



# Multiphysics modeling of lithium ion battery capacity fading process with solid-electrolyte interphase growth by elementary reaction kinetics



Yuanyuan Xie, Jianyang Li, Chris Yuan\*

Department of Mechanical Engineering, University of Wisconsin Milwaukee, Wisconsin 53211, USA

## HIGHLIGHTS

- A pseudo two dimensional multi-physics lithium ion battery model is developed.
- The elementary reaction based SEI layer generation is simulated.
- The battery multi-transport processes are coupled with SEI formation.
- The battery capacity fading processes are studied under different operating conditions.

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## ABSTRACT

A pseudo two-dimensional mathematical model is developed for a lithium ion battery, integrating the elementary reaction based solid-electrolyte interphase (SEI) growth model with multiple transport processes. The model is validated using the experimental data. Simulation results indicate that the operating temperature has great effect on the SEI layer generation and growth. Under different charging–discharging rates, it is found that high charging–discharging rate can intensify the battery capacity fading process. Different cooling conditions are then applied and show that enhanced surface convective cooling condition can effectively slow down the battery capacity fading. After that, the effect of electrolyte salt concentration and exchange current density are studied. It is found that raising the electrolyte salt concentration can improve the diffusion property of lithium ions, and stabilize the battery performance under lithium ion consumption induced resistance rising. It also suggests that improving exchange current density could greatly decrease the lithium ion battery capacity fading.

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## 1. Introduction

The rechargeable lithium ion battery is one of the most popular energy storage devices for its high energy density, low energy-weight ratio, small self-discharging and environmental suitability [1]. These beneficial properties as well as low costs have established the rechargeable lithium ion battery as a promising candidate for the next generation automotive and aerospace applications [2]. However, during the charging–discharging cycles or the storage at elevated temperature conditions, lithium ion batteries typically exhibit capacity fading process.

Numerous capacity fading mechanisms of lithium ion battery have been proposed, including electrolyte decomposition, active material degradation, surface film formation, overcharging, self-discharging, and phase change. It is believed that the irreversible

capacity loss during the first few charge–discharge cycles is primarily due to the formation of a passivating film on the negative electrode surface [3,4]. This so-called solid electrolyte interphase layer (SEI) is formed at the first time when the electrode contacts the electrolyte solvent [5]. It can isolate the negative electrode from the electrolyte solvent and minimize further reduction reactions of electrolyte components, through which the lithium ions are transported by vacancies and interstitials to reach the active electrode. Typically, the SEI consists of two distinct layers: an inorganic layer and an organic layer. The inorganic layer is a compact layer. It is close to the electrode and in several nanometers thick. The organic layer is a porous layer and on the electrolyte side, which is usually on the order of hundred nanometers thick [6]. The SEI formation can act as a barrier to prevent the electrolyte solvent cointercalation, but the excessive SEI formation may lead to undesirable lithium ions consumption and active electrode area reducing, which finally causes irreversible capacity fading. Experimental studies [7] indicated that the selection of electrolyte solvent and electrode structure could

\* Corresponding author. Tel.: +1 414 229 5639; fax: +1 414 229 6958.  
E-mail address: [cyuan@uwn.edu](mailto:cyuan@uwn.edu) (C. Yuan).

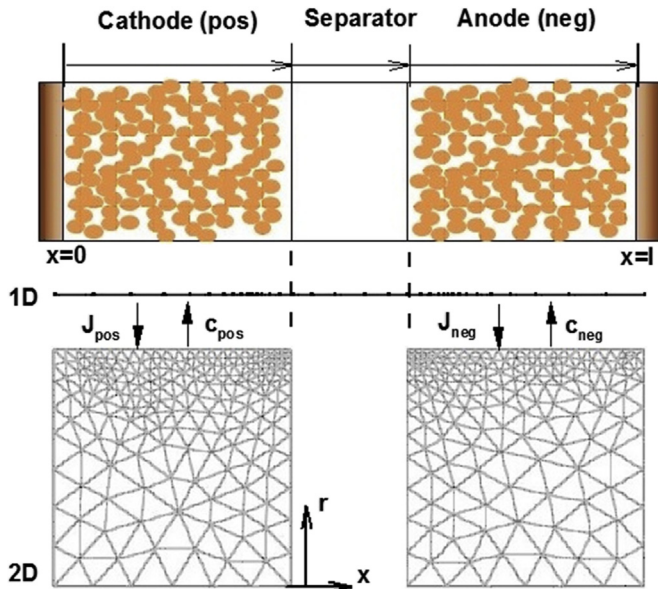


Fig. 1. Physical base and modeling approach.

have crucial effect on the formation and composition of SEI layer. Besides, during the charging–discharging cycles, the operating conditions of lithium ion battery also have been proved to play a very important role on the SEI layer growth and repair [8–10]. Due to the experimental works cannot fundamentally understand these multi-physics processes, modeling approach, as an important complementary, may provide significant advantages to reduce the experimental efforts through exploring the battery performance under different operating conditions.

In literature, various mathematical models have been proposed to reveal the formation and growth of the SEI layer [11–17]. Based on the assumption that the diffusion of electrons through the SEI layer is the rate-determining step, the parabolic law models were developed by Peled [11], Broussely et al. [12] and Ramadass et al. [13], where the side reactions were assumed to occur on the interface between SEI layer and electrolyte. Instead of assuming electron diffusion is rate-determining, Ploehn et al. [14] proposed a SEI formation model by considering the diffusion of solvent through the SEI porous layer as the rate-determining step, of which the numerical results match with the experimental observations fairly well. To study the detailed surface chemistry of SEI layer formation, elementary reaction mechanism was proposed by Aurbach et al. [15], and the reaction based SEI growth models were developed by Christensen et al. [16] and Colclasure et al. [17]. These models all focused on the SEI layer formation process while the battery level models are simplified. Since the lithium ion battery performance highly depends on the operating conditions, it is needed to couple the SEI growth model with the battery level model, so that it can provide more accurate prediction for the battery cycling behavior and the associated processes. However, few such kind multi-physics models [18–22] recently have been presented. Cai et al. [18] incorporated the energy conservation into a multi-physics lithium ion battery life model without the effect of SEI growth. Vazquez-Arenas et al. [19] combined the SEI induced capacity fading model with lithium ion battery model and studied thermal effects on the cycling process. Awarke et al. [20] also proposed a multi-physics model by coupling the electron-diffusion determined SEI growth model with lithium pouch cell model. However, none of them has considered the complicate reaction mechanisms during SEI layer formation. Since the detailed chemistry of SEI formation is critical to study lithium

ions intercalation and transport in the electrolyte solution, the objective of this paper is to develop a multi-physics lithium ion battery fading model by coupling the elementary reaction kinetics of SEI layer formation.

In this study, a pseudo two dimensional mathematical model of lithium ion battery is developed, which has bridged multi-physical transport processes with elementary reaction based SEI growth model in a coherent way. Comprehensive simulation studies are performed to investigate the effect of various operating conditions on the battery output performance and capacity fading process.

## 2. Mathematical model

A lithium ion coin cell has been utilized as the physical base of the developed mathematical model in this paper. Fig. 1 shows the schematic illustration of its structure, which consists of a negative electrode ( $\text{Li}_x\text{C}_6$ ), a separator, a positive electrode ( $\text{Li}_y\text{Mn}_2\text{O}_4$ ) and two current collectors on the electrode ends. The electrolyte solution is 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume fraction ratio of 1:2. The proposed reaction mechanisms of passive film formation on the negative electrode have indicated that the inorganic products, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), is one of the major passive film composition [15]. Although the experimental studies showed that SEI layer could also be formed on positive electrode [16,23], our following mathematical model would only consider its effect on graphite negative electrode. The governing equations of the model include elementary reactions and multi-physics transport processes.

### 2.1. Elementary reaction kinetics

According to Aurbach [15] and Newman [16], the elementary reaction steps of  $\text{Li}_2\text{CO}_3$  formation can be simplified as following,

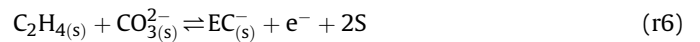
1) The adsorption–desorption reactions:



2) The film formation reaction:



3) The charge transfer reactions:



where, the subscript (s) stands for the adsorbed species, S is the available surface site. The forward and backward reaction rate coefficients,  $k_f$  and  $k_b$ , are listed in Table 1. The net reaction rate  $r_n$  can be determined as,

$$r_n = k_f^n \prod_i [c_i^{\text{Rct}}]^{s_i} - k_b^n \prod_i [c_i^{\text{Prd}}]^{s_i} \quad (1)$$

and the elementary kinetic description of charge transfer can be formulated by Butler–Volmer expression,

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