

Interfacial Phenomena for Li Electrodeposition at PC/Liquid Metal

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Electrochemical nucleation and growth phenomena must be well controlled to create the unique interface in advanced energy conversion & storage devices. The battery reversibility is often determined by the coupling phenomena between mass transfer rate and morphological variations at electrolyte/electrode interfacial phenomena. It is believed that dendrite formation at metal negative electrode determines the safety and durability. Electrochemical nucleation and growth on solid and liquid substrate are discussed.

As to the electrochemical reaction at electrolyte/liquid metal interface, the study of liquid metal batteries as energy storage devices has been reported recently [1]. The researches on electrodeposition of semiconductor materials like Si and Ge [2], actinoid elements recovery in nuclear waste fuel technology [3] include such an academic interest as well as the polarography [4]. In order to develop the advanced ultra-large scale energy storage devices with Li metal negative electrodes linked with conventional electrical network, it is indispensable to understand the Li electrodeposition mechanism on various substrates in detail. The interfacial phenomena at electrolyte/liquid metal during Li electrodeposition may provide a new design insight in the unique electrode/electrolyte interface. In this study, Li was electrodeposited on a Ga(l) electrode, and the interfacial behavior at propylene carbonate/Ga(l) interface was investigated. The surface imperfections on solid substrate provide the nucleation sites of Li to preferentially result in the dendrite growth. As an alternative electrode material, we focused on liquid metal substrate, which probably has a smoother and clearer surface in comparison with solid substrate of same metal.

Electrochemical behavior of Li^+ ion on a Ga(s) and Ga(l) in PC- LiClO_4 at 25 / 40°C was investigated. The cyclic voltammograms for Ga(s) at different scan rates showed the current density peaks which attributed to the reduction of Li^+ ion. Good linearity between current peak and square root of scan rate indicates the reduction of Li^+ ion on a Ga(s) in a diffusion-limited process while no such a correlation was observed on Ga(l) substrate. Moreover, the current-time transients curves obtained by potentiostatic polarization showed the typical maximum and local minimal current behavior ascribed to the nucleation and growth of Li were observed on Ga(s). On the other hand, a monotonously decreasing current transient phenomenon was observed on Ga(l) substrate.

In order to reveal the electrodeposition mechanism of Li on Ga(l), the interfacial behavior of Ga(l) during potentiostatic polarization was investigated. With proceeding potentiostatic operation, the liquid surface shape considerably changed from protruded to flat entirely. This phenomenon can be discussed in terms of interfacial tension difference accompanying of reduced Li metal dissolved into Ga(l). This consideration was supported by Ga-Li phase diagram and electrochemical measurements. It is hoped that the electrochemical interfacial phenomena at liquid metal/liquid electrolyte may open a new insight in the material science for large scale energy storage technology.

References:

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