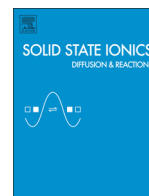




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# Numerical investigation of kinetic mechanism for runaway thermo-electrochemistry in lithium-ion cells

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## ABSTRACT

Thermal runaway of lithium-ion cells is a complex process governed by heat production due to thermal decomposition reactions and heat transport within the cells. Exothermic characteristics are simulated for solid electrolyte interface (SEI) on anode of a Li-ion cell. As a pilot study preliminary to building thermal runaway mitigation system, exothermic SEI decomposition and formation reactions are included in thermo-electrochemical 1D model in addition to lithium insertion in multi-scale model of battery kinetics. Differential scanning calorimetry (DSC) simulations of negative electrode are used to parameterize and validate the model against experiments in literature. Simulations under constant and rising ambient temperature show the onset of runaway at temperatures around 400 K.

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## 1. Introduction

Lithium-ion cells have been one of the most popular rechargeable batteries due to their attractive properties such as high energy densities, long lifetimes and absence of memory effect. However, they are mostly currently limited to portable applications especially because of safety concerns [1]. Thermal runaway can be triggered by extreme conditions like external heating, overcharge, external or internal short circuit and leads to uncontrolled heat release by various chemical reactions in the cells. Several investigations have been conducted to understand the phenomena occurring at elevated temperature [2]. It is reported that solid electrolyte interface (SEI) decomposition inside the anode is initiated at around 363–393 K [3], followed by the reaction of intercalated lithium with electrolyte. These phenomena are exothermic and decompositions of passivation layer as well as electrolyte are involved. Hence they are considered to be a part of the chain reactions which lead to severe thermal runaway of a cell. Numerical modeling is an ideal tool to understand, analyze and avoid such complex processes which are based on the interaction of heat release and heat transport. Numerical simulations have been carried out for a combination of exothermic processes by Spotnitz et al. [2], however without comparison to experimental results.

In this work, modeling and simulation of exothermic characteristics of SEI reactions are presented. The electrode model is validated against differential scanning calorimetry (DSC) experiments from literature [4].

We furthermore present a 1D full cell simulation including the exothermic reactions at elevated temperature and under temperature ramp.

## 2. Modeling and simulation

### 2.1. Approach

The thermo-electrochemical model used in this work is designed to understand electrochemical and thermochemical kinetics in the range from micro to macro scales [5]. Lithium insertion and extraction through active materials are:



They are assumed to follow the Butler–Volmer kinetics. Computational domain is 1D and is homogeneously discretized.

### 2.2. Solid electrolyte interface (SEI)

SEI is a product of solvent decomposition which mainly occurs at the surface of the negative electrode particles (typically, graphite with intercalated lithium) [6,7]. Yang et al. investigated the composition of SEI film by Fourier transform infrared and mass spectroscopy and show that  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  is the main component for ethylene carbonate (EC) solvent, and only EC is decomposed in a binary solvent consisting of ethylene carbonate–diethyl carbonate (EC–DEC) or ethylene carbonate–

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dimethyl carbonate (EC–EMC) [8]. Wang et al. studied the detailed reduction mechanisms of EC by density functional theory and concluded that the SEI film consist of two lithium alkyl bicarbonates, lithium butylene dicarbonate ( $(\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li})_2$ ) and  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  [9].

In this work, SEI is assumed to consist of  $(\text{CH}_2\text{OCO}_2\text{Li})_2$ . EC–DMC (2:1) solvent is assumed which allows the comparison with experimental DSC results of Pasquier et al. [4]. As an initial condition, we assume an SEI film thickness of  $0.1 \mu\text{m}$  [10] surrounding active material particles with a radius of  $1 \mu\text{m}$ . A volume fraction of active material in the negative electrode of 0.332 is assumed [11]. These assumptions result in an initial SEI volume fraction of 0.18. As modeling in 1D, volume-specific surfaces are also estimated as  $5.0 \times 10^7 \text{ m}^2/\text{m}^3$  and  $4.0 \times 10^7 \text{ m}^2/\text{m}^3$  for the SEI/solvent and graphite/SEI interfaces, respectively. The scaling function of the specific surfaces is introduced to realize SEI thickness dependency against volume fraction for SEI film growth.

### 2.3. Modeling of differential scanning calorimetry

DSC measures the heat flow from a sample  $\dot{Q}$  under external heating with constant rate in a constant pressure environment. The heat flow  $\dot{Q}$  shows an exo/endothermic reaction happened in the sample.  $\dot{Q}$  is obtained by taking the temperature difference between a sample and a reference. It can be written as following equation:

$$\dot{Q} - \dot{Q}_{\text{ref}} = \frac{T - T_{\text{ref}}}{R} \quad (3)$$

where  $\dot{Q}_{\text{ref}}$ ,  $T$ ,  $T_{\text{ref}}$  and  $R$  are the heat flow of reference, temperature of sample, temperature of the reference and a specific thermal resistance, respectively. This relation of Eq. (3) can be easily understood considering electric circuit: current as heat flow, resistance as thermal resistance, and temperature as voltage.  $\dot{Q}$  is derived from Eq. (3) with  $\dot{Q}_{\text{ref}}$  and  $R$  that are known as material constants of the reference.

For DSC simulations, we assume an isothermal computational domain (here: negative composite electrode consisting of active material, solvent and SEI) which we heat to a rate of 5 K/min as Pasquier et al. [4]. We obtain  $\dot{Q}$  from the calculation of thermo-electrochemistry: i.e. by integrating the heat release from all chemical reactions over computational domain.

### 2.4. SEI formation/decomposition chemistry

The SEI formation and decomposition reactions studied here are illustrated in Fig. 1.

SEI formation is a reaction involving charge transfer at negative electrode. We assume the following reaction [9]:



EC ( $\text{C}_3\text{H}_4\text{O}_3$ ) decomposes by reacting with lithium ion in anode and  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  is formed as a product (Fig. 1). In this case, there are contribution from the reaction enthalpy  $\Delta H$  and electric potential difference  $\Delta\phi$  to the heat production due to the SEI formation  $\dot{Q}_{\text{form}}$ :

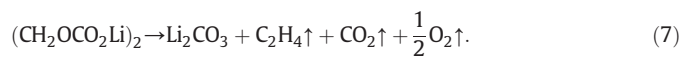
$$\dot{Q}_{\text{form}} = r(\Delta H + zF\Delta\phi) \quad (5)$$

where  $r$ ,  $z$ ,  $F$  and  $\phi$  are the reaction rate, number of moles of electrons transferred, Faraday constant and potential drop at interface, respectively. The reaction rate of SEI formation  $r_{\text{form}}$  is taken from an aging model by Safari et al. [12]:

$$r_{\text{form}} = k_f \prod_i c_i^{\alpha_i} \exp\left(-\frac{\beta F}{RT} \phi\right) \quad (6)$$

where  $k_f$ ,  $c_i$ ,  $\alpha_i$ , and  $\beta$  are the pre-exponential factor for SEI formation, concentration of species  $i$ , reaction order of and a symmetry factor, respectively. The parameters for SEI formation are given in Table 1.

On the other hand, SEI decomposition is a reaction without charge transfer which we express as follows [2]:



Metastable  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  decomposes to stable  $\text{Li}_2\text{CO}_3$  and releases gasses as shown in Fig. 1. In this case, heat released in DSC is obtained from the reaction enthalpy  $\Delta H$  according to.

$$\Delta H = Q_p \quad (8)$$

Here we assume that the reaction is under constant pressure  $Q_p$  and there is no additional work in terms of macroscopic point of view [13]. The heat flow of SEI decomposition  $\dot{Q}_{\text{decomp}}$  is derived to multiply the reaction rate of SEI decomposition  $r_{\text{decomp}}$  to the heat of reaction:

$$\dot{Q}_{\text{decomp}} = r_{\text{decomp}} \Delta H \quad (9)$$

The reaction rate of the SEI decomposition is assumed to follow the Arrhenius equation.

$$r_{\text{decomp}} = k_d c_{\text{SEI}} \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where  $k_d$ ,  $c_{\text{SEI}}$ ,  $E_a$ ,  $R$  and  $T$  are the pre-exponential factor, concentration of SEI ( $(\text{CH}_2\text{OCO}_2\text{Li})_2$ ), activation energy and temperature, respectively. Parameters used in the model are shown in Table 1.

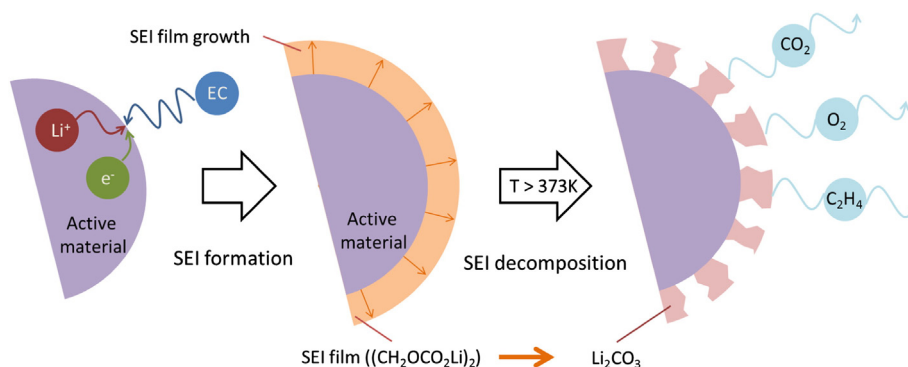


Fig. 1. Schematics of SEI formation and SEI decomposition model.

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