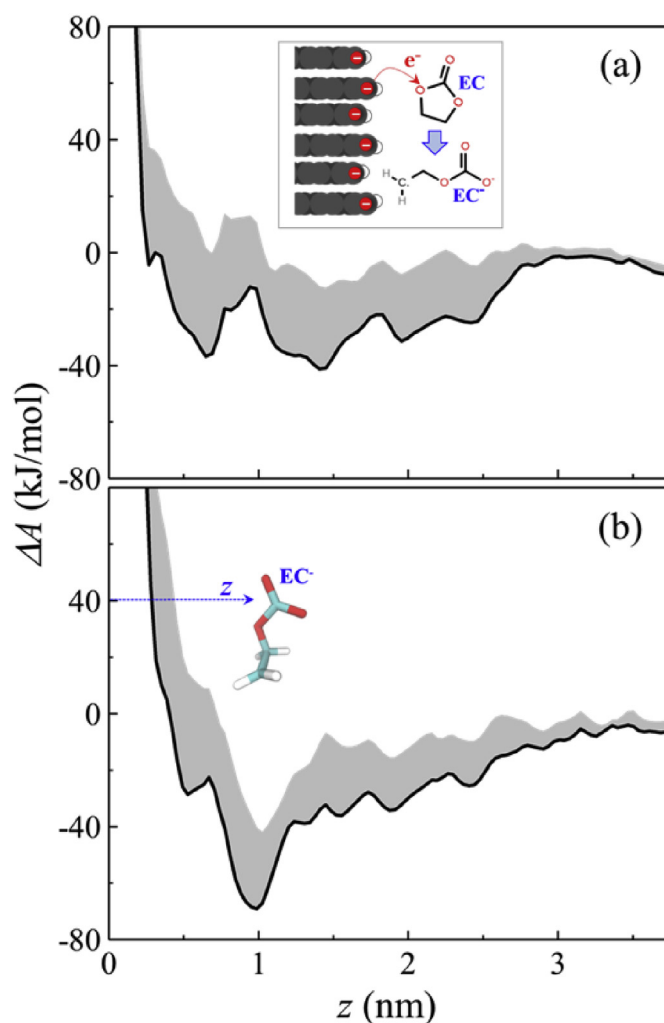
dependence of the SEI structure on its growth process, which is strongly governed by electrochemical and chemical reaction kinetics, intermediate/product diffusion, and product precipitation near the electrode. Kinetically controlled growth of the SEI layer can be well demonstrated by the strong temperature dependence of capacity fade associated with SEI formation [31]. In particular, the reaction-diffusion behavior of intermediates such as  $\text{EC}^-$  would directly influence the SEI structure and the parasitic loss of active material. Furthermore, the rate processes and in turn the SEI structure and growth can be significantly influenced by electrolyte composition and operating voltage in addition to temperature.

Previous experiments have shown that, for conventional electrolytes consisting of mixtures of EC and DMC, the EC:DMC ratio strongly affects SEI properties. Resistance associated with  $\text{Li}^+$  migrating through the SEI was shown to decrease as more DMC is added to an EC-based electrolyte [32]. This was done by comparing the area-independent activation energy of lithiation of graphite [19,32,33] to lithium titanate anode (known to form no SEI) [4]. Additionally, it was shown that the operating voltage range at which a stable SEI is formed on graphite also changes with EC:DMC ratio [18]. While the SEI structure tends to change with the solvent mixture ratio of EC:DMC [17], it has been speculated that the formation of  $\text{EDC}^{2-}$  would be more likely in systems with relatively high EC concentrations due to the increased likelihood of  $\text{EC}^-$  combination [23]. However, to explain these observations, further research is needed to gain more insight into the underlying processes of SEI formation and how they are affected by electrolyte composition, temperature, and operating voltage.

In this work, we employ classical molecular dynamics (MD) simulations combined with an advanced sampling technique to determine the structural reorganization of solvent molecules and examine its effect on the diffusion behavior of an  $\text{EC}^-$  radical anion near a graphite electrode in 1 M  $\text{LiPF}_6/\text{EC}:\text{DMC}$  electrolyte, at the onset of SEI layer formation. The relative free energy ( $\Delta A$ ) profiles for  $\text{EC}^-$  migrating from the electrode towards the bulk electrolyte are calculated and analyzed using well-tempered metadynamics simulations. The influences of solvent composition and applied voltage are considered by varying the EC:DMC molar ratio and the electrode surface charge, respectively. The predicted free energy profiles provide new insights into trapping/diffusion of  $\text{EC}^-$  near the electrode, which may directly influence evolution of the composition and structure of the SEI. The presence of free energy minima may suppress the migration of  $\text{EC}^-$  away from the electrode, which may in turn enhance its further reduction (or combination) to  $\text{CO}_3^{2-}$  (or  $\text{EDC}^{2-}$ ) near the electrode, possibly contributing to the formation of a thin and compact SEI layer. Contrarily, facile diffusion of  $\text{EC}^-$  towards the bulk electrolyte may lead to thicker, more diffuse SEI forming. The particular factors contributing to the presence (or lack) of these minima enabling the suppression of  $\text{EC}^-$  away from the electrode are discussed in detail.

## 2. Results and discussion

Fig. 1 shows predicted Helmholtz free energy ( $\Delta A$ ) profiles for  $\text{EC}^-$  in 1 M  $\text{LiPF}_6/\text{EC}:\text{DMC}$  electrolyte with EC:DMC molar ratios of (a) 1:3 and (b) 1:1, along the perpendicular direction of the electrode surface, from well-tempered metadynamics simulations [34]. The 1:1 and 1:3 mixtures of EC:DMC will hereafter be referred to as EC-rich and DMC-rich, respectively. Here, the  $z$  position is that of the carbonate C of  $\text{EC}^-$  with respect to a graphite edge, which is negatively charged with a surface charge density of  $\sigma = -9.7 \mu\text{C}/\text{cm}^2$  (corresponding to approximately 1.2 V vs.  $\text{Li}^+/\text{Li}(s)$ ), where electrolyte reduction tends to begin [1,35]). Here,  $\text{EC}^-$  is assumed to be in the ring-opened conformation which is thermodynamically favorable compared to the intact ring structure, although there may



**Fig. 1.** Relative free energy ( $\Delta A$ ) profiles with standard deviation (grey area) from the minimum energy path (black line) for the position of the carbonate C atom in reduced ethylene carbonate ( $\text{EC}^-$ ) along the axis perpendicular to the graphite electrode for (a) EC:DMC 1:3 and (b) EC:DMC 1:1. The negative electrode is charged at  $\sigma = -9.7 \mu\text{C}/\text{cm}^2$ . The inset graphic depicts the reduction mechanism of EC to  $\text{EC}^-$  by electron transfer from the graphite edge ( $z=0$ ).

exist a sizable energy barrier for the ring-opening of  $\text{EC}^-$  anion, depending on the solvation environment. Five independent metadynamics simulations with different initial configurations were conducted in order to ensure that the minimum  $\Delta A$  was sampled across the  $x$ - $y$  plane at each  $z$  position. From the multiple trials, the standard deviation in  $\Delta A$  was also calculated to approximate potential deviations from the minimum path.

From the predicted  $\Delta A$  profiles, it can be seen that the DMC-rich case [(a)] exhibits a clear minimum at  $z \approx 0.6$  nm with a shoulder at  $z \approx 0.5$  nm. Moving away from the electrode surface, another minimum appears at  $z \approx 1.4$  nm with another shoulder at  $z \approx 1.3$  nm. From here, there is a steady increase with some minor oscillations until  $z = 2.7$  nm, where the profile flattens out at  $\Delta A \approx 40$  kJ/mol (relative to the second minimum) due to the bulk-like nature of the electrolyte beyond  $z \approx 3$  nm. Contrarily, the EC-rich case [(b)] shows no clear minimum at  $z < 0.7$  nm, but rather a small dip on the order of the oscillations in the bulk. Moving away from the electrode, there is a pronounced minimum at  $z \approx 1$  nm which is followed by a gradual increase until  $z > 3$  nm where it levels off at  $\Delta A \approx 70$  kJ/mol (relative to the minimum).

Download English Version:

<https://daneshyari.com/en/article/6604033>

Download Persian Version:

<https://daneshyari.com/article/6604033>

[Daneshyari.com](https://daneshyari.com)