In-Situ Electron Microscope Observations of Electrochemical Li Deposition/Dissolution with a LiPON Electrolyte

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Abstract

This paper studies the effect of current density on electrochemical Li deposition/dissolution at glassy solid electrolyte (LiPON) interfaces with a thin-film Cu current collector by in-situ scanning electron microscopy (SEM). The Li nucleation rate and the saturation density of Li nuclei increase with increasing current density. When the current density is smaller than 300 µA cm⁻², Li islands continue to separately grow under a Cu film to the critical sizes to produce small cracks in the Cu film resulting in isolated Li rod growth from the cracks. On the other hand, a current density of 1.0 mA cm⁻² provokes the nucleation of Li islands at a number of sites. They rapidly coalesce under a Cu film in all lateral directions before cracking the Cu film, whereby Li growth is prevented.

Keywords : Li, Solid-state Electrolyte, Electrodeposition, In-situ Scanning Electron Microscopy

1. Introduction

A great deal of attention has been paid to the development of next-generation-rechargeable batteries that may store several times more energy than commercial Li-ion batteries. The research on all-solid-state-lithium batteries (SSLB) has been significantly advanced by advancements in techniques to decrease solid/solid interface resistivity and new discoveries of solid Li⁺ ionic electrolytes.⁴⁻⁷

Inorganic solid electrolyte blocks Li dendrite growth if Li metal is used as the negative electrode. This is certainly attractive because the theoretical energy density of Li metal (2062 Ah L⁻¹) is much greater than those of presently commercialized negative electrodes (<1000 Ah L⁻¹). Moreover, there are also other advantages of using ceramic electrolyte: (1) non-flammability; (2) simplified battery pack design due to no risk of electrolyte leakage; (3) longer cycle and calendar life compared to organic liquid electrolyte.

However, Li rapidly grows to penetrate through solid electrolyte during charging if there are percolated gaps between grains like in a ceramic-powder pellet. Hence, the Li anode easily touches the cathode even with solid electrolyte in some cases. Amorphous electrolyte plays a key role in blocking Li growth from the anode for using Li metal as the negative electrode in SSLB. It is thus important to study how Li metal grows and dissolves through amorphous solid electrolyte interfaces during charging and discharging. Extensive studies of electrochemical Li deposition and dissolution have not sufficiently been devoted to solid electrolyte systems.⁴⁻⁷

Previous work studied the electrochemical Li deposition and dissolution using an amorphous electrolyte of lithium phosphorous oxyxynitride (LiPON).⁸⁻¹⁰ Li deposition invokes non-uniform nucleation that leads to whisker-like growths on a LiPON layer. Consequently, analyzing every step of Li growth trajectories at fixed sites during charge-discharge processes is an important step toward understanding the mechanism of non-uniform Li growth.

In-situ electron microscope observation is a powerful approach to unveil transient electrochemical nucleation behaviors that are essentially obscure in ex-situ observations. In-situ electron microscope observations for electrochemical nucleation studies have been reported using transmission electron microscopy (TEM).¹¹ A few recent studies used atmospheric scanning electron microscopy (ASEM) for observations of Ag dendrite growth in liquid.¹² Since solid electrolytes are not volatile, conventional electron microscope techniques can be applied for observations of in-situ electrochemical experiments using this class of electrolytes. We report on the growth and dissolution of Li islands/whiskers through solid electrolyte interfaces coated with a metal current collector as a function of current density during charge-discharge processes using in-situ scanning electron microscopy (SEM).

2. Experimental

Figure 1 shows a two electrode-type-electrochemical cell for in-situ SEM observation. The majority of the electrolyte (1.25 cm × 1.25 cm) is a mirror-polished Li₁₋₃Al₀.₃Ti₁₋₇(PO₄)₃ (LATP) sheet (OHARA Co.) with a thickness of 150 µm. It was subsequently coated with LiPON layers with thicknesses of 2.5 µm on the upper and bottom surfaces by radio frequency (RF) magnetron sputtering. The details are described elsewhere."
The working electrode is a Cu film deposited onto a circular area with a diameter of 5.0 mm in the center of the LiPON-coated upper surface of the electrolyte by pulsed laser deposition (PLD). The counter electrode is a Li film with a thickness of 3–4 µm and an area of \((0.45)^2 \times \pi \text{ cm}^2\) evaporation-deposited onto the bottom of the electrolyte. This trilayered ceramic electrolyte sheet with the electrodes is clamped with thick Cu and brass plates to obtain electric contacts as presented in Fig. 1. There is a viewport with a diameter of 3.0 mm in the center of the top Cu plate. This viewport is aligned within the area of a Cu working electrode. In-situ observations of electrochemical Li deposition and dissolution were conducted through the viewport. The brass plate is attached to a Li counter electrode on the bottom. An electrochemical cell is assembled on a custom-made sample stage in an Ar-box. It is carried into a Keyence VE-9800 SEM without being exposed to air. The observations were conducted with an accelerating voltage of 10 kV. One frame during in-situ SEM observation is taken with a scan time of less than one second. A potentiostat drops (20 to 400 mV) need to be subtracted from the voltages estimated above. Hence, electrolyte ohmic resistance estimated above. Hence, electrolyte ohmic resistance is negligibly small in the present study.

The absolute values of the voltages in Fig. 2 are the sum of the overpotentials for a working electrode and the ohmic drop across electrolytes. The Li deposition current density increases as the current density increases. The deposition amount per site decreases as the nucleation density increases because the total charges are the same for all the current densities \((= 180 \text{ mC cm}^{-2})\). At a current density of \(1.0 \text{ mA cm}^{-2}\), Li rod growths are therefore not observed due to their large nucleation density. After each in-situ experiment, the displayed magnification of an SEM was lowered to observe surrounding regions outside the field of view exposed to electron beams for 180 to 3600 s. There were no clear differences in Li nucleation density and morphology between regions with and without a long exposure to electron beams.

Figure 3 shows Li deposition current density as a function of voltage. Impedance spectroscopy measurements (the inset in Fig. 3) revealed direct current (DC) resistance values of 2.5 to \(3.0 \times 10^3 \Omega\) for the entire electrolyte region. These values are close to the electrolyte resistance estimated above. Hence, electrolyte ohmic drops (20 to 400 mV) need to be subtracted from the voltages in Fig. 2 to estimate the overpotentials for a working electrode. We assume that the overpotentials for a Li counter electrode are negligible small in the present study.

The current density increases linearly in the voltage range examined in this study. This slope of the increase in current density is parallel to the ohmic drop increment. This means that the overpotentials for Li deposition are approximately constant \((~60–100 \text{ mV})\) at any current density.

Figure 4 shows nucleation density transients at different current densities \((50, 100, 300 \text{ µA cm}^{-2}\)). The nucleation density cannot be accurately measured at 1.0 mA cm\(^{-2}\) because of the rapid coalescence of Li nuclei. A transient nucleation density variation is often assumed by the following equation:\(^{15-17}\)

\[
\frac{N_t}{N_0} = 1 - \exp(-k_\text{n} t)
\]  

where \(N_0\) is the nucleation density at a time of \(t\), \(N_0\) is a saturation nucleation density, \(k_\text{n}\) is a nucleation rate constant. The nucleation rate at \(t = 0\) is as follows:

\[
\frac{d}{dt} \left( \frac{N}{N_0} \right) \bigg|_{t=0} = k_\text{n}
\]  

The general shape of a curve drawn by Eq. (1) fits well to the transient behaviors in Fig. 4. The theory behind Eq. (1) assumes that
nucleus-centered exclusion zones, which radically extend with time, deplete the free zones for subsequent nucleation resulting in the saturation of nucleation density.\(^1\) However, further studies are necessary to conclude that the above nucleation theory can be sound for electrochemical Li growth in a solid electrolyte system in the present study. This paper therefore approximates the above \(k_n\) by the nucleation rates only at the onset times (dashed lines in Fig. 4). The inset figure shows \(k_n\) as a function of voltage. In theory, \(k_n\) exponentially increases with increasing overpotential. The results in Fig. 4 show a rapid increase in \(k_n\) with increasing voltage. The ohmic loss for each sample (not shown) was evaluated by measuring its overall electrolyte resistance using the AC impedance spectroscopy.

The series of SEM snapshots in Fig. 5A show the time evolution of a Li nucleation site at 50 \(\mu\text{A cm}^{-2}\). The Cu surface slightly swells after approximately 8 minutes suggesting that a Li island initiated its growth beneath the Cu. A crack in the Cu surface starts to be significant after 15 minutes. A straight Li rod with a diameter of 1.4 \(\mu\text{m}\) appears from the crack and grows toward the left of the field of view. The growth rate of this Li rod is roughly estimated to be 2.0 \(\text{nm s}^{-1}\). This means that the local current densities for the growth of Li rods are approximately 1.5 \(\text{mA cm}^{-2}\).

When electrochemical Li dissolution is performed at a current density of 50 \(\mu\text{A cm}^{-2}\), the Li rod gradually hollows resulting in the creation of a cavity while surface layers remain undissolved as presented in Fig. 5A. The coulombic efficiency on dissolution was 85\% (cutoff voltage: 1.5 V).

Figure 5B shows an SEM image of Cu surface after all Li residues were entirely removed with distilled water. A circular hole with a diameter of approximately 1.4 \(\mu\text{m}\) is observed. The circular lid is sustained at one edge. This image helps understanding of how a Li rod grows to appear in Fig. 4A. We think that Li nuclei deform the top Cu layers by growing until the stress in deformed Cu reaches the fracture point. Eventually, Li escapes through a crack to grow. A rod-shape Li consequently grows as illustrated in Fig. 5C.

Figure 6 shows sequential SEM pictures during Li electrodeposition at 1.0 \(\text{mA cm}^{-2}\). Deformations of Cu layers due to Li nucleation are observed in all places. Isolated Li islands at 50 seconds laterally grow to coalesce at 120 seconds as delineated with dotted lines. On dissolution, the coulombic efficiency was 84\% (cutoff voltage: 1.5 V).

When the current density is smaller than 300 \(\mu\text{A cm}^{-2}\), rod-shape Li grows as shown in Figs. 2 and 5. This is because the nucleation densities are so small that Li islands continue to separately grow to the critical sizes (i.e. 1–2 \(\mu\text{m}\) in diameter) that produce cracks in a Cu film (Fig. 7A). On the other hand, adjacent Li islands rapidly coalesce under Cu layers at 1.0 \(\text{mA cm}^{-2}\). This island coalescence functions to level the Li surface (Fig. 7B). Consequently, the local stress concentrations in a Cu film are suppressed compared to the case that individual Li islands continue to grow separately. A small crack is observed at 1.0 \(\text{mA cm}^{-2}\) when the charge amount is 150 mC cm\(^{-2}\) in Fig. 6. On the other hand, the cracking occurs when the charge amount is only 40 mC cm\(^{-2}\) at 50 \(\mu\text{A cm}^{-2}\) in Fig. 5A.

The mean distance to the first nearest neighbor for random points that distribute in a two-dimensional field is described below.\(^1\)

\[
r_n^* = (2\pi N)^{-\frac{1}{2}}
\]

where \(N\) is the point number density (cm\(^{-2}\)). The average diameter of Li islands when cracks are observed in the top Cu surfaces is approximately 1.4 \(\mu\text{m}\). If \(r_n^*\) is 1.4 \(\mu\text{m}\) in Eq. (3), \(N\) is \(3.2 \times 10^7\) cm\(^{-2}\). Hence, Li islands are supposed to substantially coalesce before cracking occurs in a Cu film if the nucleation density is greater than \(3.2 \times 10^7\) cm\(^{-2}\). The nucleation density at 300 \(\mu\text{A cm}^{-2}\) (−0.16 to −0.22 V) is \(1.2 \times 10^7\) cm\(^{-2}\) in Fig. 4. Usually, the nucleation density exponentially increases with increasing kinetic energy.\(^1\) Therefore, it is likely that the nucleation density is far beyond \(1.2 \times 10^7\) cm\(^{-2}\) and much greater than \(3.2 \times 10^7\) cm\(^{-2}\) at 1.0 \(\text{mA cm}^{-2}\) (−0.5 to −0.6 V). Li islands thus rapidly coalesce over the entire area of the electrode before Cu surfaces crack at 1.0 \(\text{mA cm}^{-2}\). Li rod growth is hence suppressed at high current density because Li nuclei are too close to continue to grow to the critical sizes (1.4 \(\mu\text{m}\) in diameter) for Cu cracking without coalescing with neighbors due to increased nucleation density.

Figure 5. (A) SEM snapshots (width: 7.7 \(\mu\text{m}\)) at 5.0-minute intervals for the growth of a Li rod at 50 \(\mu\text{A cm}^{-2}\). The lower-right-corner image is taken at the same location after Li is stripped by anodic dissolution. (B) SEM image of a Cu lid after Li is entirely removed with distilled water. Scale bar: 1.0 \(\mu\text{m}\). (C) Growing Li rod from LiPON surface coated with a Cu layer.
3.2 Current densities per Li coverage area

True values of current densities for Li deposition sites are larger than the applied current density values because Li non-uniformly covers the area of a working electrode except in the case of 1.0 mA cm\(^{-2}\). The critical Li diameters to initiate cracks in Cu layers are measured in the inset in Fig. 8 and are 1.4 µm on average as described above. This value is almost independent of current densities within the range investigated in this study. The Cu film thickness seems to be the predominant factor for the critical Li island sizes that produce cracks in Cu layers. Figure 8 shows effective current densities that are calculated by dividing the applied current density values (i.e., 50, 100, 300 µA cm\(^{-2}\)) by total-Li coverage areas \((= (0.7 \mu m)^2 \times \pi \times N_s)\). Although 0.7 µm is not a good approximation for the radii of Li deposition sites when Li islands initially grow under a Cu film, the effective current densities for Li deposition sites are eventually close to 1.0 mA cm\(^{-2}\) \((= 1.3 \times 10^2 \text{nm thickness of Li per second})\) for all the current densities. This number is close to the observed growth rate \((\sim 2 \text{nm s}^{-1})\) of the Li rod in Fig. 5. These results suggest that Li\(^+\) ionic flux to each deposition site eventually becomes approximately the same in steady state after a sufficiently long duration. Hence, Li nucleation events take place in all places over the working electrode with a large overpotential when the overall current density is 1.0 mA cm\(^{-2}\) as seen in Fig. 3. Approaching 1.0 mA cm\(^{-2}\) for the local current density in any case seems to imply the presence of a specific rate-limiting step for Li deposition in this regime. The current density linearly increases with increasing voltage in Fig. 3, whereby it is unlikely that Li\(^+\) ionic transport in the LiPON layer determines the local deposition rates. The kinetic energy to grow Li rods at 1.0 mA cm\(^{-2}\) is possibly smaller than the nucleation energy under a Cu film overcoming strain energies in Cu and Li. This model needs to be further examined.

4. Conclusions

We have observed transient behaviors of electrochemical Li deposition and dissolution that occur through the charge transfer across LiPON electrolyte interfaces coated with a Cu current collector film using an in-situ SEM technique. The use of a glassy electrolyte without grain boundaries effectively prevents Li growth toward the cathode.

At lower current densities \((\leq 300 \mu \text{A cm}^{-2})\), Li nucleation densities are small enough for individual Li islands to continue to grow separately. Consequently, Li islands initiate cracks in Cu surfaces. Li rods begin to grow through those cracks. The Li nucleation rate at Cu/LiPON interfaces increases with increasing overpotential. The nucleation densities do not show further increases after certain durations. On the other hand, Li nucleation events take place in the entire region of Cu/LiPON interfaces at 1.0 mA cm\(^{-2}\). Li islands readily coalesce under a Cu film to laterally extend in all directions. Li rod growths are therefore effectively prevented.

The use of a non-volatile solid electrolyte offers the unique benefit that an electron microscope can be directly coupled with electrochemical experiments without substantial efforts to modify sample cells used in bulk experiments. This study has revealed how Li grows after the nucleation takes place beneath a Cu current collector by in-situ SEM. In-situ electron microscope techniques may have great potential for new surface analyses in solid-state electrochemistry that cannot be easily addressed in liquid electrolyte systems.
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References