The influence and mechanism of transition metal ions dissolution in lithium-ion batteries

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Abstract: Lithium-ion battery (LIB) has been extensively applied in the field of power vehicles and energy storage. Extending the service life is the research priority. Transition metal (TM) ions dissolved from the cathode are considered a key factor affecting battery electrochemical properties. To reveal comprehensively the mechanisms of influence of TM ions at the full-cell level, this paper reviews the recent efforts of the exploration of TM ions affecting lithium-ion batteries using conventional metal oxide as cathode matched with graphite, silicon-containing, or Li metal as anode, respectively. The existence of TM ions in electrolyte or solid electrolyte interphase (SEI) films can change the morphology, the structure as well as the component concentration of the SEI films and accelerate the side reaction as a catalyst. In the comparison of different TM ions, the failure mechanism could be diverse, and it is proved that Mn ion is the most detrimental and extensively studied. However, in some special lithium-ion battery systems, TM ions are even in favour of electrochemical performance by forming LiF-rich SEI components.

Keywords: lithium-ion battery, transition metal dissolution, crosstalk.

1. Introduction

The lithium-ion battery is an electrochemical device that converts electrical energy and chemical energy by mobile Li^+, which intercalates into or deintercalates from its anode and cathode. Driven by the demand for higher performance in the field of electric vehicles (EVs), LIBs are expected to have a long-life span, low cost, high thermal stability, and high specific energy. To enhance the service life of LIB, numerous cell failure studies have been conducted and metal-ion dissolution has been normally considered as one of the main reasons. Metal-ion dissolution belongs to one type of electrode crosstalk, which means the compounds generated at one electrode by chemical or electrochemical side reactions migrate to the other electrode and further participate in other reactions in the full cells.

With stable crystal lattices, transition metal oxides compose the majority of the cathode materials in LIB, which provide tunnel or layer structures as lithium ions diffusion pathways. However, the cathode could react with electrolyte or undergo structure change as the delithiation during charging, leading to the dissolution of TM ions that further proceed through the separator and accumulate on the anode. In spite of the low amount, the electrochemical properties will be significantly affected, such as capacity attenuation, coulomb efficiency reduction, impedance increase, and even the risks of thermal runaway. This process is accelerated and deteriorated by high temperature, high voltage, and chemical state change during cycling, etc. In 1994, Tarascon first proved the release of metal ions from lithium manganese oxide (LMO) and the increase of Mn on the Li surface during charge and discharge cycling by Rutherford backscattering [1]. Since then, the advanced characterization equipment and newly developed measurements allow further exploration of the factors influencing TM dissolution degree and mechanism of TM on capacity fade in various lithium-ion battery systems. Nevertheless, there is yet no consensus on how these reactions are triggered and evolved in the full materials.

In this review, it is systematically discussed about the recent advances of TM ions influence in different lithium-ion cell systems. This paper focuses on lithium-ion secondary batteries that are commercialized or have commercial potential as well as those cutting-edge, containing conventional metal oxide cathodes and graphite, silicon-containing, or Li anodes. Li-S and Li-O_2 batteries are excluded.

2. The influence and mechanism of TM ions

The studies of TM ion dissolution began with Mn ions, while the relevant mechanism is intricate and has not yet been completely perceived. Among different TM ions, disproportionation reaction ($2Mn^{3+}(s) \rightarrow Mn^{2+}(aq) + Mn^{4+}(s)$) and HF acid corrosion are commonly considered as the reason for Mn ions dissolution. However, they are not convincing enough to explain the increase of Mn ions concentration on the anode at higher potential conditions [2]. Therefore, other mechanisms such as phase transformation, surface reconstruction or vacancy evolution, etc. have also been suggested to supply the dissolution mechanism in the high potential range. There are fewer studies on TM ions in terms of ternary Li-ion batteries, yet the same theories are still applicable.

After dissolution, TM ions tend to form a solvated structure with the solvent of the electrolyte and migrate toward the anode, driven by the concentration gradient and or electric field. In addition, Shkrob et al. proposed that there is another migration mechanism in that electrolyte decomposition products work as chelating agents to accelerate the TM ions dissolution and form stable neutral complexes, finally diffusing on the anode. Whatever the migration mechanism is, it is undisputed that TM ions can not only affect the stability of SEI films but also change the reactivity and decomposition degree [3].

2.1. *Effects of TM ions crosstalk in graphite-based battery*

To compare the influence and affection of different TM ions in the full batteries, a frequently used experimental method is considered effective, especially in ternary lithium batteries systems, adding bis(trifluoromethane) sulfonimide (TFSI) salts with transition metal ions of ternary cathode materials into the same base electrolyte to simulate the effect of metal ion dissolution on the entire battery. This is caused by the high solubility of TFSI salts with all of Li^+, Ni^{2+}, $Mn^{2+,}$ and Co^{2+} so that the effect of TFSI ions can be offset by comparing TFSI salts of Li+ and other transition metal ions.

Jung. et al. investigated the deposition and influence of Ni, Mn, and Co ions, derived from NMC622, on the graphite anode by using operando X-ray absorption spectroscopy (XAS). Based on no impact of TFSI-anion on cycling performance, they assembled NCM622/ graphite battery with a base electrolyte consisting of 1M $LiPF_6$ and ethylene carbonate (EC) / ethyl methyl carbonate (EMC)=3/7 (wt/wt) and the counterpart with TFSI salts of Ni^{2+}, Mn^{2+}, and Co^{2+} respectively. The final concentrations of TM ions were 30 mM or 60 mM. Their research showed that the dissolution of TM ion was significant, with an almost stoichiometrically linearly increase at high potentials (>4.6 V) and a prominent acceleration at 4.8 V. XAS analysis revealed that the valences of both Ni and Coon the graphite anode were +2, while that of Mn could be +2 or +3, or a mixture of the two oxidation states. The aging mechanism of three transition metals was regarded as the major reason for cycling capacity deterioration, which was the loss of active lithium due to the decomposition of the SEI components with the catalytic action of deposited metals. Among the three transition metal ions in NMC622, deposited Mn led to a more detrimental effect and more serious associated loss of cyclable lithium ions [4].

In 2016, Wandt et al. used real-time XPS to study the valence states of Ni, Mn, and Co on the graphite electrode after dissolution and found that Mn existed in the form of Mn^{2+} and was not relevant to the state of charge (SOC), while its oxidation state was closely related to the existence of electrolyte. Without electrolyte, Mn^{2+} was gradually reduced to Mn (0) while Co and Ni always existed in the form of +2 [5]. To figure out the mechanism of dissolved TM ions affecting the electrolyte and SEI layer, Solchenbach et al. compared and studied the effects of Ni^{2+} and Mn^{2+} on the decomposition reaction of the electrolyte and SEI layer. They added TFSI salts of Ni and Mn into the combination of ethylene carbonate and $LiPF_6$ as well as a uniquely designed double-chamber reaction cell and online electrochemical mass spectrometry, as shown in Figure 1. The graphite working electrode was positioned in chamber "1", and the Li opposite electrode was placed in chamber "2", and the two chambers were separated by glass ceramics conducting lithium ions. Either TFSI salts of Ni or Mn were added only into the upper chamber where the graphite working electrode was located [6]. The discrepancy in composition and content of gas production indicates that both Ni^{2+} and Mn^{2+} could promote the reduction of EC, while Mn^{2+} exhibited a stronger promoting effect and can continuously facilitate EC decomposition. Compared with Ni^{2+}, the decomposition of the electrolyte caused by Mn^{2+} cannot be effectively inhibited. Through a series of special experimental designs, they proposed the principle of the decomposition of the electrolyte and SEI membrane catalyzed by Mn^{2+} (Figure 2. (a)), including five paths. 1. Mn^{2+} was adsorbed into SEI membrane; 2. Mn^{2+} diffused through the SEI film and was reduced to Mn(0); 3. Mn(0) catalyzed the decomposition of alkyl lithium (LEDC) in SEI film to produce Li_2CO_3 and C_2H_4, while itself was oxidized to produce Mn^{2+}; 4. Mn(0) catalyzed EC decomposition to produce C_2H_4; 5. Mn^{2+} was reduced to Mn(0) by the negative electrode. In this cycle, Mn eventually acted as a catalyst, causing the electrolyte and SEI film to decompose continuously [7]. The formation of Li_2CO_3 caused by catalysis of TM ions on the electrolyte was supported by experiments of Joshi et al. using X-Ray Photoelectron Spectroscopy (XPS). Moreover, the SEI film was observed 4 times thicker and non-uniform, which was caused by the reduction reaction of TM ions and increased inorganic components [8].

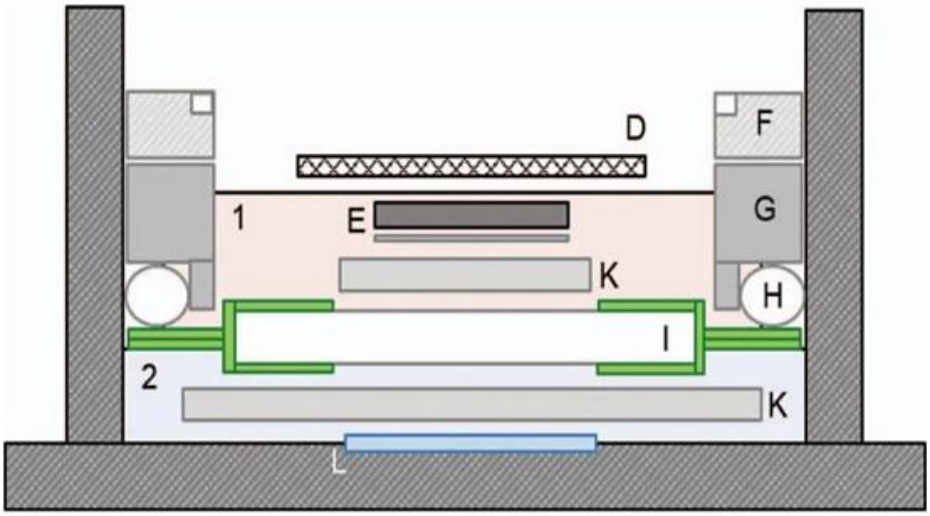
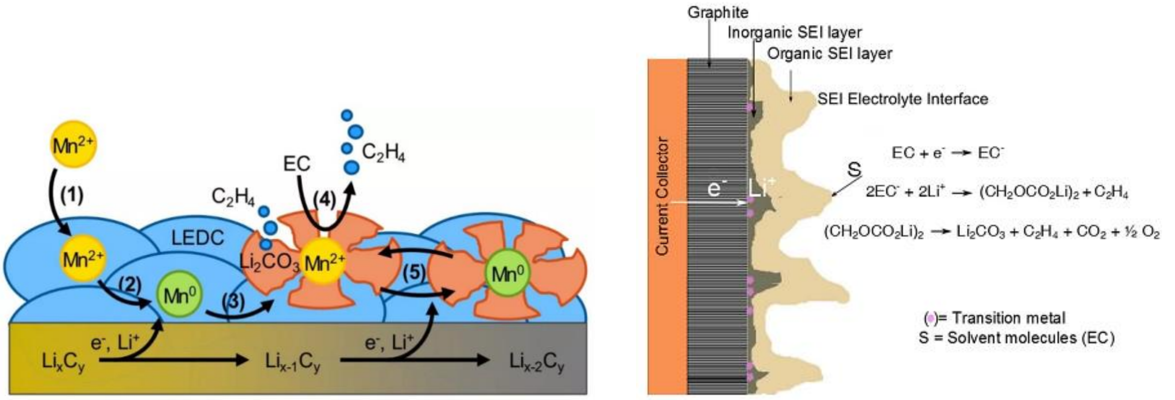
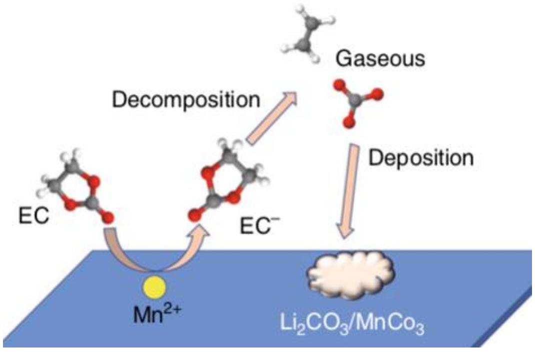


Figure 1. Schematic cross-section of two-chamber reaction cell for electrochemical mass spectrometry [6].



(a) (b)



(c)

Figure 2. Different mechanism of negative effects of TM ions. (a) Diagram of Mn catalytic decomposition of electrolyte and SEI film [7]. (b) Schematic of SEI layer growth influenced by TM ions on a graphite electrode [8]. (c) Schematic diagram of manganese-catalytic solvent decomposition [9].

However, the valence state of Mn is still controversial. Doron Aurbach's team conducted a series of electrochemical tests in the electrolyte system with $LiPF_6$(1M), EC/DMC=1/1(w/w) using lithium manganate/graphite full battery. X-ray absorption near edge structure (XNEAS), electron paramagnetic resonance (EPR), inductively coupled plasma spectroscopy (ICP), and other testing methods were used to prove that Mn mainly exists in the valence state of +3 in the electrolyte. The results of EPR combined with ICP show that in the full (4.2 V) and lean (3.0 V) batteries state, the trivalent manganese in the electrolyte accounted for 80%, while in the cycling process, the trivalent manganese in the electrolyte accounted for only 60%. At the same time, the disproportionation reaction rate of Mn^{3+} in the organic electrolytic liquid system was very slow [10].

In addition, Wang et al. proposed different explanations for the effects of Mn^{2+}. The solvation reaction energy of Mn^{2+} in the electrolyte was calculated using the density function theory. It was found that solvent molecules and anions such as EC and $TFSI^-$ were more inclined to react with Mn^{2+} to form a solvation structure than Li^+. Furthermore, the solvated structure of PF_6^- and Mn^{2+} had higher reactivity so that it was easier to decompose, and the decomposition product PF_5 would promote the further decomposition of carbonate solvents, thus aggravating the deterioration of lithium-ion battery performance. Their studies have shown that the solvated Mn^{2+} on the negative electrode surface tended to transfer the obtained electrons to the EC molecules and PF_6^- anions to form a solvated structure, thus continuously catalyzing the decomposition of solvent and lithium salts [9].

Li et al. compared the difference in electrochemical properties between high-concentration and conventional concentration electrolytes in graphite/Li half battery systems and revealed that high-concentration electrolytes can improve the reduction stability of electrolytes by increasing the LUMO value of Li^+ and Mn^{2+} solvation structure. Finally, the continuous reduction decomposition and Mn^{2+} deposition on the graphite surface was inhibited. This research suggested that Mn^{2+} affected the properties of graphite by forming a solvation structure different from Li^+ [11].

2.2. *Effects of TM ions crosstalk on silicon-containing anode-based battery*

Although crosstalk of TM dissolution on graphite-based anodes has been extensively studied, mechanistic insights related to Si-based anodes are barely reported.

In the study of Zhang et al., SiOx/Gr anodes with high, medium, and low concentrations of TM ions were formed by changing the charge upper voltage and duration in the condition of high voltage. The results show that with the increase of TM ion content on the SiOx/Gr electrode, irreversible electrode expansion would be intensified. It may be due to the accelerated decomposition of the electrolyte catalyzed by TM ions, leading to the structure of the dominant organic species. This made SEI thick, non-uniform, and non-protective, failing to inhibit continuous electrolyte breakdown during cycling [12].

To reveal the separate effects of TM ions on the electrochemical properties of LIBs with Si/Gr composite anodes, a specific number of Ni, Co, and Mn were artificially added into the electrolyte. Co $(TFSI)_2$, Ni $(TFSI)_2$, Mn $(TFSI)_2$ of 20 mM, and LiTFSI of 40 mM were mixed with blank electrolytes, respectively. The extent of adverse effects of TM ion on Si-containing electrodes followed the order of $Co^{2+} < Ni^{2+} < Mn^{2+}$. This trend mainly resulted from the different mechanisms of Mn, Ni, and Co on the SiOx/Gr electrode. The results of TOF-SIMS showed that Co ion had a limited effect on the degradation reaction of $LiPF_6$ salts, but had a significant effect on solvent decomposition, resulting in more organic components in SEI layers. Conversely, the Ni ions were more possible to promote the degradation of $LiPF_6$ salts. In addition, Mn ion can induce both solvent and $LiPF_6$ decomposition, resulting in the thickest SEI layer, highest resistance, and lowest performance [12].

Currently, to pursue high specific energy, Ni-rich or Mn-rich layered ternary cathode materials are developed due to higher discharge capacities. However, TM ions dissolution can be aggravated by adjusting the ratio of metal elements or ternary cathode materials.

Kim et al. assembled three diverse full cells containing Si as anode and NMC111, NMC532, or NMC811 as the cathodes. High-performance liquid chromatography (HPLC) coupled with electrospray ionization mass spectroscopy (ESI-MS) and XPS was used to analyze the decomposition reaction of the electrolyte and component of SEI. The results showed that the decomposition degree was more correlated to the concentration of Mn ions rather than Ni ions. The inorganic-rich, fluorinated SEI can be easier formed in NMC811 with the lowest Mn ions dissolution, which meant more stable and robust [13].

In another research by Kim et al., they studied the crosstalk effects of three kinds of cathodes on the chemical properties of cells coupled with silicon (Si) anode, NMC532, NMC811, and $LiFePO_4$, respectively. Using XPS and time of flight-secondary ion mass spectrometry (TOF-SIMS), the silicon anode with LFP was found to have the thinnest, highly fluorinated, inorganic-rich SEI layer and formed less Li-O-containing SEI components derived from the degradation of electrolyte, which caused of LFP/Si system to have higher cycling stability [14].

2.3. *Effects of TM ion crosstalk on lithium-metal anode-based battery*

Lithium metal anode is one of the effective ways to achieve high energy density LIBs, and the influence of TM ion on lithium-metal anode has rarely been studied.

Langdon et al. first investigated the crosstalk of TM ions in LIBs with $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ and lithium-metal as electrodes. It is shown that TM ions had minimal effect on the due to the following reasons the concentration of TM ions could be diluted in the thick SEI film of lithium-metal anode (LMA) and the decomposition product from LMA could have more negative effect than TM ions for capacity fading, leading to the minimal effect of TM ions on LMA [15].

Li et al. researched the crosstalk of TM ions with ether electrolytes and ester electrolytes, respectively, in NCM811/Li system. They found that the low stability of ether-based electrolytes against oxygenation resulted in a large number of TM ions dissolution, inducing dendrite growth and rapid cell failure. On the contrary, the carbonic ester electrolyte showed lower plating/stripping stability and higher electrochemical performance at 4.5 V with little crosstalk effect. By introducing 10 mM TFSI salts of Ni and Mn in ether electrolytes to investigate the crosstalk effect, Ni^{2+}-rich electrolyte led to the formation of whisker-like lithium, while in terms of Mn^{2+}-rich electrolyte, lithium evolved into dendrite form and deposited lithium was distributed in an island pattern. These showed that Ni and Mn ions can induce the growth of lithium dendrites and further aggravate the electrolyte side reactions [16].

Betz et al. assembled Li metal anode with $LiFePO_4$, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, and $LiNi_{0.5}Mn_{1.5}O_4$ respectively, and used a scanning electron microscope (SEM) to observe the morphology difference. The porous structure of the lithium deposition film appeared in all three systems, both NMC 622 and LFP can result in the emergence of nodule-like lithium deposition on the Li metal surface, while small spherical deposits for LNMO cathode. This means a high concentration of Mn ions contributed the most to lithium dendrite growth. To support this conclusion, 200 ppm $Mn\ (TFSI)_2$ was artificially introduced into the electrolyte and Li/Li battery was assembled. Results showed that the anode evolved in a similar pattern in the same experiment condition, compared with the LNMO cathode [17].

However, Tan et al. proposed that the crosstalk effect caused by an increased formation cycle voltage significantly facilitates the formation of LIF-rich SEI, which could benefit the cycling performance. It was explained that the LIF-containing SEI was caused by the NMC positive electrode, which had a natural attraction to negatively charged anions, and was influenced by the amount of TM ions. Then the anions of lithium salts were oxidized, and F-containing free radicals subsequently migrate to the anode and further react with Li to form LiF [18].

3. Conclusion

Recently, lots of efforts have been put into the study of how TM ion crosstalk contributes to lithium-ion battery performances. Herein, combined with a brief introduction of experimental methods and their advantages, this paper pioneers a review of the mechanism of TM ions influence on conventional lithium-ion batteries with conventional metal oxide as the cathode as well as graphite, silicon-containing, or Li metal as the anode. The TM ions are normally detrimental to the properties of full cells, while some research suggested that the crosstalk of TM ions may benefit the cycling performance under certain conditions. The mechanism of failure could be caused by the combination of SEI morphology change, influence on solvation structure, or catalytic reaction. Hence, the stability of SEI is affected. Furthermore, different metal ions are also diverse in the degree of deterioration and the explanation of catalysis, such as Mn ions are verified to accelerate the decomposition for both lithium salts and solvents, compared with Ni and Co ions predominantly for lithium salts and solvents respectively. As the most impactive TM ion, the valences of Mn in electrolyte and SEI films are still controversial. Nevertheless, it undoubtedly exists in various valence states. Actually, TM ions could lead to different gas emissions, reaction species, and heat releases, which also contribute to performance deterioration. Further research should pay attention to the change and influence of crosstalk species by in situ characterization technique. Intensive investigation of crosstalk mechanisms of TM ions will guide and optimize the design of battery components in full cells and the highly fluorinated SEI formation promoted by TM ions could be further explored and expected to enhance electrochemical performance.

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