

Construction of Dynamic Alloy Interface for Uniform Li Deposition in Li-Metal Batteries

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Abstract

It is well accepted that a lithiophilic interface can effectively regulate Li deposition behaviors, but the influence of the lithiophilic interface is gradually diminished upon continuous Li deposition that completely isolates Li from the lithiophilic metals. Herein, we perform in-depth studies on the creation of dynamic alloy interface upon Li deposition, arising from the exceptionally high diffusion coefficient of Hg in the amalgam solid solution. As a comparison, other metals such as Au, Ag and Zn have typical diffusion coefficients of 10-20 orders of magnitude lower than for Hg in the similar solid solution phases. This difference induced compact Li deposition pattern with an amalgam substrate even with a high areal capacity of 55 mAh cm⁻². This finding provides new insight into the rational design of Li anode substrate for the stable cycling of Li metal batteries.

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It is well accepted that a lithiophilic interface can effectively regulate Li deposition behaviors, but the influence of the lithiophilic interface is gradually diminished upon continuous Li deposition that completely isolates Li from the lithiophilic metals. Herein, we perform in-depth studies on the creation of dynamic alloy interface upon Li deposition, arising from the exceptionally high diffusion coefficient of Hg in the amalgam solid solution. As a comparison, other metals such as Au, Ag and Zn have typical diffusion coefficients of 10-20 orders of magnitude lower than for Hg in the similar solid solution phases. This difference induced compact Li deposition pattern with an amalgam substrate even with a high areal capacity of 55 mAh cm⁻². This finding provides new insight into the rational design of Li anode substrate for the stable cycling of Li metal batteries.

1. Introduction

Nowadays, Li metal anode is among the most popular topics in the field of battery research due to its ultra-high theoretical capacity (3860 mAh g^{-1}) and low electrochemical redox potential (-3.04 V vs. the standard hydrogen electrode).^[1-4] Yet the uncontrolled Li plating/stripping is a fatal problem for its practical application.^[5-7] Especially, unevenly distributed electric fields cause lithium ions to deposit irregularly, resulting in large amounts of dendritic or mossy lithium on the surface of Li metal electrode.^[8-10] On the other hand, P-zone metal anodes (Si, Sb, Sn, Ge...) possess high capacities with little risks of dendrites due to the inward diffusion of deposited Li atoms driven by the essential alloying reactions.^[11-18] The surface alloying process has been successfully applied to Li metal anodes to regulate Li deposition behaviors.^[19-23]

Electrochemical deposition morphology is largely affected by the substrate properties such as absorption energy, nucleation barrier, ionic mobility and exchange current density.^[24-28] Certain substrate with definite solubility in Li is preferable for reducing Li deposition barriers.^[29] For example, the formation of solid-solution alloy at the Li-rich region allows much reduced Li nucleation potential for Au substrate.^[30] The doping of small amount of Mg into Li substrate also greatly alters the surface energy and results in distinct deposition morphologies from pure Li substrate.^[31,32] Nonetheless, the substrate influence is gradually decayed during Li accumulation due to the fact that the original surface is gradually covered by deposited Li and thus the uncontrolled morphologies remain unavoidable in practical Li metal cells with large areal capacities and high current densities.

Hg is a unique metal that is thermodynamically and kinetically favorable to form alloys with many metals.^[33-35] For example, the alloying reaction is readily processed by casting Hg drops onto Li foil without further treatment at room temperature.^[36] The Li-Hg composite anodes with Li amalgam on the top and Li metal at the bottom afford fast adsorption of Li deposition in electrochemical cells, that is, the elimination of dendrite morphologies at high current densities. In fact, the amalgam layer can be easily peeled off from Li foils and served as an alloy substrate due to the flexible, self-supported and ultra-thin characteristics. Unlike regular metal substrates, Li-Hg interface is kinetically maintained even with a high plating capacity, which is distinct amalgams from other metal substrates that can only form Li-M (M=metal) at the surface. The uniquely super-fast diffusion of Hg atoms in the Li-rich Li-Hg solid solution phase affords fresh amalgam interface during electrochemical Li deposition.

2. Results and discussion

To study different Li-M solid solution formation and their influence on Li deposition, we first compared binary Li-M phase diagrams with selected metals Hg, Ag, Au and Zn, respectively. **Figure 1** a shows phase diagrams of these Li-M solid solution compositions in the range of Li atomic ratio near 100%.^[37] The solubility of Li in the metal substrates significantly improve the deposition interface and lead to much reduced overpotential upon Li nucleation.^[30] The assembly of the cells comprised of Li metal and various substrates are presented in Figure 1b, in which Li foil was used as the counter electrode and the substrate for Li deposition. The Ag, Au and Zn thin foils were purchased and cut into desired size for use. LiHg film electrodes were synthesized by the simple drop-casting method.^[36] 5 μL Hg was coated onto 10 cm^{-2} pure Li foil to spontaneously form thin alloy film (about $\sim 7 \mu\text{m}$ in thickness). LiHg film has a lightweight areal density of 7 mg cm^{-2} and composition of $\text{Li}_{0.46}\text{Hg}_{0.54}$ (Figure S1).

In Figure 1c, the LiHg film shows a two-step feature in the curve. The onset of voltage sharp-drop is attributed to the vast Li deposition on the surface of the LiHg electrode at a large current density of 2 mA cm^{-2} . However, the voltage is rapidly recovered to above 0 V vs. Li^+/Li due to the formation of Li-Hg alloys. After Li is saturated in the amalgam, Li deposition appears as indicated by the flat curve below 0 V. Thus, LiHg substrate exhibits 3 distinct steps upon Li deposition: the initial Li nucleation, the subsequent alloying between Li and LiHg, and the Li deposition on the lithiated amalgam. This feature is not presented for other metal substrates, which only have the sharp dip and the following flat curve below 0 V. The deposition behaviors of Li on Au, Ag and Zn substrates in this study is consistent with the previous studies by other groups.^[38-40] The unique Li deposition process on the amalgam substrate is correlated to the fast Li-Hg alloying reaction that allows immediate Li diffusion into the amalgam phase above 0 V. This assumption is also verified by the violent alloying upon the contact between fresh Li and Hg even at room temperature

when prepared the LiHg film substrate (Figure S2).

We performed in-depth studies to understand the Li-Hg alloying process. **Figure 2** a shows cross-section scanning electron microscope (SEM) images of LiHg film with different Li deposition capacities (0.0, 2.3, 3.1, 5.0, 9.0, 55.0 mAh cm⁻², respectively) at 2 mA cm⁻². A two-layer morphology is clearly shown with the Li capacity of 2.3 mAh cm⁻². In Figure 1c, the lithiation of LiHg film is completed above 1.5 mAh cm⁻², followed by Li deposition on the amalgam surface. The two-layer morphology of the electrode confirms the electrochemical process. Both layers gradually expanded upon the increase of Li deposition capacities, but the compact electrode feature is maintained even with a high volume of 55 mAh cm⁻². The growth of the bottom layer indicates it was not simply a lithiation-deposition process. Instead, the amalgam layer was actively involved in the Li deposition even after Li was saturated in the amalgam solid solution phase to yield the compact Li layer with smooth surface (Figure S3–S5).

The structures of deposited electrodes were analyzed with ex-situ XRD shown in Figure 2b and Figure S6. The as-prepared LiHg film is consisted intermetallic compounds of LiHg₃, Li₃Hg and trace amounts of metallic Li or Li-rich Li-Hg solid solution. The initial lithiation convert LiHg₃ into Li₃Hg within 10 min deposition (Li capacity of 0.34 mAh cm⁻²) and have completely evolved sole Li₃Hg phase after 20 min (~0.67 mAh cm⁻²). This fast phase transformation is crucial to guide the initial Li diffusion into the inner phase at a high current density. With increased Li plating time to 80 min (~2.70 mAh cm⁻²), Li₃Hg is the main phase in the pattern as indicated by the 23.520°, 27.220° and 38.860° peaks, corresponding to the (111), (200), (220) diffractions. The growth of the characteristic diffraction peaks indicates the alloying reactions were dominant process in electrodes. The diffraction peak at 35.920° is emerged and strengthened in subsequent process (>80 min), suggest the nucleation and accumulation of lithium atoms on the surface of the amalgam. Combined electrochemistry, SEM and XRD results, the alloying process (stage I) is the phase transition from LiHg₃ to Li₃Hg, while the subsequent Li deposition gives high compact Li layer with the involvement of Hg (stage II) (Figure 2c).

As discussed above, it is highly possible that the Li deposition process on the top of the amalgam layer is affected by Hg to obtain compacted growth of Li layer. To examine this assumption, Energy disperse spectroscopy (EDS) mappings, HR-TEM and Cs-corrected TEM were employed to explore the composition and structure of the Li layer (**Figure 3**). The electrodes with a Li capacity of 5 mAh cm⁻² were selected for the analysis of the compositions of the Li layer. First, the electrode was examined by SEM and EDS mapping. The EDS mapping clearly confirm the existence of Hg atoms in the Li layer at micron scale (Figure 3a). Next, a sample was carefully prepared by FIB (Figure S7) obtained from the top layer of the electrode. The average thickness of the sample is ~3 μm to avoid any contamination from the bottom Hg-containing layer. It is not easy to probe Li by EDS, but the electron energy loss spectroscopy (EELS) spectrum still shows strong Li signals at 56.0 eV in this sample (Figure 3b).^[41,42] XPS spectra confirm Hg 4f peaks at 101.9, 103.9 eV as well as Li peak at 54.9 eV. The peaks can be assigned to the metallic mercury and lithium (Figure 3c and d) with the atomic ratio 1:99 for Hg:Li (Figure S8).^[43,44] In addition, HR-TEM tests of the sample further confirm Hg is distributed in the Li layer (Figure 3e–h). All the combined results suggest Hg can diffuse upward along with the electrochemical deposition by forming a dynamic alloy interface to regulate Li deposition pattern, as shown in the SEM images in Figure 2.

In contrast, other selected substrates (Ag, Au and Zn foils) exhibit different deposited Li

morphologies under the same electrochemical condition (2 mA cm⁻², 5 mAh cm⁻²). The porous and loosely packed dendrites are clearly observed on the surface of these substrates upon Li deposition, and there is little Ag, Au and Zn being detected in the deposition layer (**Figure 4** a–c), a sharp contrast to observation on the LiHg substrate. The absence of Ag, Au and Zn are also evidenced by the XPS analyses with the deposited Li layer (Figure S9). These results imply the critical role of surface alloying process in avoiding dendritic morphologies. Along with the coverage of the initial interface upon Li plating, the alloying function becomes weaker and dendritic morphologies appear for Ag, Au and Zn substrates (Figure 4d).

To understand the inherent different lithiation behaviors between Hg and other metals, the diffusion coef-

ficient (D) of each metal was calculated in the Li-rich Li-M alloys. As shown in the phase diagrams, the Li-rich zone has a solid solution phase for the selected metals M (Hg, Au, Ag and Zn). The alloy diffusion theory can be explained with Darken equation in a binary A-B alloy:^[45]

$$D = D_{A-B} = D_A x_B + D_B x_A (1)^{[46,47]}$$

Where A and B refer to Li and M (Ag, Au, Zn and Hg), respectively. D_{Li} and D_M are intrinsic diffusion coefficient of Li and M, and x_{Li} and x_M are concentration of Li and M in this study. For the Li-rich solid solution phase, it has $x_{Li} \sim 100\%$ and $x_M \sim 0$, thus the above equation can be simplified as $D = D_M$ (M=Ag, Au, Zn or Hg). D_M can be calculated according to the

diffusion equation:

$$D_M = D_0 \exp \left(\frac{-Q_{sd}}{RT} \right) (2)^{[48,49]}$$

In which, R is the ideal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the room temperature ($T = 298 \text{ K}$), D_0 is the frequency factor of the atom and Q_{sd} is the diffusion activation energy, respectively. D_0 and Q_{sd} of Ag, Au, Zn and Hg atoms are shown in **Table 1**, respectively.^[45] By equation (2), the diffusion coefficient of Ag, Au, Zn and Hg atom is calculated as 1.8×10^{-31} , 1.0×10^{-30} , 1.1×10^{-15} , $1.55 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$, respectively. It is clearly that D_{Hg} is 28, 27 and 12 orders of magnitude higher than for D_{Ag} , D_{Au} and D_{Zn} , respectively. Meanwhile, the radial distance R (or net displacement) of an atom can be estimated by the follow equation.

$$R = \sqrt{D * t} (3)^{[50]}$$

Where t represents diffusion time (s), D is the interdiffusion diffusion coefficient ($\text{mm}^2 \text{ s}^{-1}$). Thus, the radial distance R of each metallic atom can be up to 4.2×10^{-16} , 1.0×10^{-15} , 3.2×10^{-8} , $3.9 \times 10^{-2} \text{ mm s}^{-1}$, respectively. The results reveal Hg can migrate as much as 3-14 orders of magnitude farther than for other metals (**Figure 5 a**). Ideally, the plating capacity of 2 mAh (2 mA cm^{-2} current with 1 hr time and 1 cm^2 square condition) corresponds to a thickness of $\sim 9.7 \text{ } \mu\text{m}$. According to the calculated radial distance R , the super high Hg diffusion coefficient allows a migration distance of $39 \text{ } \mu\text{m s}^{-1}$, which indicates Hg can easily migrate from the LiHg substrate to the top electrolyte/electrode interface to mitigate the formation of Li dendrites through the alloying process. Instead, Ag (Au or Zn) has very limited diffusion distance of $4.2 \times 10^{-13} \text{ } \mu\text{m}$ (1.0×10^{-12} or $3.2 \times 10^{-5} \text{ } \mu\text{m}$) within the same time. The significant difference on metal diffusion coefficient reveals these metals can only regulate Li plating patterns with small current density and capacity, while Hg substrate is capable of evolve to a dynamic Li-Hg interface for uniform Li deposition (Figure 5b).

Further studies on plating/stripping cycling were compared between Zn substrate and LiHg film at 2 mA cm^{-2} and areal capacity of 2 mAh cm^{-2} . The upper voltage was set 1.0 V when evaluated the Coulombic efficiencies. The cell with a LiHg film shows stable stripping/plating over 400 hrs, and the Li|LiHg film cell exhibits superior Coulombic efficiency (100%) over 160 cycles (**Figure 6 a and b**). The stable potential hysteresis indicate a LiHg film can effectively guide Li deposition and stripping behaviors by avoiding dead lithium and dendrites formation (Figure 6c). The Li|Zn cell exhibits a short-circuit phenomenon and unstable coulombic efficiency in the initial cycles (Figure 6d). Full cells were also assembled with a high LiFePO₄ (LFP) loading of 12 mg cm^{-2} . LiHg film|LFP full cell delivers a stable capacity about 100 mAh g^{-1} after 100 cycles at a high rate of 2C (1C=170 mA g^{-1}), while the Zn foil|LFP cell shows obvious capacity decay only in 40 cycles (Figure 6e-g).

3. Conclusion

In summary, it is the first time to propose the concept of dynamic alloying interface to regulate Li deposition pattern. The exceptionally high diffusion coefficient of Hg allows its rapid migration from the substrate to the top electrolyte/electrode interface, thus effectively mitigate the formation of Li dendrites at high plating current (2 mA cm^{-2}) and capacities (5 mAh cm^{-2}). This unique feature is distinct from other metals such as Au, Ag and Zn, which only work with the initial Li plating onto the substrates. This study provides new insight into the rational design of the plating substrates. Metals with low melting points such as Hg, Ga and In may play a critical role in tailoring substrate compositions. Further progress is expected with these

metals for the design of binary or ternary alloy substrates, or accurate control of coating species on regular Cu substrates.

4. Experimental Section

Materials: The pristine self-supported LiHg film was obtained by coating method in an argon-filled glovebox with <0.1 ppm O_2 and H_2O . The preparation of LiHg film was as follows: (1) mercury droplet was spread onto the pure lithium metal to spontaneously form LiHg film by a brush; (2) this film was peeled off the pure lithium metal, the thickness of the film is about $7 \mu\text{m}$ in thickness; (3) the obtained thin film was cut into squares of $1 \times 1 \text{ cm}^2$ by a scissor as electrode. After weighing of this self-supported film, the surface load of LiHg film is 7 mg cm^{-2} , and the surface load of Hg was 6.8 mg cm^{-2} ($5 \mu\text{L}$ liquid phase Hg was coated on 10 cm^{-2} Li foil), thus the surface load of Li was 0.2 mg cm^{-2} . The commercial Ag, Au and Zn foils have the same $1 \times 1 \text{ cm}^2$ squares by a scissor with LiHg film, whose possess thickness of 10, 2 and $10 \mu\text{m}$, respectively. LiFePO_4 (LFP) cathode material was provided by Lishen company with mass loading of 12 mg cm^{-2} .

Physical Characterization: Scanning Electron Microscope (SEM) studies were carried out on Environment Scanning Electron Microscope with a field emission gun (Quanta FEG 250). X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex 600 desktop at 40 kV and 20 mA (Cu K α radiation). Transmission Electron Microscope (TEM) analysis was used on a High-Resolution Transmission Electron Microscope with FEG (Talos F200 X) at 200 kV (HR-TEM) and Transmission Electron Microscope with A Probe Corrector (Titan Themis Cubed G2 60-300) (Cs-TEM). Focused Ion Beam (FIB) sample was synthesized on FIB-SEM system (Helios Nanolab 460HP) at 5 kV and 30 kV (Ga ion beam etching). X-Ray Photoelectron Spectroscopy (XPS) characterization were measured with an X-Ray Photoelectron Spectroscopy (Escalab 250Xi) spectrometer. Optical images were conducted with a Keyence VHX-950F microscope and cell phone.

Electrochemical Evaluation: Coin half cells and full cells were assembled in an Ar-filled glove box (O_2 and H_2O level below 0.1 ppm). In half cells, Ag, Au, Zn foils and LiHg film were acted as working electrodes and pure lithium metal (thickness of $600 \mu\text{m}$) as counter electrode. In full cells, LFP electrode worked as cathode (12 mg cm^{-2} of mass load), the LiHg film and Zn foil anodes were pre-deposited Li capacity of 4 mAh cm^{-2} . The electrolyte was 1.0 M lithium bis-(trifluoromethane-sulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 vol/vol) without any additives. About $100 \mu\text{L}$ of electrolyte was used in each coin cell to standardize the experiment. The three piece of separators with Al_2O_3 coating layer (Celgard 2400) was placed in the middle of two electrodes to protect from short-circuit in the cells. All electrochemical tests were carried out on LAND-CT 2001A multichannel battery tester (Wuhan, China) at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were conducted on a Princeton PARSTAT 2273. The frequency was ranged from 1 MHz to 0.01 mHz with an alternating voltage signal amplitude of 5 mV.

Conflicts of interest

There are no conflicts to declare.

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Table 1. The frequency factor (D_0) and diffusion activation energy (Q_{sd}) of Ag, Au, Zn and Hg atom.

| | Ag | Au | Zn | Hg |
|--|---------|---------|--------|-------|
| D_0 (mm ² s ⁻¹) | 40.000 | 10.700 | 13.000 | 0.011 |
| $Q_{sd} \cdot 10^3$ (J mol ⁻¹) | 184.600 | 177.000 | 91.600 | 4.850 |

Figure 1. a) Phase diagrams of Li-M (M=Hg, Ag, Au and Zn, respectively). The regions where Hg, Ag, Au and Zn dissolved are denoted as (Li), δ (Li), (Li) and β (Li); b) a schematic of Li|substrate cell and the formation of Li-rich solid solution alloys upon Li deposition; c) Li plating profiles of four cells at 2 mA cm⁻² and 5 mAh cm⁻².

Figure 2. Morphology and structure evolution with different Li plating capacities at 2 mA cm⁻². a) The cross-sectional SEM images of LiHg electrodes with areal capacity of 0.0, 2.3, 3.1, 5.0, 9.0 and 55.0 mAh cm⁻²; b) the electrochemical profiles and corresponding ex-situ XRD patterns with controlled Li capacities; c) the schematic illustration of morphology evolution of LiHg substrate upon Li deposition.

Figure 3. Composition analyses for the sample with a plating capacity of 5 mAh cm⁻². a) The SEM image and corresponding EDS mapping of Hg; b) EELS spectrum of Li signal for the FIB sample; c, d) XPS spectra of Hg and Li of the FIB sample; e, f) HAADF image and corresponding EDS mapping image from HR-TEM; g, h) the low, high HAADF images and corresponding EDS mapping from the Cs-corrected TEM model, where Hg agglomeration are clarified as bright domains in the dark Li zones due to the super energy exposure of Cs-corrected TEM and significantly different atomic weight of the two elements.

Figure 4. a–c) The cross- and top-sectional SEM images and corresponding EDS mapping images with Li deposition capacity of 0 mAh cm⁻² and 5 mAh cm⁻²: a) Ag foil, b) Au foil and c) Zn foil. d) The schematic diagram of the morphology evolution from pristine electrode to the subsequent plating process for Ag, Au and Zn.

Figure 5. a) The histogram of theoretical diffusion equal distance R and diffusion coefficient D of Ag, Au, Zn and Hg in the Li-rich solid solution phases; b) the schematic upon Li atoms deposition on different substrate foils (Ag, Au, Zn foil and LiHg film).

Figure 6. The electrochemical performance of cells assembled with Zn foil and LiHg film electrodes with a prelithiation capacity of 4 mAh cm⁻². a) Stripping/plating-time curves at 2 mA cm⁻² and 2 mAh cm⁻²; b–d) Coulombic efficiencies and corresponding stripping/plating curves at 2 mA cm⁻² and 2 mAh cm⁻²; e–g) LiHg film|LFP and Zn foil|LFP full cell performance: e) cycling performance, f) and g) capacity-voltage curves at various cycles.

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