Showcasing a study on long cycling lithium metal batteries by a group of researchers led by Prof. Qiang Zhang (2019 Journal of Materials Chemistry Lectureship winner) from Tsinghua University.

Crosstalk shielding of transition metal ions for long cycling lithium–metal batteries

The Mn ions dissolved from the cathode are involved in the formation of the solid electrolyte interphase (SEI), inducing the emergence of Mn content and the decrease of Li₂O and LiF components in the SEI accounting for inhomogeneous lithium nucleation. A graphene-coated separator was proposed to obstruct Mn ions by adsorption for lithium protection, prolonging the lifespan of lithium metal batteries under harsh conditions.

See Jia-Qi Huang, Aibing Chen, Qiang Zhang et al., J. Mater. Chem. A, 2020, 8, 4283.
Crosstalk shielding of transition metal ions for long cycling lithium–metal batteries†

Xue-Qiang Zhang, Xin-Meng Wang, Bo-Quan Li, Peng Shi, Aibing Chen and Qiang Zhang

Lithium–metal batteries (LMBs) comprising a lithium anode and high-specific-capacity manganese (Mn)-based cathode provide a promising high-energy-density system. However, this full cell suffers from poor cycling life under practical conditions. In this contribution, the effect of transition metal ions, e.g., Mn ions, dissolved from the cathode on the failure of lithium anodes was investigated in a working cell. Mn ions are involved in the formation of the solid electrolyte interphase (SEI), inducing the emergence of Mn content and a decrease in the Li2O and LiF components in the SEI; this results in inhomogeneous lithium nucleation. Furthermore, the direct chemical reaction between Mn ions and lithium anodes results in anode corrosion. For the crosstalk shielding of Mn ions, a graphene-coated separator was proposed to obstruct Mn ions by adsorption for lithium protection, prolonging the lifespan of LMBs under harsh conditions. This study not only highlights the impact of dissolved transition metal ions, such as Mn ions, on the stability of lithium anodes but also affords a practical strategy to shield the crosstalk of transition metal ions for anodic protection in both present lithium-ion and next-generation batteries.

Introduction

In the pursuit of high-energy-density rechargeable batteries to meet the increasing demands of portable electronics and electrical vehicles, lithium (Li)–metal batteries combining Li anode with high-specific-capacity transition metal oxides as cathodes have emerged as a promising energy storage system. The high specific capacity (3860 mA h g⁻¹) and low reduction potential (−3.04 V vs. standard hydrogen electrode) enable the Li metal to be one of the most competitive candidates. For using transition metal oxides as cathodes, manganese (Mn)-based oxides, such as LiNi₀·₅Co₀·₅MnₓO₂ (NCM) and xLi₂MnO₃·(1 − x)LiMO₂ (M = Ni, Co, Mn, or their combination, denoted as LM-rich NCM), have attracted increasing attention due to their high voltage, high specific capacity, and moderate structural stability. In particular, the specific capacity of LM-rich NCM has exceeded 300 mA h g⁻¹, and the energy density of practical Li–metal batteries is supposed to be over 400 W h kg⁻¹. Furthermore, the employment of Mn-based cathodes also reduces the reliance on limited cobalt sources, rendering advantages of low cost and nontoxicity.

However, the short lifespan and safety issues have severely hindered the practical applications of Li–metal batteries. A high-performance Li–metal battery highly depends on a Li anode with a stable solid electrolyte interphase (SEI), which dictates the deposition behaviors and utilization efficiency of Li during cycling, ultimately leading to the failure of Li–metal batteries. In general, the formation of SEI can be impacted by the solvation of Li ions in the electrolyte, adsorption of solvated Li ions on the surface, temperature, and so on. While employing Mn-based cathodes to pair with Li anodes, a new challenge emerges, which further complicates the formation of SEI. Transition metal ions, such as Mn ions, can dissolve from cathode due to the irreversibly structured, chemical, and electrochemical instability and then migrate to anode and degrade it severely, which prevents the application of almost Mn-based cathodes. In currently available Li-ion batteries with a graphite anode, Mn ions have been proven to be involved in the SEI of graphite, catalyzing the decomposition of the electrolyte and changing the components of SEI, which obviously deteriorates the performance of graphite anodes. As per X-ray absorption near-edge spectra, the valence state of Mn ions in the SEI is Mn(II), as proven by Qiu, Amine, and co-workers. Nevertheless, the effect of the dissolution of Mn ions on a Li anode remains an undeveloped area. The SEI on a Li anode is more sensitive and fragile when compared with the SEI of graphite.
on graphite due to the highly reactive nature of Li dendrites and large volume change of a Li anode during cycles. Moreover, the deposited Li is directly exposed to Mn ions, unlike the intercalated Li ions in the graphite anode.

In this contribution, the role of Mn ions on the formation process of SEI and the subsequent deposition of Li was investigated by introducing anhydrous manganese(II) bis(tri-fluoromethanesulfonyl)imide (Mn(TFSI)$_2$) into the carbonate electrolyte in an electrolytic cell, and a new and practical strategy was proposed to shield crosstalk of Mn ions in a Li-metal battery using the NCM cathode. Concretely, Mn ions interfere with the formation of SEI and regulate the components of SEI, resulting in the emergence of Mn ions and a decrease in the contents of Li$_2$O and LiF when compared to those of the original SEI. This significantly destroys the uniformity of the SEI. Consequently, the nucleation and deposition of Li become sparse and irregular in the presence of Mn ions. In addition, the chemical reaction between Mn ions and Li metal also corrodes the Li anode, which further deteriorates the utilization efficiency of Li anodes. In response, a graphene-coated separator was demonstrated to obstruct the crosstalk of Mn ions by adsorption, prolonging the lifespan of Li-metal batteries under practical conditions.

**Experimental**

**Materials**

Lithium (Li) metal foils (33 or 500 μm) were purchased from China Energy Lithium Co., Ltd. and were directly used as received. Lithium hexafluorophosphate (LiPF$_6$) and Mn(TFSI)$_2$ were purchased from Tokyo Chemical Industry Co., Ltd. Fluoroethylene carbonate (FEC) and dimethyl carbonate (DMC) were purchased from Alfa Aesar Chemical Co., Ltd. All the solvents and Li salts were directly used as received. The electrolyte composed of 1.0 M LiPF$_6$ dissolved in FEC/DMC (1 : 4 by volume) with or without 50 mM Mn(TFSI)$_2$, except when explicitly mentioned otherwise. The NCM cathode was acquired from Shaanxi Gnnano Co., Ltd. with an areal capacity of 2.5 mA h cm$^{-2}$ (measured value). Commercial Celgard 2400 was used as the polypropylene (PP) separator. All the materials were kept and used in a glove box with oxygen and water contents below 0.1 ppm.

**Preparation of graphene-coated PP (G@PP) separators**

Graphene was prepared according to an earlier report. Typically, graphene oxide was prepared by a modified Hummers’ method. The as-prepared graphene oxide was ground into a fine powder, heated to 250 °C for 2 h, and then to 950 °C for 30 min at a heating rate of 30 °C min$^{-1}$ under argon protection. Graphene was obtained after naturally cooling to room temperature.

The G@PP separator was fabricated via a filtration process. Typically, 1.8 mg graphene was dispersed in 20 mL N-methyl-2-pyrrolidone (NMP) by a combination of ultrasonication for 1.0 h and shearing for 3 min. Then, 0.2 mL PVDF/NMP (1.0 mg mL$^{-1}$) dispersion was added into the graphene/NMP dispersion, followed by ultrasonication for 20 min. The mass ratio between the binder and graphene was 1 : 9 in the dispersion. The dispersion was filtered through a piece of PP separator (diameter: 4.0 cm) and subsequently dried at 60 °C for 12 h. The graphene loading on the PP separator was controlled to be approximately 0.15 mg cm$^{-2}$.

**Materials characterization**

Li-metal anodes or deposited Li were firstly washed with DMC three times to completely remove the residual electrolyte and then dried until the solvent was thoroughly volatilized in the glove box. The Li-metal anodes were protected with argon in a homemade container to avoid contact with air during the transferring process before performing the characterizations. The morphologies of the deposited Li were characterized by a scanning electron microscope (SEM, JSM 7401F, JEOL Ltd., Japan) operated at 3.0 kV. The graphene was characterized using a JEM 2010 transmission electron microscope (TEM, JEOL Ltd.) at 120.0 kV, and the mapping by energy-dispersive X-ray spectrometry (EDS) was performed using a TEM equipped with an EDS unit from Oxford Instruments. X-ray photoelectron spectroscopy (XPS) experiments were carried out using a scanning X-ray microprobe (Quantera SXM, ULVAC-PHI, Inc.) operated at 250 kV and 55 eV with monochromated Al-K$_{α}$ radiation.

**Electrochemical measurements**

The electrochemical reduction decomposition of the electrolyte was measured by cyclic voltammetry (CV) using a copper current collector as the working electrode and Li as the counter and reference electrodes at a scan rate of 0.5 mV s$^{-1}$ within 2.0 V and 0.01 V vs. Li/Li$^+$. An H-type electrolytic cell was employed to determine the effect of Mn ions on intrinsic Li deposition without pressure. Mn ions were only introduced into the Li anode side and then the effect of Mn ions on Li deposited on the Cu substrate could be observed. The electrolyte with Mn ions was separated from the electrolyte without Mn ions by a PP or G@PP separator. The current density of deposition was 0.2 mA cm$^{-2}$ and the capacities were 0.2 and 1.0 mA h cm$^{-2}$ for nucleation and final morphology, respectively. The electrolytic cell was assembled and sealed in a glove box and then tested at 25 °C.

Li|Cu and Li|NCM cells were assembled in standard 2032 coin-type cells in an Ar-filled glove box with oxygen and water contents below 0.1 ppm. Li|Cu cells were tested at a current density of 1.0 mA cm$^{-2}$ and capacity of 1.0 mA h cm$^{-2}$, where a Li foil (500 μm) with a diameter of 16 mm and Cu foil with a diameter of 17 mm were used. The Li|NCM batteries were monitored in the galvanostatic mode within a voltage range of 3.0–4.3 V using the LAND multichannel battery cycler, where an ultrathin Li foil (33 μm) with a diameter of 15 mm and NCM cathode with a diameter of 13 mm were used. The amount of electrolyte was 7.7 g A$^{-1}$ h$^{-1}$. The Li|NCM batteries were firstly cycled at 0.1C for two cycles and then cycled at 0.4C (1C = 180 mA g$^{-1}$).
Results and discussion

Changes in SEI formation

The intrinsic effect on the formation of SEI and Li deposition induced by Mn ions was investigated in an H-type electrolytic cell. The use of an electrolytic cell excludes the impact of pressure in coin cells on SEI and Li deposition.\(^{41,42}\) Mn(II) ions have been considered as the most common state of existence of Mn ions in an electrolyte.\(^ {43}\) Anhydrous Mn(TFSI)\(_2\) was selected to eliminate the side-effects of water and no disturbance from the TFSI anion is expected.\(^ {43}\) Mn ions were only introduced into one side (Li reservoir) of the H-type electrolytic cell and then the effect of Mn ions on deposited Li on Cu substrates on the other side can be investigated (Fig. 1a and S1†). A PP separator is placed between the electrolytes with and without Mn ions. In terms of electrolytes, a FEC cosolvent was used for further clarification to investigate the severe challenges induced by Mn ions toward Li anodes, although FEC is considered to be an effective additive to protect graphite anodes and has emerged as a promising additive to ensure uniform Li deposition.\(^ {44}\)

The effect of Mn ions on the electrochemical formation process of SEI was directly identified by a CV test. The reduction of Mn ions occurs during the formation of SEI \(( ca. 1.3 \text{ V} \text{ vs. Li/Li}^+\), Fig. 1b) in the presence of Mn ions in the electrolyte. The reduction in the decomposition potential of FEC is \( ca. 1.1 \text{ V} \) without Mn ions in the electrolyte. In contrast, the typical reduction decomposition of FEC is suppressed with Mn ions in the electrolyte, indicating that the electrochemical decomposition of the electrolyte and the formation processes of SEI are disturbed by the presence of Mn ions. Thereafter, XPS was employed to investigate the change in the components of SEI. Obviously, Mn(II) ions were detected in the SEI upon Li deposition, although there are no Mn ions initially on the Cu side (Fig. 1b), illustrating the fact that a commercial PP separator cannot block Mn ions due to its straight pores. The valence state of the Mn ions in the SEI on Li metal is also consistent with that on the graphite anode. In the Li 1s spectra (Fig. 1c), the content of oxygen-contained components, such as Li\(_2\)O, decreases significantly while Mn ions are involved into the formation of SEI, proving that the normal decompositions of solvents are disturbed because the oxygen-contained components are mainly from solvent.\(^ {45}\) Recently, the role of Li\(_2\)O in enhancing the uniformity of SEI in addition to LiF has also been demonstrated, particularly for FEC-based electrolytes.\(^ {36,46,47}\) In the F 1s spectra (Fig. 1d), the \( -C-F \) components obviously increase and the LiF content decreases in the presence of Mn ions. MnF\(_2\) exists in the F 1s spectra. It is well known that LiF facilitates uniform Li deposition.\(^ {48-50}\) A significant change in the components of SEI can be mainly induced by two aspects: (1) disturbing the electrochemical decomposition of the electrolyte to form the SEI (as shown by the CV test); (2) Mn ions can also react with the decomposed products in the newly formed SEI, as demonstrated in earlier works.\(^ {36,38}\) The significant change in the components of SEI in the presence of Mn ions can deteriorate the uniformity of SEI.

Li nucleation

The homogeneity of SEI dictates the subsequent nucleation and growth of the deposited Li, inducing different morphologies of Li-metal anode and finally determining the cycle life of Li batteries. The intrinsic influence of Mn ions on deposited Li is further investigated in an electrolytic cell by excluding the disturbance of pressure during the plating process. In the absence of Mn ions, the nucleation of deposited Li is regular and compact at a capacity of 0.2 mA h cm\(^{-2}\) with the introduction of FEC as the cosolvent (Fig. 2a), which induces a LiF-rich SEI to regulate uniform Li deposition.\(^ {44}\) The nucleation of Li grows with an increase in the capacity to 1.0 mA h cm\(^{-2}\), yielding smooth and compact Li columns (Fig. 2b). In contrast, the nucleation of Li at the same deposition capacity is irregular and sparse in the presence of Mn ions in the electrolyte (Fig. 2c). With an increase in capacity, the deposited Li exhibits non-compact and corrosive morphology (Fig. 2d). The corrosive morphology of Li is induced by the direct displacement reactions between Li and Mn ions during long-time immersion (Fig. S2†), which also illustrates that Mn ions can penetrate the SEI and SEI cannot totally block Li metal from electrolyte corrosion.

Mn ions were then introduced into working Li/Cu coin cells to evaluate the utilization efficiency and lifespan of the Li anode (Fig. 2e). The coulombic efficiency (CE) of the Li/Cu cells without Mn ions is 93% after 60 cycles. With the addition of 5 mM Mn ions, the CE initially decreases to 90% and then rapidly decays after only 25 cycles. Furthermore, CE continuously and rapidly decreases during the entire life when the concentration increases to 50 mM, where the positive effects on uniform Li led by FEC is counteracted by the presence of Mn ions. The presence of Mn ions severely deteriorates the stability of Li anode because of the following mechanisms (Fig. 2f). Mn ions dissolve from the Mn-based cathode and cross the

---

Fig. 1 (a) Schematic diagram of an electrolytic cell employed for electrodeposition. Mn ions are only introduced into the Li side. XPS spectra of SEI after etching for 1 min on Li deposited on a Cu substrate in an electrolytic cell with and without crosstalk from Mn ions: (b) Mn 2p, (c) Li 1s, and (d) F 1s. Inset in (b) shows the CV curves of the electrolyte with and without Mn ions.
separator to arrive at the anode surface. Firstly, Mn ions regulate the electrochemical and chemical reactions of SEI formation. The uniformity of SEI cannot be effectively maintained with decreased Li$_2$O and LiF and increased components containing –C–F bonds. Consequently, the inhomogeneous and irregular nucleation of Li results in the formation of non-compact Li deposition. Secondly, Mn ions can penetrate the SEI to corrode Li via displacement reactions. The utilization efficiency of the deposited Li significantly reduces during cycling, which accounts for the short lifespan and instability of Li anodes.

**Crosstalk shielding by graphene-coated separators**

Bulk doping, surface coating, core–shell structure, and gradient strategies of the cathode are currently used effective routes to suppress the dissolution of Mn ions,\textsuperscript{22,51,52} protect graphite anodes, and enhance the cycling performance of Li-ion batteries. However, the effect, cost, and technical complexity of the present strategies are unsatisfactory, although several improvements in lifespan have been achieved. Therefore, a new and practical strategy has become imperative in addition to suppressing the dissolution of Mn ions. As an indispensable part of batteries, the general function of a separator is to ensure electron insulation between the anode and cathode. In a working battery, Mn ions dissolve from the cathode and then cross the separator to degrade the Li anode. Therefore, protecting the Li anode can be significantly improved if this crosstalk of Mn ions is obstructed by modifying the separator.

In order to protect the Li anode from the disturbance of Mn ions, a G@PP separator (Fig. 3a) was proposed to block the crosstalk of Mn ions. The specific surface area of graphene is 609 m$^2$ g$^{-1}$ and the pore volume is 2.1 cm$^3$ g$^{-1}$, as reported earlier.\textsuperscript{53} The thickness of graphene on a PP separator by filtration is ca. 25 μm and the areal mass loading of graphene is 0.15 mg cm$^{-2}$ (Fig. 3b). The through pore of a PP separator was covered by graphene (Fig. S3†). When the PP separator was substituted by a G@PP separator and the same current density and deposition capacity as those used above were employed in an electrolytic cell, compact and uniform Li deposition was achieved, similar to that obtained when an electrolyte without Mn ions was used, proving that Mn ions are blocked by the G@PP separator (Fig. 3c). Elemental Mn on the surface of graphene was also detected by the EDS to validate the above-mentioned argument (Fig. S4†). Therefore, Mn ions directly cross the through pores of the PP separator, disturb the electrochemical and chemical formations of uniform SEI and nucleation, and react with metallic Li, ultimately resulting in noncompact and corrosive Li deposition (Fig. 3d). In contrast, Mn ions tend to be adsorbed within the numerous pores of graphene when they cross the G@PP separator, which ensures that the Li anode remains far away from the Mn ions and preserves the original SEI and deposition morphology.

**Crosstalk shielding in a working battery**

The effectiveness of a G@PP separator was further evaluated by using Li|NCM523 batteries under harsh conditions, such as an ultrathin Li anode (33 μm), a high loading cathode (2.5 mA h cm$^{-2}$, measured value), and lean electrolytes (7.7 g A$^{-1}$ h$^{-1}$). NCM523 is a routine cathode in currently available Li-ion batteries for electrical vehicles, where elemental Mn contributes toward the structural stability of NCM.\textsuperscript{24} However, the dissolution of Mn ions also occurs.\textsuperscript{55} In comparison to mild conditions in most publications including a thick Li anode (>200 μm), a low loading...
cathode (<1.0 mA h cm⁻²), and flooded electrolytes (>30 g A⁻¹ h⁻¹), the employment of an ultrathin Li, a high loading cathode, and lean electrolytes facilitates the revealing of the intrinsic issues within the Li anode. The potential issues concealed under mild conditions, such as short lifespan and electrolyte depletion, are revealed under practical conditions, which can further promote the progresses of Li batteries. Furthermore, 80% retention of the initial capacity is considered to be the benchmark of the cycle life in present Li-ion batteries, which is also appropriate for Li batteries aiming for practical applications.

The initial discharge capacity of Li|NCM523 batteries with a PP or G@PP separator is ca. 2.5 mA h cm⁻² (Fig. 4a). The capacity of batteries with a PP separator rapidly decays after 45 cycles and approaches the benchmark of 80% retention on the 62nd cycle. The decay of batteries also accompanies an increase in overpotential (Fig. 4b). While a G@PP separator was employed towards cathode, batteries exhibit stable operation for 100 cycles without any abrupt roll-down. Moreover, the effect of the types and layers of separators were also excluded (Fig. S6†). The overpotential of batteries using a G@PP separator marginally decreases. The cycled Li anode was disassembled from Li|NCM523 batteries for further investigations. Corrosive and noncompact Li was deposited when the PP separator was used (Fig. 4c). In contrast, smooth and compact Li (diameter: 10 μm) was formed in the presence of a G@PP separator (Fig. 4d). After 50 cycles, several isolated Li deposits (marked in white dashed circles) were observed with a PP separator (Fig. 4e). However, there are no obvious isolated Li deposits when using a G@PP separator, revealing that Li can be utilized with very high efficiency (Fig. 4f). Isolated Li cannot be utilized because contact is lost with the current collector; further, because of gradual accumulation, a dead Li layer gets coated on fresh Li, increasing the resistance of Li batteries. The formation of isolated Li originates from the inhomogeneous SEI and Li deposition. Due to the inhomogeneous stripping rate of Li ions induced by heterogeneous SEI, the deposited Li can break from the middle part, which loses contact with the current collector, induces the loss of fresh Li, and decreases the utilization efficiency of Li. Moreover, the chemical reactions between Mn ions and Li also results in the loss of fresh Li. The employment of a G@PP separator can protect the SEI and Li anode from Mn ions, thereby increasing the utilization efficiency of Li and prolonging the cycle life of Li batteries under harsh conditions.

Conclusions

The effect of transition metal ions from Mn-based cathodes on Li-metal anodes was systematically investigated in an electrolytic cell and practical Li|NCM523 batteries. Furthermore, a fresh and practical strategy to obstruct the crosstalk of Mn ions was proposed by designing a graphene-coated separator. Mn ions can cross the pore of the PP separator and deteriorate the stability of the Li anode. The presence of Mn ions interferes with the electrochemical decomposition of the electrolyte. For instance, the reduction of Mn ions emerges and the decomposition of FEC is disturbed, as revealed by the CV test. Moreover, Mn ions can react with the fresh decomposition products of the electrolyte, changing the final components of the SEI. Li₂O and LiF decrease and the components containing –C–F bonds increase in the presence of Mn ions in the electrolyte (where FEC is used as the cosolvent), which destroys the homogeneity of the original SEI with abundant Li₂O and LiF and induces sparse and irregular Li nucleation. Furthermore, the direct chemical reaction between the Mn ions and Li also corrodes the Li anode. Therefore, noncompact and corrosive Li is generated during repeated cycles. Isolated Li easily forms due to the inhomogeneous SEI and noncompact Li, which results in the loss of fresh Li, low utilization efficiency of Li anode, and rapid decay of practical Li batteries. When a G@PP separator was employed, the crosstalk of Mn ions was blocked by adsorption into the numerous pores, protecting the Li anode against damage from Mn ions and prolonging the lifespan of Li batteries. This work provides a fresh perspective into the failure mechanism of Li anode in presence of Mn ions dissolution and highlights the impact of crosstalk of the transition metal ions on the stability of the Li anode. Furthermore, it also affords a novel strategy to deal with the crosstalk of transition metal ions for not only Li-metal batteries but also present Li-ion, silicon-based, sodium-based, and other rechargeable batteries.

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

This work was supported by National Key Research and Development Program (2016YFA0202500 and 2016YFA0200102), National Natural Science Foundation of China (21676160, 21825501, and U1801257), and China Postdoctoral Science Foundation (2018M631480).

Notes and references

50 T. Li, X. Q. Zhang, P. Shi and Q. Zhang, Joule, 2019, 3, 2647–2661.
58 Y. Li, W. Huang, Y. Li, A. Pei, D. T. Boyle and Y. Cui, Joule, 2018, 2, 2167–2177.