Degradation of the solid electrolyte interphase induced by the deposition of manganese ions

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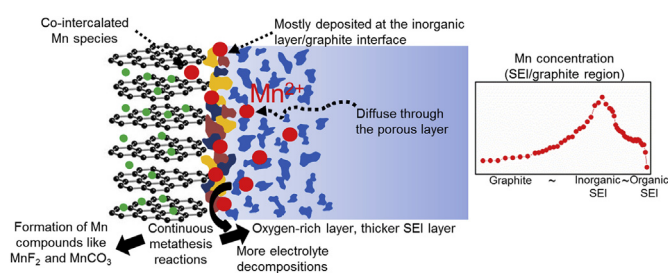
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GRAPHICAL ABSTRACT

ABSTRACT

The deposition of manganese ions dissolved from the cathode onto the interface between the solid electrolyte interphase (SEI) and graphite causes severe capacity fading in manganese oxide-based cells. The evolution of the SEI layer containing these Mn compounds and the corresponding instability of the layer are thoroughly investigated by artificially introducing soluble Mn ions into a 1 mol L^{-1} LiPF$_6$ electrolyte solution. Deposition of dissolved Mn ions induces an oxygen-rich SEI layer that results from increased electrolyte decomposition, accelerating SEI growth. The spatial distribution of Mn shows that dissolved Mn ions diffuse through the porous layer and are deposited mostly at the inorganic layer/graphite interface. The Mn compound deposited on the anode, identified as MnF_2, originates from a metathesis reaction between LiF and dissolved Mn ion. It is confirmed that ion-exchange reaction occurs in the inorganic layer, converting SEI species to Mn compounds. Some of the Mn is observed inside the graphite; this may cause surface structural disordering in the graphite, limiting lithium-ion intercalation. The continuous reaction that occurs at the inorganic layer/graphite interfacial regions and the modification of the original SEI layer in the presence of Mn ions are critically related to capacity fade and impedance rise currently plaguing Li-ion cells.

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1. Introduction

The capacity and power fading of lithium-ion (Li-ion) batteries are complicated processes that are very challenging to understand and resolve, especially at elevated temperatures [1–6]. Although the mechanisms responsible for the degradation of Li-ion batteries cannot be simplified and explained by one or two phenomena, the

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dissolution of the active materials and the instability of the solid electrolyte interphase (SEI) are two of the key phenomena responsible for the degradation. These two phenomena, in particular, cannot be considered independent at elevated temperatures, since a significant amount of the ions dissolved at elevated temperatures move to the anode side and modify the SEI layer. Consequently, transition metal dissolution from the cathode materials not only influences the reversible capacity of the positive electrode, it also influences the reversible capacity of the negative electrode.

The dissolution of active materials from the cathode side clearly causes the loss of usable materials from the positive electrode. These dissolved transition-metal ions subsequently re-deposit on the positive electrode, forming an electrically insulating layer of oxides and fluorides [4,7]. Moreover, the dissolved ions diffuse to the negative electrode, where they are deposited, influencing both the chemical degradation of the SEI layer and the self-discharge of the lithiated anode [8,9]. These phenomena are especially important for manganese-based electrodes, such as $LiMn_2O_4$, $LiMnO_2$, $Li_{1+x}Mn_2O_4$, and $Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$, since the manganese-based oxides are more vulnerable to dissolution in the electrolyte than other cathode materials, especially at elevated temperatures [10]. It has been also reported that the amount of Mn deposited is significantly greater than that of other transition metals, such as Ni and Co [11]. Thus, in manganese-based cells, a considerable amount of Mn ions is expected to be continuously dissolved and deposited during prolonged storage/cycling at elevated temperatures.

The instability of the SEI on the anode is severe especially at elevated temperatures; two factors, i.e., temperature and dissolved Mn ions, considerably contribute to degradation of the SEI layer [2,3,8,9]. Fig. 1 shows a simple schematic of the degradation of the SEI on the graphite that occurs at elevated temperatures. As shown in the figure, two different mechanisms are associated with the degradation of the SEI: (1) Elevated temperatures directly induce the dissolution, breakdown, and conversion of the SEI layer, which make the original SEI layer to be a defective layer [1–3]. This defective layer causes the consumption of cyclable lithium ions and additional decomposition of the electrolyte to reform the layer, resulting in the growth of the SEI layer. (2) The dissolved Mn ions also induce side reactions associated with the deposition of the Mn
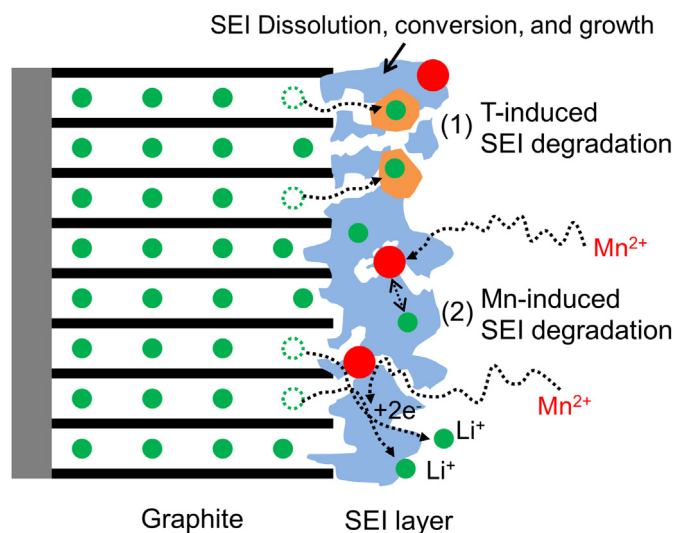
ions, resulting in a defective layer [8,9,12]. During the deposition process, Mn ions can interact with the chemical species in the SEI layer, and deposited Mn compounds can promote a catalytic reaction that results in more decomposition of the electrolyte. In addition, the deposition of the dissolved Mn ions can make lithium ions in the lithiated graphite to deintercalate during the reduction process [8]. Thus, degradation of the SEI layer proceeds in the presence of the dissolved Mn ions, reducing capacity and power of a Li-ion battery. At elevated temperatures, these two phenomena simultaneously occur and are coupled to each other, which make understanding the mechanism of SEI layer degradation more complex.

To simplify the problem and get a better insight into the influence of Mn deposition on capacity fade, several studies have been conducted by artificially introducing soluble Mn ions into the electrolytes. Either a defined amount of the manganese perchlorate $[Mn(ClO_4)_2]$ has been dissolved in $LiClO_4$-based electrolytes or the anodic dissolution of Mn metal has been carried out using electrolysis [9,12–15]. These previous studies provide limited information that is only applicable to $LiClO_4$-based electrolyte systems because, in each case, a lithium salt ($LiClO_4$) was used as the electrolyte. Moreover, the presence of hydrofluoric acid (HF), which is an important reason for Mn dissolution in $LiPF_6$-based electrolytes, has been ignored in $LiClO_4$-based electrolyte systems. A recent study tried to mimic the conditions in $LiPF_6$-based commercial cells by immersing $LiMn_2O_4$ powder in the electrolyte at the high temperature for several days [16]. However, this preparation could cause the degradation of the electrolyte during the storage, producing byproducts such as HF, PO_3F^{2-}, and $PO_2F_2^-$ in the electrolyte [17]. In addition, it is difficult to achieve the desired amount of dissolved Mn ions in the electrolyte.

So far, a number of efforts have been made to understand the influence of Mn deposition on anode performance, the interaction mechanism between dissolved Mn ions and the anode/electrolyte interface, and the oxidation state of the deposited Mn. The deterioration of anode performance induced by Mn deposition has been clearly observed with increased reduction current and interfacial impedance [12–16,18]. However, earlier studies have shown conflicting results about the mechanism responsible for Mn compound deposition and the oxidation state of the deposited Mn compound. This makes it difficult to have a clear understanding of what happens at the anode/electrolyte interface as a result of the deposition of Mn ions. It was initially proposed that the dissolved Mn ions could be reduced electrochemically by the low potential, based on the known standard redox potential of Mn/Mn^{2+} (1.87 V vs. Li/Li^+) [12]. Another hypothesis was that the reduction of the Mn ions on the anode surface occurs chemically, via the chemical activity of the lithiated graphite [18]. Another possibility has recently been proposed that a metathesis reaction occurs between the dissolved Mn ions and some species in the SEI layer, rather than reduction during Mn deposition on the anode [16]. Even when the deposited Mn compound was not clearly identified, the 2 + oxidation state of Mn deposited on anodes was predominantly observed [9,13,19]. However, recent studies also suggested that a metallic form of Mn can be formed on the anode [14,20,21]. The Mn compounds reported to date are summarized in Table 1.

Despite the research described above, the precise mechanism of the interaction between dissolved Mn ions and the anode/electrolyte interface is still being debated and remains a challenging topic. To shed further light on the mechanism of capacity fade driven by deposited Mn, it is necessary to understand how the dissolved Mn ions cause SEI degradation. The identification and spatial distribution of Mn compounds at the anode/electrolyte interface are also essential to understand the mechanisms of Mn deposition as well as the Mn-induced SEI degradation. The goals of

Fig. 1. A schematic description of the SEI instability that occurs in cycled or stored Li-ion batteries at elevated temperatures.