Modeling the degradation mechanisms of C_6/LiFePO$_4$ batteries

Dongjiang Li[a], Dmitri L. Danilov[a,b], Barbara Zwikirsch[c], Maximilian Fichtner[c], Yong Yang[d], Rüdiger-A. Eichel[a,e], Peter H.L. Notten[a,b,f,*]

[a] Forschungszentrum Jülich, Fundamental Electrochemistry (IEK-9), D-52425, Jülich, Germany
[b] Department of Electrical Engineering, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands
[c] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), D-89081, Ulm, Germany
[d] State Key Lab for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen, 361005, China
[e] RWTH Aachen University, D-52074, Aachen, Germany
[f] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands

HIGHLIGHTS

- Capacity losses of C_6/LiFePO$_4$ batteries are investigated under storage and cycling.
- SEI formation is the main reason for capacity loss at moderate temperatures ($\leq 40^{\circ}$C).
- Cathode dissolution at elevated temperatures ($>40^{\circ}$C) accelerates capacity loss.
- SEI formation model and cathode dissolution model are developed.

ARTICLE INFO

ABSTRACT

A fundamental electrochemical model is developed, describing the capacity fade of C_6/LiFePO$_4$ batteries as a function of calendar time and cycling conditions. At moderate temperatures the capacity losses are mainly attributed to Li immobilization in Solid-Electrolyte-Interface (SEI) layers at the anode surface. The SEI formation model presumes the availability of an outer and inner SEI layers. Electron tunneling through the inner SEI layer is regarded as the rate-determining step. The model also includes high temperature degradation. At elevated temperatures, iron dissolution from the positive electrode and the subsequent metal sedimentation on the negative electrode influence the capacity loss. The SEI formation on the metal-covered graphite surface is faster than the conventional SEI formation. The model predicts that capacity fade during storage is lower than during cycling due to the generation of SEI cracks induced by the volumetric changes during (dis)charging. The model has been validated by cycling and calendar aging experiments and shows that the capacity loss during storage depends on the storage time, the State-of-Charge (SoC), and temperature. The capacity losses during cycling depend on the cycling current, cycling time, temperature and cycle number. All these dependencies can be explained by the single model presented in this paper.

1. Introduction

Ageing has become an important research topic since batteries are widely applied in portable electronic devices, electric vehicles and smart grid energy storage, *etc*. Long calendar and cycle life are critical for Li-ion batteries in these applications [1,2]. Understanding the aging mechanisms is essential for improving the life-span of Li-ion batteries.

The SEI formation and electrode material degradation are considered to be the main reasons for battery aging. It has been unraveled that the SEI formation on the anode is the major cause of battery capacity losses [3–9]. Considerable efforts have been made to study the structural and chemical composition of SEI layers [10–20]. It has been found that the SEI affects the performance of Li-ion batteries in two different ways. On the one hand, it immobilizes cyclable lithium in the battery, which is therefore no longer available for the energy storage and, subsequently, leads to irreversible capacity losses. On the other hand, it protects the anode surface from solvent co-intercalation, preventing exfoliation of the graphene sheets. Experimental studies demonstrate that the SEI is composed of a thin inner SEI layer and a more porous and extended outer SEI layer [10–12]. The inner SEI-layer is dense and prevents the surface of the anode from direct contact with the electrolyte, thereby suppressing co-intercalation of the solvent. The

---

inner layer of SEI is good Li^+ ionic conductor. The outer SEI layer, on the other hand, is porous, enabling fast transport of solvated Li^+ ions.

Although considerable efforts were made to study the SEI experimentally, the understanding of lithium immobilization is still limited due to the complexity of the SEI formation reaction, which was found to be highly dependent on the electrode voltage, electrode surface morphology and the composition of the electrolyte. Modeling is a powerful tool to study the SEI formation process. However, only a limited number of studies refer to the SEI growth process, which are still under discussion [6–9,21–31]. Some authors assumed the electron tunneling process to be rate-determining for SEI formation [5,6,24,30] while others regarded solvent diffusion through the SEI layer as a rate-limiting step [27–29].

Apart from the SEI formation, cathode dissolution at elevated temperatures is considered to be another important process during battery aging [7,9,32–35]. The dissolved transition metal ions can be transported to the anode and can subsequently be deposited on the graphite surface [7,9]. Both the metal dissolution and the subsequent reduction can directly lead to a decrease of the battery capacity. Furthermore, the deposited metal clusters will speed up the SEI development by facilitating the transport of electrons [7,9,32].

An electrochemical model has been developed in our previous work in order to simulate the SEI growth at room temperature [5,6]. In the present work we extended the SEI formation model to various cycling currents, storage at different SoC and temperatures. Apart from the SEI formation, the cathode dissolution and Fe plating at anode at elevated temperatures will also be modeled in the present work. The model has been validated by experimental data. Good agreement between simulations and experiments is found in all cases.

2. Model development

Cyclable Li^+ ions and electrons are originally stored in the $LiFePO_4$ electrode in $C_6/LiFePO_4$ (LFP) batteries after manufacturing. The maximum battery capacity (Q_{max}^0) therefore equals to the total amount of cyclable Li^+ ions in the cathode materials ($Q_{LiFePO_4}^0$). During charging (ch) electrons are extracted from the $LiFePO_4$ electrode and flow into the graphite electrode via the outer circuit. Simultaneously, Li^+ ions are transported from the $LiFePO_4$ electrode via the electrolyte to the graphite electrode to safeguard the system electro-neutrality. The reverse reactions take place during discharging (d). The main electrochemical storage reactions of LFP batteries can be described by Ref. [6].

$$C_6 + Li^+ + e^- \underset{d}{\overset{ch}{\rightleftarrows}} LiC_6 \tag{1}$$

$$LiFePO_4 \underset{d}{\overset{ch}{\rightleftarrows}} FePO_4 + Li^+ + e^- \tag{2}$$

Electrons extracted from the lithium iron-phosphate electrode can also be partially consumed by many processes, such as parasitic side reactions taking place at the graphite electrode during cycling and storage, leading to irreversible capacity losses. The detailed capacity loss mechanisms during cycling and storage will be discussed in the following sections.

2.1. The SEI formation model

The formation mechanisms and composition of SEI layers have been widely investigated. Although there are still some debates, it has been generally accepted that the SEI layers are composed of inorganic and organic Li salts, and constitute the dense inner layer and porous outer layer, respectively, as schematically shown in Fig. 1. The inner SEI layer is an electronic insulator. It also prevents solvents from passing through and co-intercalating into the graphene layers. Therefore, it is assumed, that solvent reduction takes place at the interface between the inner and outer SEI layers.
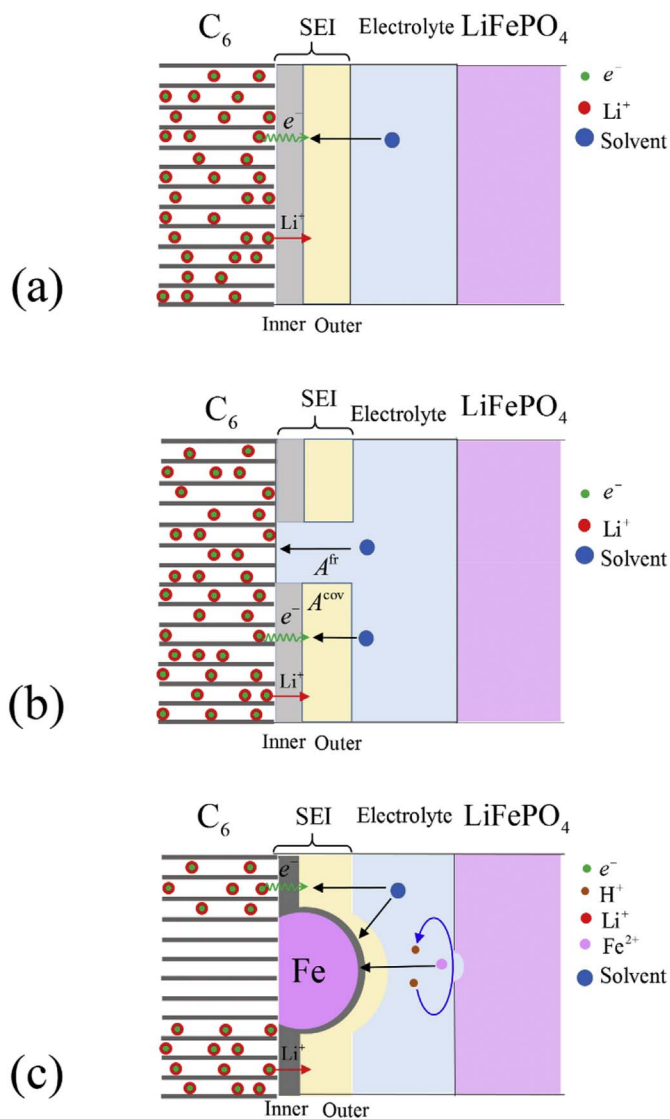

Fig. 1. Schematic representation of SEI formation on the graphite electrode inside a LFP battery under storage (a) and cycling (b) conditions. (c) The influence of elevated temperatures on aging processes inside LFP batteries [7,9].

Electrons at the graphite electrode surface can, however, tunnel across the inner SEI layer to the Lowest Unoccupied Molecular Orbital (LUMO) of the solvent. Literature reports several values for the Fermi level of metallic Li and LiC_6 [36–38]. In the present work we adopt the results reported by Wertheim et al. [38], namely -2.36 eV for Li and -2.80 eV for LiC_6 vs vacuum. For Ethylene Carbonate (EC) in the presence of Li^+ ions the LUMO was found to be -2.99 eV [6]. This value is below the Fermi level of the lithiated graphite and, therefore, EC will be reduced, presuming that electrons can pass the energy barrier by tunneling.

The SEI development starts when the voltage of the negative electrode declines below 1.0 V vs Li^+/Li [12,15,17]. Therefore, the SEI is developed during the activation procedure immediately after the end of battery manufacturing process. The quality of the SEI formed during this activation process determines the battery cycling performance in their application. An ideal SEI layer formed during the activation procedure can dramatically decrease the further SEI formation rate and, therefore, maintain a high battery coulombic efficiency. However, in practice the SEI layers continue to grow during battery operation, leading to continuous irreversible capacity losses.

During (dis)charging, Li^+ ions can readily penetrate both the inner