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Temperature Effects on the Nucleation and Growth of Li at Cu/LiPON Interfaces

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Abstract

This study investigates how Li plating/stripping at Cu/LiPON interface change at temperatures around 100 °C.

1. Introduction

Lithium metal has been regarded as an attractive anode candidate with a high theoretical specific capacity. However, dendrite formation has been a crucial problem in making lithium metal anode into practical use for a secondary battery. On the other hand, all-solid-state-lithium battery has been expected as a most promising battery system to enable highly reversible Li metal anode. This expectation has actually been supported by a fact that inorganic solid-state electrolyte generally has an enough large shear modulus large exceeding the critical value that Monroe and Newman have predicted to be necessary to prevent dendrite formation. However, it has recently been recognized that suppression of dendrite formation and improvement in Coulombic efficiency are not as easy as mentioned above. It poses that there is still a lack of fundamental understanding of Li plating/stripping on solid-state electrolyte. Metal electrodeposition in liquid electrolytes has been studied by many authors since a couple of centuries ago. However, since previous studies on the Ag whisker growth from α-AgI crystals, metal electrodeposition/dissolution on solid-state electrolytes have not as often been studied as for liquid electrolytes. Understanding the mechanism of Li electrodeposition/dissolution on oxide solid-state electrolyte is indispensable to design highly reversible Li metal anode in oxide-based-solid-state battery. We have developed a model for the Li nucleation at metal current collector (CC)/LiPON interface by taking into consideration the effect of mechanical work, which only exists in the solid/solid interfacial system. This paper reports the effect of temperature on the kinetic factors of the Li nucleation on metal-CC/LiPON interface. The nucleation rate exponentially increases with increasing the temperature following the Boltzmann distribution function. The nucleation barrier corresponds to the nucleation Gibbs energy, which is supposed to be determined by the sum of each difference in surface/interfacial work, electrochemical work, and mechanical work for a solid/solid interfacial system. This study particularly focuses on how the Li nucleation rate increases as a function of overpotential at each temperature. This is because such measurements enable quantitative estimations for the dependence of the Li nucleation barrier on the temperature. This will also likely be to help understand each of surface/interfacial and mechanical work contributions for the Li nucleation at metal-CC/LiPON interface.

2. Experimental

The details of the cell fabrication steps were described elsewhere. The top and bottom surfaces of a $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) sheet (1.25 cm × 1.25 cm, Ohara Co.) were coated with 2.5-μm-thick LiPON layers by radio frequency (RF) magnetron sputtering at a power density of 1.1 W cm^{-2}. A Cu CC film with a thickness of 30 nm was deposited on the top LiPON surface by pulsed laser deposition (PLD) using 4th harmonic Nd:YAG laser with a laser power of 400 mW. A 1.0-μm-thick Cu CC film was deposited by RF sputter-deposition. The CC area was controlled to be 5.0 mm in diameter using a physical mask. A 2-to-3-μm-thick Li film with a diameter of 9.0 mm was deposited on the bottom LiPON surface by vacuum evaporation deposition.

Electrochemical impedance measurements were carried

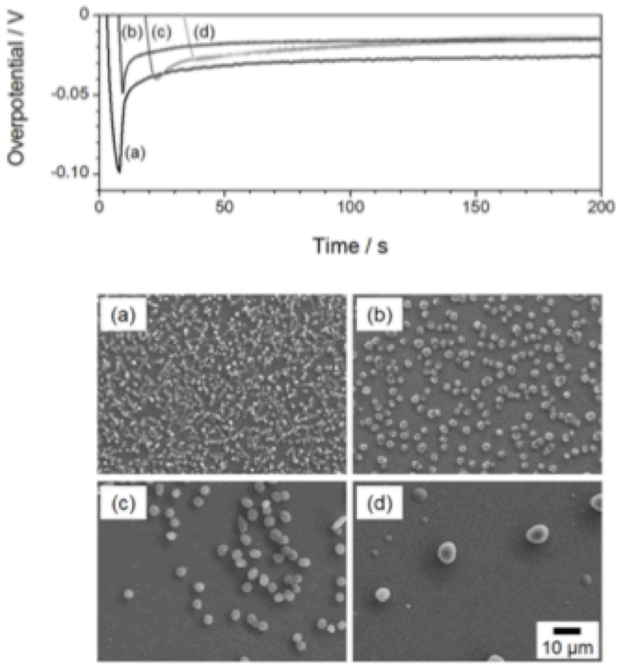

Figure 1. (Top) Overpotential transients during Li plating at 100 μA cm^{-2} with 30-nm-thick-Cu CCs. (Bottom) SEM images of Cu CC surfaces after Li plating at 100 μA cm^{-2} for 1800 s. (a) 25 °C, (b) 60 °C, (c) 80 °C, and (d) 100 °C.

out with voltage amplitude of 20 mV in the frequency range from 3×10^6 to 1 Hz. Li electrodeposition and dissolution were performed under galvanostatic conditions at 1.0 mA cm^{-2}. This current density value was averaged over the entire area of a CC film of 5.0 mm in diameter. The Li plating duration was fixed at 1800 seconds, and the Li stripping was terminated at the cut-off voltage, which was set to be +1.5 V. The measurement temperature was varied from 25 to 100 °C. All the electrochemical measurements were performed in an Ar-filled-glove box with a dew point lower than −70 °C. The samples were transferred into the SEM chamber without the exposure to air when SEM observations were conducted.

3. Results and Discussion

Figure 1(Top) shows overpotential transients during Li plating at 100 μA cm^{-2} for 1800 s at (a) 25 °C, (b) 60 °C, (c) 80 °C, and (d) 100 °C. The overpotential is calculated by subtracting the ohmic loss from the voltage value for each measurement. The height of the negative peak (nucleation overpotential) decreases with increasing the temperature. **Figure 1**(Bottom) shows SEM images of Cu CC surfaces after Li plating at each temperature. The number density and average size of Li particles decreases and increases, respectively, with increasing the temperature. It is considered that Cu/Li and Li/LiPON interfacial energies are lower at higher temperatures to decrease the nucleation Gibbs energy, and the diffusion of Li adatoms along the Cu/LiPON interface was promoted to decrease the number density of Li deposition sites. We will also show the results of *in-situ* SEM observations for Li plating/stripping reactions on LiPON electrolytes at different temperatures.

4. Conclusions

Li plating was conducted on Cu-coated-LiPON electrolytes at various temperatures from 25 to 100 °C. The nucleation overpotential decreases with increasing the temperature. Moreover, the nucleation number density also decreases with increasing the temperature. The diameter of each plated Li particle is larger at a higher temperature. It is considered that the interfacial energy of Li/LiPON and Li/Cu interfaces decrease due to the increased temperature whereby the Li nuclei radii are supposed to increase at a higher temperature. This leads to the decrease in local current density. Hence, the nucleation overpotential decreases.

Acknowledgements

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References

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