



Forward and reverse differential-pulse effects applied in the formation of a solid electrolyte interface to enhance the performance of lithium batteries



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ABSTRACT

In Li-ion batteries, the solid electrolyte interface (SEI) plays a crucial role in transferring Li ions into active materials through an electrochemical driving force. SEI is a composite layer containing of inorganic and organic components, which are fabricated by the salt degradation products and partial or complete reduction products of the solvent of the electrolyte at the battery's initial charge-discharge cycle. The chemical properties of SEI and the electrochemical driving force must be mutually optimized so as to strengthen its integrity, while minimizing irreversible SEI formation; thereby suppressing the decomposition at high temperatures. In this study, we investigated a new method of creating the SEI, i.e. the forward and reverse differential-pulse (FRDP) method, which balances the reaction kinetics of SEI formation. Furthermore, the use of the FRDP method also creates a SEI with a modified kinetic reaction route that affects battery performance. Here, we present data from the first charge-discharge and cycle performance at a high rate and a high temperature, obtained using scanning electron microscopy, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy, and Li⁺-diffusion kinetics analysis. Our findings indicate that the use of the FRDP method for generating the SEI results in a 58% reduction in the SEI's ionic diffusion activation energy and a 4.5% increase in battery capacity at room temperature, while increasing battery performance at 60 °C stability compared to batteries in which the SEI is formed using the constant-current method.

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1. Introduction

Li-ion batteries are widely used as a source of rechargeable power for portable electronic devices. In addition to their potential use in various current and future devices, Li-ion batteries have potential to be used in high-power systems such as electric vehicles (EVs) and hybrid EVs. The high reliability and uniform standard of the EV battery design is postulated to be comparable to that of batteries manufactured for current 3C (Communications, Computers and Consumer Electronics) applications. To obtain high power, the rapid ionic transfer that results from the electrochemical reaction, which occurs at the electrode/electrolyte interface, must be accelerated. In lithium batteries, this electrode/electrolyte interface is named the solid-electrolyte interface (SEI) or the passivation layer, and it is used for de-solvating Li ions that are solvated, due to the carbonates' high

dielectric constant. During the initial charging of these batteries, Li ions are extracted from the cathode and intercalated into the anode through a non-aqueous electrolyte, such as ethylene carbonate (EC), propylene carbonate (PC), or ethyl methyl carbonate (EMC). When these carbonates contain a lithium salt (LiPF₆), a complex SEI layer including organic and inorganic compounds can be readily generated on the anode's surface through a reduction reaction [1,2]. Typically, when the SEI's organic compounds contain (CH₂OCO₂Li)₂, ROCO₂Li and RCO₂Li, they enhance the battery life and the charge-transfer rate because they provide ion-hopping sites on the highly functional groups (-C=O and -C-O-) of the SEI [1,3]. However, ensuring the formation of the organic compounds is challenging because the electrochemical reaction of the cyclic carbonates undergoes substantial mutations. Zhang *et al.*, demonstrated that a two-electron pathway is used for the electrochemical decomposition of EC and a one-electron pathway is used for the decomposition of PC because the electron-donating group, -CH₃, augments the electron density within the cyclic structure [1] and thereby restricts the flow of electrons and generates an organic compound [1,4]. Research conducted using electrochemical impedance spectroscopy (EIS) has

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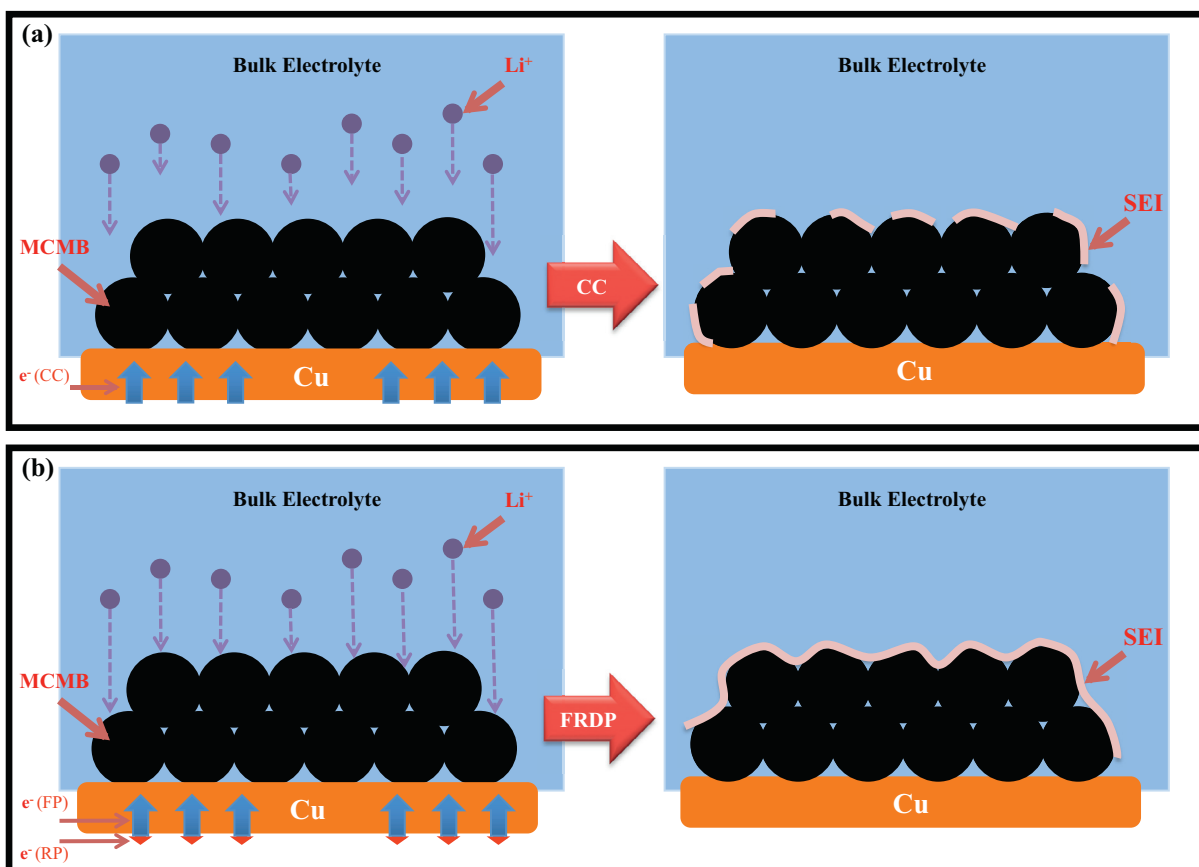


Fig. 1. The solid electrolyte interface formation concepts of lithium ion battery applied by (a) CC and (b) FRDP charging protocols.

revealed that the SEI is formed in two early stages [5]: in the first stage, a porous, highly resistive, and dimensionally unstable SEI layer grows before Li ions intercalate into graphite, whereas the second stage occurs concurrently with the intercalation of Li ions and generates a highly elaborate and conductive organic SEI layer.

Several reports have indicated that diverse approaches can control the formation of an effective SEI in Li-ion batteries. Electrolyte additives, which are low-molecular-weight monomers that exhibit high reduction potentials, are used for reinforcing SEI formation and preventing the polarization of the electrochemical reaction. Chemical compounds based on vinylene carbonates [6,7], sulfones [8], maleimides [9–13], and phosphates [14,15] were previously developed for generating an SEI that prevented the exfoliation effects on carbon when PC was used as the solvent: using this process, a 3D electrochemically active surface area was formed and frame-retardant applications were improved. However, large-scale solubility and electrochemical stability of the additives in electrolytes cannot be readily maintained. Recently, considerable attention has been devoted to modifying the surface of electrodes or particles by using so-called artificial SEI-formation methods such as atomic layer deposition/molecular layer deposition (ALD/MLD) [16,17], solid state synthesis [18], and radio frequency sputtering coating [19]. Miller et al., used coarse-grained lattice models for studying the reductive reaction of Li⁺ and showed that pulse charging can be used to suppress dendrite formation on the anode's surface when the polarization is high: the analysis also revealed that dendrite formation is linked to the competition between the timescales of Li⁺ diffusion and the reduction of SEI formation. Miller et al., suggested the use of short pulse durations shifts this competition

in favor of Li⁺ diffusion and thus lowers the propensity for dendrite formation [20].

Previous results [4,20] have indicated that DP charging affects the formation and the composition of the SEI layer in distinct and dynamic ways; however, the dynamic electrochemical equilibrium of both Li⁺ diffusion and the electron transfer must be re-examined because Li⁺ diffusion is extremely slow compared with electron conduction. We conducted this study to determine whether balanced SEI formation on the anode surface can be achieved by further refining the DP protocol.

In this study, we investigated the use of a new forward and reverse differential-pulse (FRDP) method developed for SEI formation. Fig. 1 shows the SEI formation concepts of the charging protocols of CC and FRDP. Owing to Li⁺ diffusion in the bulk electrolyte being much slower than electron transfer in the current collector, we anticipate that the diffusivity of Li⁺ can be enhanced by the reverse pulse (RP) effect.

Fig. 1 a shows that the slow movement of lithium ions achieves a non-uniform SEI formation from electron transfer in the CC protocol; in contrast Fig. 1 b shows that the RP approach causes the uniform movement of lithium ions resulting in a homogeneous SEI layer. We examined the reaction kinetics, the charge–discharge characteristics, cycle performance, and the electrochemical properties of Li-ion batteries in which an SEI film was grown. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to examine the composition and the morphology of SEI films prepared using FRDP and CC protocols. Our results can help guide the development of a new concept that can be applied in the preparation of elaborate SEI layers in commercial Li-ion batteries.

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