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Volumetric variation confinement: Surface protective structure towards high cyclic stability of lithium metal electrode†

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Surface protective structure to efficiently improve the cyclic stability and life-time of the lithium metal electrode is investigated. By volumetrically confining plated lithium metal in the inter-space of ceramic porous layer and isolating the confined lithium via reinforced skin-layer from the attack of electrolyte solvents, Coulombic efficiency of the protected lithium metal electrode reaches very high values "97-99%.

Li metal is the dreaming anode material for high-energy secondary batteries owing to its ultrahigh capacity (3860 mAh g⁻¹) and the lowest reduction potential (-3.04 V vs. S.H.E.).²⁻¹² It had been employed in commercial rechargeable batteries of Li-MSi₂ (M: Ti, Mo) before 1990s.³ However, this type of batteries was quickly obsolete from the market after serious safety accident of battery explosion caused by Li dendrite internal-shorting the cell.⁴ Since then, carbonaceous materials, which only have tenth of the theoretical capacity of Li metal, were widely adopted as anode to construct much safer system, namely the prototype of Lithium Ion Batteries (LIBs). After decades of development since its commercialization in 1991 by Sony, the energy density of LIBs was nowadays close to its upper limitation, ca. 300 Wh kg⁻¹, taking into account all the established advanced materials in each component. Therefore Li metal regained its paramount role under the spotlight of scientific community and industry, to further raise the energy density of rechargeable batteries.

The strategies to prevent internal short-circuit of Li metal based batteries have been devoted with considerable efforts due to the overwhelming impact of the safety accident. Till to date, the rigid membranes, such as polymer and ceramic electrolytes, were considered as the most representative approaches to address this drawback. These types of technologies were developed for the probable applications, especially in electric vehicles, by some pioneering companies, such as SEEO, Polyplyus, and Bolloré. However, their commercialization progresses were unsatisfactorily delayed due to the strict working conditions and/or low cost-effectiveness.⁵⁻⁸ Recently a novel approach to utilize the competitive adsorption of alkali ions (Cs⁺, Rb⁺) has presented a remarkable effectiveness in suppressing the dendrite growth.⁹⁻¹⁰ These results demonstrated the suitable morphological controllability of the lithium growth with appropriate remedies.

Besides the dendrite growth, another hurdle to be conquered is the massive lithium loss per cycle due to the strong reducibility of lithium metal, which chemically reduces the electrolyte solvents.¹¹⁻¹² Although this challenge is not directly linked to the serious safety risk, the continuous loss of lithium source persistently limited the electrode life-time. To address this drawback, various electrolyte additives were screened to construct the stable Solid Electrolyte Interphase (SEI) layers.¹³⁻¹⁸ However, the investigated surface layers suffer from the limited mechanical strength and cannot provide stable isolation of lithium from the attack of solvents in dynamic conditions. Recently, it has been reported by Cui et al. that the Coulombic efficiency could be significantly improved via nano-structured layer coating on the Li metal surface.¹⁹⁻²¹ However, it requires special and delicate preparative conditions, such as nano-scale coating, in the aim to establish suitable structure of the protective layers in good contact with lithium.

In our opinion, the huge volumetric variation, particularly on the surface, is the special challenge of Li metal anode, when compared to graphite. The infinite volumetric change of the Li metal anode during cycling can easily tear the state-of-art SEI layer, which can tolerate ~10% volumetric variation as in graphite anode and enable its operating life-time for thousands of cycles. After cracks of SEI layers, the electrolyte solvents easily permeate across the fissures and chemically react with lithium metal to produce RCO₂Li, RCOOLi and ROLi species in corresponding electrolytes in both plating and dissolution processes, as shown in Scheme 1a.²²⁻²⁵ These side reactions consume large amount of lithium, and seriously
deteriorate the surface homogeneity, which may facilitate the dendrite growth. Therefore, the confinement of the surface volumetric change during Li cycling should be a promising direction to improve the adaptability of Li metal anode in secondary batteries.

Based on the aforementioned strategy, we develop a novel protective structure to keep lithium metal from the attack of solvents. This protective structure consists of a ceramic porous layer which provides inter-space to confine lithium growth and a reinforced skin-layer to improve the mechanical tolerance of the surface protective structure (Scheme 1b). In this work, Al₂O₃ is used as the backbone material of the porous layer due to its good chemical stability with lithium.²⁶⁻²⁷ Various electrolyte additives are explored to check their feasibility to form the reinforced skin-layer in our system. It should be noted that the carbonate-based electrolyte was investigated in this work, instead of the ether-based electrolyte exhibiting much better stability with lithium.²⁸⁻³¹ to explore the possibility to replace graphite anode by lithium metal in LIBs.

The investigated systems are electrochemically evaluated in Cu│Li cells. As shown in Fig. 1a, the bare Cu electrode with regular electrolyte (1M LiPF₆ in 1:1 Ethylene Carbonate, EC and Dimethyl Carbonate, DMС) exhibits very poor Coulombic efficiency in the 1ˢᵗ cycle, as low as ~65%. The lost lithium should be consumed in the chemical reactions with carbonate solvents, and accumulated on the copper surface as the coral-shape species shown by the Scanning Electron Microscopy (SEM) (Fig. 2a). The side reactions continuously took place during cycling and leaded to drastic dendrite growth (Fig. 2b, c) and very poor performances (average Coulombic efficiency of 47% for 50 cycles, Fig. 1b). The electrode containing porous layer tested under regular electrolyte presents improved Coulombic efficiency in the first cycle, ~78%. Absence of rod-shape species on the surface demonstrates that lithium should be deposited in the inter-space of the porous layer (Fig. 2d). However, it seems that the lack of mechanical tolerance caused the porous layer cracks and the inner dendrite growth (Fig. S1, †) as well as the capacity drop (average Coulombic efficiency of 59% for 50 cycles, Fig. 1b) upon cycling.

To improve the mechanical resistance and protective isolating effect of the skin-layer, various additives (Vinylene Carbonate, VC, Fluoroethylene Carbonate, FEC and Hexamethylene diisocyanate, HDI) are explored for their compatibility in the system of Cu electrodes containing porous layers (Fig. S2a, †). For an addition of 300 mM additive in the regular electrolyte, all the used additives raise the first-cycle efficiency up to ~90%, which is close to the graphite materials. However, only FEC achieved an average efficiency as high as 97.6% stabilized for over 50 cycles (82% for VC and 22.4% for HDI). Except the poor performances with HDI probably due to the low ionic conductivity of its reduced products in SEI layer (obviously increased over-potential on the charge-discharge profiles, Fig. S2b, †), the difference in Coulombic efficiency between VC and FEC should be related to the mechanical properties of the skin-layers, as discussed in next paragraph. It should be noted that only utilizing optimized electrolytes (FEC in regular electrolyte) with bare copper electrode cannot achieve the high Coulombic efficiency obtained in presence of porous layer. For example, the Coulombic efficiency quickly dropped from 88% of the 1ˢᵗ cycle to 35% of the 50ᵗʰ cycle, with an average efficiency of 78% (Fig. 1b), indicating that the use of FEC significantly improve the mechanical tolerance of the SEI layer, however, is incapable to hinder the heterogeneous Li growth underneath the skin-layer.

The difference of electrochemical performances in the systems with various additives should be related to the structural stability of the skin-layers (SEI layers). Since few studies exist to probe the mechanical strength of the SEI layer at micro-scale, here we employ Atomic Force Microscopy (AFM) to examine the difference of their SEI layer stability. Fig. 3 shows the SEI layers obtained from various electrolytes. It clearly shows that SEI layers formed in FEC and VC-based electrolytes were denser and thicker than these formed in EC and HDI-based electrolytes. A careful look revealed that the SEI layers from EC and HDI-based electrolytes composed of loose precipitates (Fig. 3a, d); while the SEI layers from FEC and VC-based electrolytes composed of rod-like structures (Fig. 3b, c). In order to semi-quantitatively analyse the difference of their SEI layer stability, we use AFM tip to scratch the SEI layers. It was found that the SEI layers formed in EC (Fig. 4a) and HDI-based electrolytes can be easily scraped off by the AFM tip under contact mode (typical imaging conditions, for example 2 V of vertical deflection signal of photo-detector) after one or two scans. The SEI formed in VC-based electrolyte is much stable than these formed in EC and HDI-based electrolytes, however, after repeating scans (~5 scans) by AFM tip under contact mode (5 V of vertical deflection signal of photo-detector), the SEI layers can still be scraped off (Fig. 4b). One should note that the SEI layers formed in the FEC-based electrolyte is very stable and cannot be scraped off at all even a maximal force was applied (Fig. 4c, d). This optimal mechanical feature also conducted to the structural stability of the whole protective structure upon cycling (Fig. 2e, f). As shown in the cross-section of the disassembled electrode after cycling (Fig 2g, h), no layer cracks and inner dendrites were found, the deposited Li metal was effectively confined in the porous layer (~25 μm) with smooth powder form, which filled the initial void space of the porous layer (Fig 2i). Reciprocally, the SEI layer growing on the porous layer suffers much less mechanical pressure from the smoothly confined Li metal. As consequence, both the Li metal confined in the porous layer and deposited underneath can be efficiently protected by the stable SEI layer for long cycling.

To confirm the metal state of deposited lithium in our optimal system, the protected electrodes with different depths of lithium deposition are evaluated by Magnetic Properties Measurement System (MPMS), since in the electrode constitution, only lithium metal is paramagnetic and all the other components are diamagnetic (Tab. S1, †). As shown in Fig. S3, † and Fig. 5, the magnetic susceptibility of deposited lithium (by subtracting the magnetic susceptibility of the charged electrode by this of discharged electrode) of the electrodes almost presented a linear relationship with the deposited lithium amount. It is worth noting that the magnetic...
susceptibility of a pure lithium foil also obeyed this linear relation. It implies that the lithium metal is well protected from the attack of electrolyte solvents by our optimal system. One should note that this is the first time by the use of MPMS to probe the Li metal quantity in an isolated space.

To better understand the improved performances by the use of our protective structure, Li|Li symmetrical cell was cycled within a voltage window of -0.5~0.5 V with a current density of 2.125 mA cm\(^{-2}\). As shown in Fig. 6a, the bare system only cycles for 8 h before the polarization rising to ±0.5 V. The Electrochemical Impedance Spectroscopy (EIS) results indicate that the interfacial-charge-transfer resistance, \(R_s\), quickly augmented to 120 Ω cm\(^2\) at the end of test (Fig. 6b). Combined with our SEM images, the accumulated products originating from the side reactions between lithium and solvents should impede the charger transfer (Fig. 2b, c). In contrast, our optimal system has worked for more than 160 h, ~20 times longer than the unmodified system. Different from the control sample, it presents a low and stable interfacial-charge-transfer resistance, which is stabilized at ~8 Ω cm\(^{-2}\) for ~140 h and slowly augmented to ~18 Ω cm\(^{-2}\), in the whole testing period. However, the bulk resistance, \(R_b\), slowly increased since 40 h (20 Ω cm\(^2\)) and accelerated to augment from 110 h (24.3 Ω cm\(^2\)) to 160 h (45 Ω cm\(^2\)). In our optimal system, the rising polarization should be related to the depletion of electrolyte. According to the Coulombic efficiency (~97%) of the protected Cu|Li cell, ~2~3% plated lithium reacted with solvents during each cycle. Consequently, the theoretical consumption of electrolyte is calculated to be ~29.5 μL (i.e. the rest volume of electrolyte is ~40.5 μL) at the end of cycling. By calibrating the \(R_s\) values as function of electrolyte volume (Fig. 6c), we find that the initial and final values of \(R_s\) (10 and 45 Ω cm\(^2\)) in the protected system separately correspond to 68.8 and 34 μL remained (i.e. a loss of 34.8 μL during cycling). These results inform that a very small consumption of plated lithium in side reactions still exists even in the optimally protected system. Thus, the further improvement on cyclic stability should be emphasized on the quality of the surface protective layer.

Finally, the effect of the optimal protective system is evaluated in Cu|LiFePO\(_4\) cells (Fig. S4,†). The cells were tested under 0.2 C rate (0.1 mA cm\(^{-2}\)) between 3~4 V. The protected system exhibits a Coulombic efficiency of 74.5% for the 1\(^{\text{st}}\) cycle, corresponding to 0.26 mAh lithium and 0.8 μL solvent consumed to build the skin layer, which is consistent with that of the Cu|Li cell (consumption of ~0.22 mAh lithium and 0.7 μL solvent). The average Coulombic efficiency is ~97.5% from 2\(^{\text{nd}}\) to 50\(^{\text{th}}\) cycles (Fig. S4c,†), which is also similar to that of the Cu|Li cell. Since the amount of lithium is limited, the discharge capacities slowly dropped from 112.1 mAh g\(^{-1}\) at the first cycle to 111.6 and 95.6 mAh g\(^{-1}\) at the 2\(^{\text{nd}}\) and 30\(^{\text{th}}\) cycles, and attained 33.6 mAh g\(^{-1}\) at the 50\(^{\text{th}}\) cycle (Fig. S4b,†). In contrast, the capacity of the control system plummeted from 151.3 to 30.6 mAh g\(^{-1}\) in the first charge-discharge cycle and further dropped to 4.1 mAh g\(^{-1}\) in the 3\(^{\text{rd}}\) cycle (Fig. S4a,†).

Conclusions

We have demonstrated a novel method to protect lithium electrode from attack of electrolyte solvents. The synergetic effect of the porous layer and reinforced skin layers forming the protective structure allows the isolation of the smoothly confined Li inside the porous space located at Li metal surface. The resulting Coulombic efficiency could reach an average value of 97.5% over more than 50 cycles, even in using highly reactive carbonate-based electrolyte. This simple and efficient protective structure could provide a novel approach to develop the promising rechargeable Li metal batteries. A further work to match detailed porous structure to the efficiency in Li metal protection will be investigated by our group, in the aim to reveal an optimal porous structure to maximize the protective efficiency in keeping a minimal space occupied by the porous layer. The optimized structure is expected to achieve a more practical application in battery system.

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Notes and references

Scheme 1 Volumetric surface variation during repeated Li deposition/dissolution in (a) unprotected system with state-of-art SEI layers and (b) protected system with the volumetric confining surface layer (porous + skin layers).

Fig. 1 Cycling performances of Cu/Li cells. (a) Voltage profiles of the 1\textsuperscript{st} cycle. (b) Coulombic efficiencies with current density of 0.5 mA cm\textsuperscript{-2}. The amount of Li plated in each cycle is 1 mAh cm\textsuperscript{-2}.

Fig. 2 SEM images of the dendrite formation on the bare Cu electrode after the 1\textsuperscript{st} (a) and 50\textsuperscript{th} cycle (b, c). Top view of the porous layer on the Cu electrode after the 1\textsuperscript{st} cycle (d) and after the 50\textsuperscript{th} cycle in addition of FEC (e, f). Cross-section view of the porous layer on the Cu electrode after the 50\textsuperscript{th} cycle is shown in (g) with amplified zone in (h), and its initial state before cycling in (i).

Fig. 3 AFM images of SEI layers formed in (a) EC, (b) FEC, (c) VC, and (d) HDI-based electrolytes. Scale bar: 1 μm.

Fig. 4 Scratched patterns result from the SEI layers formed in (a) EC and (b) VC-based electrolytes. Scale bar: 2 μm. SEI layers formed in FEC-based electrolyte before (c) and after (d) the scratch. Scale bar: 1 μm.
Fig. 5 Magnetic susceptibility of the deposited metal lithium in the inter-space of the porous layer, the point at 10 mAh corresponds to a reference measured with a Li foil.

Fig. 6 Cycling tests of Li│Li cells. (a) Voltage profiles versus cycling time. (b) Interfacial-charge-transfer resistance, $R_i$, and bulk resistance, $R_b$, during cycling times. The calibration of bulk resistance, $R_b$ versus electrolyte volume is shown in (c). The estimated electrolyte volumes before and after cycling in protected system are shown in red points.
Scheme 1

(a) Bare system

SEI layer

\[ \text{Li metal} \]

Repeated Li deposition/dissolution

\[ \text{Li metal} \]

\[ \text{Li metal} \]

\[ \text{Li metal} \]

\[ \text{Li metal} \]

(b) Modified system

(porous + skin layers)

SEI layer

\[ \text{Li metal} \]

\[ \text{Li metal} \]

\[ \text{Li metal} \]

\[ \text{Li metal} \]

\[ \text{Al}_2O_3 \text{ particle} \]
Figure 1

(a) Voltage (V) vs. Capacity (mAh cm\(^{-2}\))

(b) Efficiency (%) vs. Cycle number

Legend:
- Black line: Bare Cu
- Orange line: Cu + porous layer
- Blue line: Cu + FEC
- Red line: Cu + porous layer + FEC
Figure 2
Figure 4
Figure 5

- Experimental data
- Linear Fit of Magnetic Moment

Magnetic susceptibility * 10^10

Deposited lithium capacity (mAh)
Figure 6
Composite surface protective structure to keep Li metal from the electrolyte attack and enable Coulombic efficiency as high as 97-99%.