Li Plating/Stripping Reactions on Oxide Solid Electrolytes

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An inorganic-solid-state electrolyte can play a role as a separator for suppressing Li dendrite formation. Moreover, the solid-state electrolytes are non-flammable thereby guaranteeing high safety. This property is important for large-scale applications such as electric vehicles. Hence, all-solid-state-lithium battery (SSLB) has been recognized as a strong candidate for a next generation battery realizing the use of a high capacity Li metal anode.

However, it has been reported that the short-circuiting also occurs with solid-state electrolytes. Therefore, in order to realize stable charge/discharge cycles of SSLB using the Li metal anode, it is necessary to understand the nucleation/growth/dissolution at solid/solid interfaces and dendrite formation associated with these processes. This study investigates how the nucleation/growth, dissolution, and dendrite formation of Li occur on inorganic-solid-state electrolytes such as $Li_7La_3Zr_2O_{12}$ with various kinds of metal current collectors (CCs) using an *in-situ* scanning-electron microscopy (SEM) technique.

Figure 1 shows the voltage transient and *in-situ* SEM images during Li plating on Ta-doped $Li_7La_3Zr_2O_{12}$ (Toshima Manufacturing Co.) coated with a Cu-current-collector film. The diameter and thickness of the Cu film were 5.0 mm and 30 nm, respectively. The applied current density was 100 μA cm^{-2}. After starting the measurement, the negative voltage peak soon appeared indicating the Li nucleation. It was observed that Li rods began to grow through cracks in the Cu film after the nucleation. The voltage then increased to −40 mV to show an almost steady state. However, the short-circuiting eventually occurred at (h). This is likely because Li dendrites penetrate through the electrolyte. The number density of the nucleation sites was actually smaller than at Cu/LiPON interface in the previous studies [1,2]. Local current densities estimated from the growth rates of the Li rods were greater than 100 mA cm^{-2}. This large current density is supposed to trigger the dendrite formation through the most vulnerable paths, which are probably along grain boundaries. Additionally, these results deny that dendrite formation occurs after the voltage exceeds a certain threshold.

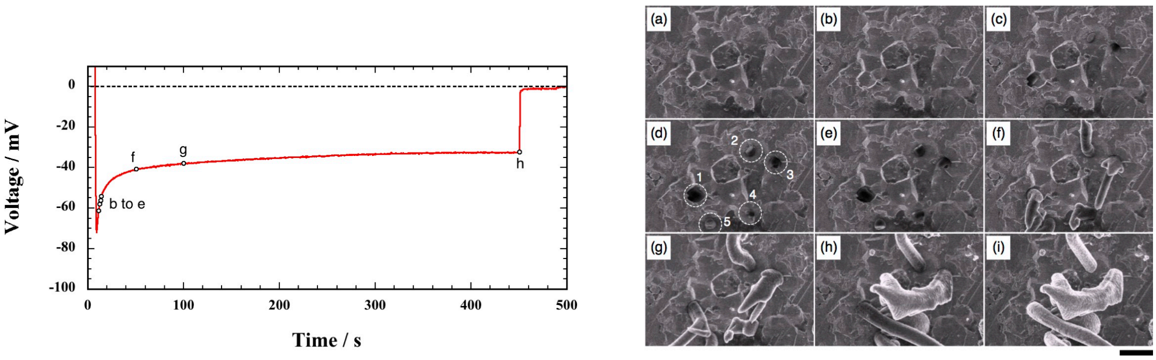

Fig. 1. (Left) Voltage transient during Li plating on Ta-doped $Li_7La_3Zr_2O_{12}$ coated with a 30-nm-thick-Cu-current-collector film at 100 μA cm^{-2}. (Right) *In-situ* SEM images during Li plating with the voltage-transient in the left figure. Each image was taken at (a) 0, (b) 11, (c) 12, (d) 13, (e) 14, (f) 50, (g) 100, (h) 450 s, and (i) after the Li plating. The dotted-line circles in (d) indicate the nucleation sites (five in total). Scale bar: 5 μm

References:

[1] M.Motoyama, M.Ejiri, and Y.Iriyama, Electrochemistry 82 (2014) 364−368.
[2] M.Motoyama, M.Ejiri, and Y.Iriyama, J. Electrochem. Soc. 162 (2015) A7067−A7071.