New insights into “dead lithium” during stripping in lithium metal batteries

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1. Introduction

The target of carbon-neutral and net-zero emissions drive the highly efficient and sustainable conversion and storage of renewable energy [1]. The safe energy storage systems are essential to utilize renewable energy and achieve cleaner environment [2,3]. Lithium (Li) metal with a theoretical capacity of 3860 mAh g⁻¹ and an electrode potential of −3.04 V versus standard hydrogen electrode is highly recognized as the eternal promising alternative anode for next-generation rechargeable batteries [4–8]. Nevertheless, the major issue of Li metal batteries (LMBs) is the low Coulombic efficiency (CE) and safety issues from the inactive Li accumulation. The metallic Li which is isolated from the lithium anode (named dead Li⁰) consists the major component of the inactive Li. We systematically and meticulously investigated the formation and evaluation of dead Li⁰ during stripping process from electron transfer, the oxidation of Li⁰ to Li⁺ and the diffusion of Li⁺ through solid electrolyte interphase (SEI). The above-mentioned processes were regulated by adjusting the contact sites of electron channels, the dynamic rate of conversion from Li⁰ to Li⁺, and the structure as well as components of SEI. The design principles for achieving less dead Li⁰ and higher CE are proposed as a proof of concept in lithium metal batteries. This new insight sheds a comprehensive light on dead Li⁰ formation and guides the next-generation safe batteries for future application.

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efforts have been made to investigate the evolution of dead Li$^0$. For instance, Dasgupta and co-workers demonstrated that the dead Li$^0$ concentrated on the Li metal anode introduced a tortuous pathway for Li$^+$ transport and thereby increased in total electrode overpotential \cite{34}. Xu et al. developed a physics-based model to understand how dead Li$^0$ affects the apparent capacity loss in LMBs \cite{35}. Tewari et al. found that the amount of dead Li$^0$ formed during stripping increased with decreasing current and increasing temperatures via a synergistic computational and experimental approach \cite{36}. The systematic understanding of dead Li$^0$ formation during stripping process is scarce but essential to suppress dead Li$^0$ formation for the safer and longer-lifespan LMBs \cite{37,38}.

In this contribution, the formation and evaluation of dead Li$^0$ was systematically and meticulously investigated during stripping process from electron transfer, the oxidation of Li$^0$ into Li$^+$ and the diffusion of Li$^+$ through SEI \cite{35,39}. Concretely, when maintaining the electron channels on Li anode, the recovered dead Li$^0$ and less dead Li$^0$ formation can be achieved via modifying the contact sites of electron channels. The higher rate of conversion from Li$^0$ to Li$^+$ renders chaotic Li stripping, while the more amount of dead Li$^0$ is formed. The Li$^+$ diffusion in SEI is subsequently controlled and the extraordinary SEI composed by faster Li$^+$ conductor guarantees less dead Li$^0$ formation. This work affords a comprehensive understanding of dead Li$^0$ formation that guides the design principles to enable less dead Li$^0$ and higher CE of future LMBs.

2. Experimental

2.1. Materials

The Li metal foils (500 $\mu$m) were purchased from the China Energy Lithium Co., Ltd. The 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), and Li bis(trifluoromethansulfonyl)imide (LiTFSI) were provided by Tokyo Chemical Industry Co., Ltd. The Lithium nitrate (LiNO$_3$) was bought from Shanghai Aladdin Bio-Chen Technology Co., Ltd. Copper foil, Poly tetra fluoroethylene (PTFE) rings, and Celgard 2400 polypropylene (PP) membranes were purchased from Shenzhen Kejing Star Technology Co., Ltd. The electrolyte of DD was 1.0 M LiTFSI in DOL/DME (v:v = 1:1) and DD-N was DD with 5wt% LiNO$_3$. All materials were preserved and adopted in a glove box with O$_2$ and H$_2$O contents below 1.0 ppm.

2.2. Materials characterization

The JSM 7401F scanning electron microscope (SEM) and the JEM 2010 transmission electron microscope (TEM) were utilized to observe the morphology of the samples. The samples were protected in Ar in a home-made container to avoid the sample contact with air during transfer process before characterization. The Cu foil in half cell after cycles was washed carefully with DME to fully remove residual Li salt and other impurities. The amount of metallic Li is monitored through Titration gas chromatography (TGC). The detail steps of TGC are: (1) the as-detected electrode disassembled from coin cell and put into a headspace bottle in glove box, (2) 0.5 mL H$_2$O injected into the headspace bottle, (3) 5 mL gas in the headspace bottle transferred into the gas chromatography (GC) after reaction and shaking, (4) the area of H$_2$ peak obtained, and (5) the amount of Li$^0$ gained from the as-established H$_2$ calibration curve. The calibration curve was plotted and fitted through the seven sample of as-measured metallic Li (0.56, 1.04, 1.23, 1.46, 1.91, 2.77, and 3.07 mg) and the corresponding area of H$_2$ peak from GC. A shi-madzu GC-2014 Tracera equipped with a thermal conductivity detector was employed to measure the amount of H$_2$, which can be used to calculate the amount of Li metal based on the following reaction:

$$2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2 \uparrow$$

2.3. Electrochemical measurement

2.3.1. In-situ observation of Li plating/stripping

A homemade optical cell with quartz window was employed to in-situ observe \cite{40,41}. Li foil and Cu wire were adopted as the counter electrode and working electrode, respectively. The Cu wire was 3.0 cm in length and 0.01 cm in diameter. The DD electrolyte was used in the cells. The in-situ observation in this contribution was carried out under a microscope and recorded by a charge coupled device camera. The Solartron 1470E electrochemical workstation (Solartron Analytical, UK) was utilized for galvanostatic Li plating and stripping. The homemade optical cell was observed at 5.3 mA cm$^{-2}$ with a capacity of 0.44 mA h cm$^{-2}$ for every Li plating/stripping process.

2.3.2. Half cell assemble and electrochemical measurements

Half cells were assembled using a Cu foil and a Li metal foil as electrodes, and a Celgard 2400 PP membrane as the separator. In order to relieve the pressure in particle cell, a PTFE ring was placed between Celgard 2400 PP membrane and Cu foil, which could be specified in the main manuscript. The diameter of Cu foil was 13.0 mm. The thickness and diameter of Li metal foil were 500 $\mu$m and 16.0 mm, respectively. The outside and inside diameters of the PTFE ring were 14.0 and 16.0 mm, respectively. The as-assembled half cells were monitored in galvanostatic mode using a Land CT2001 multichannel battery tester. The cells were firstly discharged with the capacity of 2.0 mA h cm$^{-2}$ at a given current density of 1.0, 2.0, 5.0 or 10.0 mA cm$^{-2}$ and then charged until the voltage reached 1.0 V at the current density of 1.0, 2.0, 5.0 or 10.0 mA cm$^{-2}$.

3. Results and discussion

The in-situ optical microscope (OM) was employed to monitor the formation of dead Li$^0$ during repeated Li plating/stripping. The Li is quickly extracted from several active sites on the Cu wire at 5.3 mA cm$^{-2}$ with a capacity of 0.44 mA h cm$^{-2}$. Obviously, the final morphology of Li plating is rugged accompanied by local bulges and caves (Fig. 1a and e). During the subsequent 1st stripping process (Movie S1), the whole outline of Li deposition is rugged accompanied by local bulges and caves (Fig. 1a and e). The in-situ observation in this contribution was carried out under a microscope and recorded by a charge coupled device camera. The Solartron 1470E electrochemical workstation (Solartron Analytical, UK) was utilized for galvanostatic Li plating and stripping. The homemade optical cell was observed at 5.3 mA cm$^{-2}$ with a capacity of 0.44 mA h cm$^{-2}$ for every Li plating/stripping process.

In the images with higher magnification as Fig. 1f revealed, the more local stripping rates are faster as shown the naked Cu wire in red circle (Fig. 1b). During the 2nd plating, the Li metal draws out from the root of origin electrode (Movie S2). The inactive Li formed during 1st stripping process is jacked up by the new Li deposition as shown in the yellow outline (Fig. 1b and c). The inactive Li which is accumulated on the surface of anode severely hinders the transmission of Li ions and therefore leads to the more serious uneven Li deposition in the following each cycle \cite{35,42,43}. Beside of root-growth, the tip growth can be observed on the working Li metal anode (Fig. 1g) because these sites retain the electron channels with the anode. The behavior of the 2nd stripping step is similar with the 1st stripping step (Movie S3). The constant morphology after 2nd stripping compared with the morphology after 2nd plating demonstrates abundant inactive Li formed during stripping process.
Based on the above observation, inactive Li is formed during stripping process and accumulated on the electrode surface at the subsequent cycles, which is harmful for the battery performance and safety (Fig. 2a). In order to further explore the structure and components of inactive Li, TEM was employed to investigate the Li plating and stripping behavior after 1st cycle at the current density of 1.0 mA cm\(^{-2}\) with a capacity of 2.0 mAh cm\(^{-2}\). The lattice fringe spacing of domains indicates the contribution of metallic Li (Fig. 2b), suggesting the metallic Li unreacted during the 1st stripping process. Both Li_2O and Li_2CO_3 can be identified through the lattice plane distance as shown in the Fig. S1, which is the importance component of the SEI layer. The TGC was further utilized to measure the amount of dead Li\(^0\) from the area of H\(_2\) peak area. As the Fig. 2d shown, the peaks of H\(_2\) reacted from H\(_2\)O and the Cu foil after 1st cycle with 1.0 mA cm\(^{-2}\) are at 2.65 min and the area of H\(_2\) peak is 24624. The area ratio of peaks at 3.82 min and 5.81 min is 1:3 and these two peaks also appear in the air sample. Herein the two peaks can be assumed as leaked O\(_2\) and N\(_2\) in air. The as-established H\(_2\) calibration curve and equation are displayed in Fig. S2. Based on the equation of H\(_2\) calibration curve, the capacity of dead Li\(^0\) can be measured as 0.337 mAh precisely while the capacity of inactive Li is 0.538 mAh from the voltage–time curves during Li plating and stripping process. Hence, SEI components retain the capacity of 0.201 mAh and the dead Li\(^0\) is the main component in inactive Li.

The dead Li\(^0\) is directly formed during the stripping process because the partial metallic Li cannot immediately convert into Li\(^+\) but is wrapped by insulated SEI [44–50]. The stripping processes involve the following stages: the electron transfer in solid phase, conversion of the Li atom to the Li\(^+\) and Li\(^+\) diffusion though SEI [51,52]. The detailed investigations of each stage will be exhibited in the further contribution.

The key factor of dead Li\(^0\) formation is blocked electron transfer. To recover the electron channel between dead Li\(^0\) and anode, the external force was applied to the anode with some inactive Li after five cycles at different current density with 2.0 mA h cm\(^{-2}\) per cycle (Fig. 3a). The anode accumulates the irreversible capacity of 5.61 mAh cm\(^{-2}\) after five cycles at the current density of...
1.0 mA cm$^{-2}$ (Fig. 3b). The irreversible capacity of Li mainly comes from the formation of dead Li$^0$, which can be observed through the SEM (Fig. 3c). When the external force applied, the anode subsequently exhibits the revived capacity of 0.14 mA h cm$^{-2}$ at 1.0 mA cm$^{-2}$ and continues to release a revived capacity of 0.37 mAh cm$^{-2}$ at reduced current density of 0.1 mA cm$^{-2}$ (Fig. 3d). When the current density increased to 2.0, 5.0, and 10.0 mA cm$^{-2}$ during cycles, the revived capacity can also appear under the function of external force (Fig. S3). The external force can rupture the partial SEI around the dead Li$^0$ and above the Li anode. The dead Li$^0$ with cracked SEI will revive due to the renewable electron channels linked under the function of external force. Therefore, when constructing more electron channels, the active Li will be guaranteed ceaseless electron transfer and converted into Li$^+$ largely during stripping process (Fig. 3a). The carbon papers (CPs) are adopted as the Li hosts to ensure abundant electron channels. As a result, the diameter of a CP is 8.04 and 8.26 μm at the initial and 1st cycle, suggesting the Li wrapping a CP during plating process and removing from a CP totally as the function of more electron channels during stripping process (Fig. S4). Similar achievements made by Li host have been also found in some literatures [53–60], which is because of not only the reduced local current density but also the increased electron channels through our model experiments. The constant and sufficient electron channels are the necessary condition for more reversible Li$^0$ reaction during Li stripping process and less dead Li$^0$ formation.

The conversion rate of the Li atom to Li$^+$ depends on the stripping current density. A series of stripping current density from 1.0 to 10.0 mA cm$^{-2}$ at the same plating current density with a plating capacity of 2.0 mAh cm$^{-2}$ in the Li | Cu half cells were employed to adjust the conversion rate. Fig. 4a demonstrates that their average CE of initial 30 cycles (the Li stripping capacity/Li plating capacity during initial 30 cycles) range from 48.72% to 92.21%. The average CE reduces as the stripping current density reducing under the same plating current density, suggesting the faster conversion rate results in lower CE and more inactive Li (Fig. S5). Besides, when changing the plating current density, the average CE almost steadies under the same stripping current density. This indicates that the CE is more corresponding with the stripping rate not the plating rate (Fig. S6). Therefore, more targeted strategies for controlling Li stripping process are essential to reduce the dead Li$^0$ formation as well as improve the CE. When the cells last until 50 cycles, the average CE during initial 50 cycles still obeys the abovementioned principles (Fig. S7). The amount of dead Li$^0$ is further measured through TGC and the results demonstrate that the capacity of dead Li$^0$ is 0.837, 0.876, 1.332, and 1.561 mA h cm$^{-2}$ at the stripping current density of 1.0, 2.0, 5.0 and 10.0 mA cm$^{-2}$ after 5th cycle (Fig. 4b). The capacity of dead Li$^0$ has a linear relationship with the accumulated inactive capacity during the initial 5 cycles (Fig. S8). The cumulative dead Li$^0$ continues to increase the battery safety risks during cycles, while the higher stripping current density will deteriorate battery performance because of the more dead Li$^0$ forming.

To further explore the Li$^+$ diffusion in the SEI during stripping process, 5% LiNO$_3$ is added into the DD electrolyte (1.0 M LiTFSI in DOL/DME (v:v = 1:1)), which can be donated DD-N electrolyte. The DD-N electrolyte will construct the uniform SEI with high ionic conductivity [61,62]. This is because the SEI formed in DD-N contains abundant Li components with high Li$^+$ conductivity, such as Li$_3$N and LiN$^x$O$^y$, which have been verified in the previous publications [40,63,64]. The evener and higher conductive SEI achieves the ordered Li$^+$ diffusion from every position of the surface of anode (Fig. 5a). Therefore, the average CE in DD-N during initial 30 cycles are 98.3%, 98.3%, 98.4%, and 67.8% at the same plating current density of 1.0 mA cm$^{-2}$ and the stripping current density of 1.0, 2.0, 5.0, and 10.0 mA cm$^{-2}$, separately, which are significantly higher.
compared with DD electrolyte (Fig. 5b and S9). The morphology of Li anode using the DD-N electrolyte after 1st cycle can further certificate the less dead Li$^0$ forming under the function of ordered Li$^+$ diffusion (Fig. 5c and d). The ordered Li$^+$ diffusion from the surface of anode to the electrolyte can prevent the abundant metallic Li from being wrapped by insulated SEI.

4. Conclusions

The dead Li$^0$ are the major components of inactive Li on the working Li anode, which not only induce the low CE but also hinder the mass transfer of Li$^+$ at some sites where the dead Li$^0$ accumulates. The formation and evaluation of dead Li$^0$ was systematically explored from the processes of electron transfer, conversion of Li$^0$ into Li$^+$, to Li$^+$ diffusion in SEI by adjusting the contact sites of electron channels, the dynamic rate of conversion from Li$^0$ to Li$^+$ and the structure and component of SEI. According to the above results and discussion, the design principles of Li anode are proposed to reduce the dead Li$^0$ formation as follows: (1) sufficient electron channels to ensure continuous electron transfer to the deposition Li, (2) slow charge transfer rate to guarantee the inter Li$^0$ diffusion to the surface of anode, and (3) uniform and fast ion-conducting SEI to prevent the local block of Li$^+$ diffusion. This work describes the comprehensive understanding of dead Li$^0$ formation and guides to reduce dead Li$^0$ for developing the future LMBs with higher CE.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.