



# A Thermodynamic Perspective for Formation of Solid Electrolyte Interphase in Lithium-Ion Batteries



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## ABSTRACT

This work studied the formation and growth of solid electrolyte interphase (SEI) under the assumption that the formation of an SEI layer is associated with the nucleation and growth of disk-like islands at the interface between an active material and nonaqueous electrolyte solution (NES). The supersaturation of NES favors the nucleation of the islands via lowering the Gibbs free energy with the contribution of interfacial energy and mismatch strain energy to the nucleation process. Using a modified Lifshitz-Slyozov-Wagner model, the growth of the disk-like islands is analyzed. Explicit kinetic estimation for the change of the density and mean dimension of the islands as well as the degree of supersaturation of NES with time is obtained. The degree of supersaturation at time  $t$  is found to be proportional to the square root of time.

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## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the most popular power source for portable electronic devices due to their long cycle life and high energy density. Recent development in hybrid electric vehicles and electric grids has witnessed new demands for lithium-ion batteries of high energy density and stability. One of the critical issues in the development of LIBs is the formation of solid electrolyte interphase (SEI, named by Peled [1]), which forms at the electrolyte/electrode interface in the first stage of electrochemical discharge/charge [2]. Ideally, SEI will allow Li ions to pass and block electrons to the surface of electrodes to avoid electrolyte decomposition. Currently, the structure and composition of SEI, though widely studied, are still not fully understood. Major components in SEI, including inorganic substances, i.e.,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$ , and  $\text{LiF}$ , and organic substances, i.e.,  $\text{LiCH}_3$ ,  $\text{LiOCO}_2\text{CH}_3$  and  $\text{ROLi}$  (R is an organic group dependent on the solvent), have been reported, as reviewed by Verma [3]. In general, an SEI layer, once formed, is not fixed in chemistry and properties. Lee et al. [4] observed that the SEI layer in cells with high degradation is thicker than that in cells with low degradation. Bryngelsson et al. [5] suggested that the SEI layer becomes thicker at low potentials. In addition, temperature has an even more pronounced effect on the evolution of SEI [6,7]. Matsuoka et al. [8] and Jeong et al. [9]

suggested that adding additives, such as vinylene carbonate (VC), can effectively improve the performance of LIBs via facilitating the formation of a dense and solid SEI layer and thus greatly suppressing the decomposition of solvent. In general, the evolution of SEI layers, including growth, dissolution, and aging, plays an important role in determining the long-term performance of LIBs [10,11].

There are various models for the formation of SEI. Based on the X-ray photoelectron spectroscopy results, Kanamura et al. [12] suggested that SEI is a multi-layer structure. Peled et al. [11] suggested that an SEI layer is a mosaic microphase. Aurbach [13,14] presented a scenario for the formation of a multilayer film on the Li electrodes. Edström et al. [15,16] suggested a two-layer SEI structure with a dense inorganic layer close to the electrode surface and a porous organic or polymeric layer on top of it. All of the works reveal the layered structure of SEI in which the main components consist of the substances from the reductive decomposition of nonaqueous electrolyte solution (NES). However, they did not address the formation and growth mechanism of SEI, which likely play an important role in determining the performance of lithium-ion batteries.

Recently, Zheng et al. [17] visualized the SEI formed on the silicon anode material three-dimensionally through a scanning force curve method, using a scanning probe microscope. A partial coverage (95%) of SEI on the anode was observed even after adding 2 wt% VC in electrolyte. Their results reveal the presence of single-, double-, and multi-layered structure of highly inhomogeneous SEI and suggest that the insoluble species in the NES form the first

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**A list of symbols**

$C$	molar concentration of NES
$C_{\infty}$	molar concentration of saturated NES
$C_R$	equilibrium molar concentration at the edge of an SEI island
$R_{c_0}$	initial radius of an SEI island
$\bar{R}$	mean radius of SEI islands
$R_c$	critical radius of SEI islands
$t$	time
$S$	spreading parameter
$v_{\bar{R}}$	growth rate of SEI islands
$v$	critical volume of total molecules or atoms in an SEI island
$x$	critical dimension of an SEI island
$\Delta G_T$	change of total Gibbs free energy
$\Delta G_S$	change of surface energy
$\Delta G_V$	change of volumetric Gibbs free energy
$\Delta G_T (v_c)_{\max}$	maximum change of total Gibbs free energy
$\Delta \mu$	change of the Gibbs free energy introduced by moving unit volume of molecules or atoms from the bulk NES phase to the interior of an SEI island
$\gamma$	interfacial free energy
$\varepsilon$	mismatch strain
$\Omega$	atomic volume of solute atoms
$\rho/z$	dimensionless size of an SEI island
$\rho_{\max}$	maximum dimensionless size of an SEI island
$\Delta$	degree of supersaturation of NES
$\Delta_0$	initial degree of supersaturation of NES
$\lambda$	coefficient of convective mass transfer
$\theta$	dimensionless time

layer of the SEI film on the anode surface via absorption, nucleation and growth, following with the deposition of the reduced and formed lithium salts either on the formed-in-advance SEI islands or on bare areas which depends on thermodynamic and/or kinetic factors.

Winter [10] pointed out that the protective properties of SEI were overemphasized. He suggested that the limited SEI performance may result from the fact that the protective SEI components are less (or even not) cation-conductive and conductive components are less protective. However, it doesn't preclude the consistent acceptance of the concept of passivation film due to simplicity and reasonability, i.e., a denser SEI layer usually brings in better performance of LIBs [8,9,17]. Due to the complex nature of SEI, the very first layer of SEI formed upon the contact between anode and an electrolyte solution may be of particular importance to the protective function of SEI [1,2], and thus should be understood theoretically.

Well-known models like single particle model and porous electrode model proposed by Pinson et al. [18] have demonstrated the capability in the prediction of the capacity fade of LIBs, based on the formation mechanism of SEI. However, the studies were focused on the prediction of life time rather than on the mechanism of the SEI formation and growth. Yan et al. [19,20] applied the classical nucleation theory (CNT) model to explain the formation of SEI on graphite electrode substrates. They assumed a nucleus of spherical cap and used the change of total Gibbs free energy to determine the critical size of nucleus. It is believed that the SEI thickness ranges from  $\sim 20$  to several hundred angstroms [15–17,21]. Thus, the model of a spherical cap for the SEI nucleation [19] may not be able to capture the limit to the thickness of the SEI

layer. In addition, the observation of the formation of flat flake structures of  $\sim 0.9$  nm in thickness on the surface of HOPG (highly oriented pyrolytic graphite) electrode [22] suggests that a model different from the model of a spherical cap is needed to explain the formation of flat flake.

Considering the observation of the formation of the flat flake structures on the surface of HOPG electrode [22], the model proposed by Yan et al. [19] is modified with the constraint of the SEI thickness. Instead of using a spherical cap for the nuclei of SEI, disk-like islands of a fixed thickness qualitatively in accord with the flat flake structures are used in analyzing the formation and growth of SEI. In addition, the mismatch strain between the SEI and active materials is introduced in the model, and the LSW (Lifshitz-Slyozov-Wagner) theory is modified to provide a kinetic image for the growth of SEI.

## 2. Mechanistic model

Consider the nucleation of an SEI island on the surface of an active material, as schematically shown in Fig. 1. The following assumptions are made to establish the mechanistic model:

- The surface of the active material is flat and smooth.
- There is little change of temperature and pressure during the formation and growth of SEI.
- The small nucleus is in a disk-like shape with a fixed height of  $h$ .
- The composition of the nucleus is homogeneous and uniform.

For the heterogeneous nucleation of a disk-like island, the total change of Gibbs free energy  $\Delta G_T$  can be calculated as

$$\Delta G_T = \Delta G_V + \Delta G_S, \quad (1)$$

where  $\Delta G_V$  is the change of the volumetric Gibbs free energy and  $\Delta G_S$  represents the contribution of interfacial free energies. For a spontaneous nucleation process,  $\Delta G_T$  must be negative. The term  $\Delta G_S$ , which is controlled by the absorption and de-absorption of atoms or molecules near the interfacial region and proportional to the interfacial area, is positive. Thus,  $\Delta G_V$  plays a critical role in the SEI nucleation which can be expressed as

$$\Delta G_V(v) = v\Delta\mu + vM\varepsilon^2, \quad (2)$$

where  $v$  is the volume of total molecules or atoms in the SEI island, and  $\Delta\mu$  is the change of the Gibbs free energy when moving unit volume of molecules or atoms from the bulk NES phase to the interior of the SEI island. Here, we assume that  $\Delta\mu$  is independent of the size of the SEI island. Note that  $\Delta\mu$  is positive for unsaturated NES and negative for supersaturated NES. The second term represents the mismatch strain energy due to the composition difference between the active electrode material and the NES components, where  $M$  is the biaxial modulus and  $M^2$  represents the mismatch strain energy density (strain energy per unit volume).

The term  $\Delta G_S$  is calculated as

$$\Delta G_S = (2\pi Rh + \pi R^2)\gamma_1 + \pi R^2(\gamma_2 - \gamma_3), \quad (3)$$

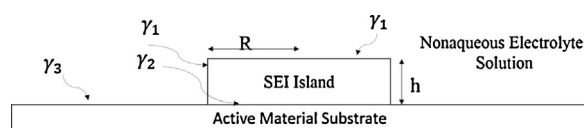


Fig. 1. Schematic of the nucleation of a disk-like island.

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