Unravelling the Effects of Additive on Li Growth Mechanism by *In-Operando* Transmission X-ray Microscopy

Chen-Jui Huang(黃貞睿)[1], Hsien-Chu Tao(陶賢竹)[1], Shi-Kai Jiang(蔣仕凱)[1], Pei-Lun Hsieh(謝佩倫)[1], Wei-Nien Su(蘇威年)[2], Chun-Chieh Wang(王俊杰)[3], and Bing-Joe Hwang(黃炳照)[1,3]*

[1]Department of Chemical Engineering, National Taiwan University of Science and Technology.

[2]Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

[3]National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

Abstract

Ever since the inventory of Li-ion batteries, various anode materials such as graphite and metal alloy have been extensively studied and commercialized. Yet, the capacity and energy density of these anodes still fall behind the growing demands of high performance battery for high power electric vehicles. Recently, metallic Li anode has been revisited and gain great research interest since it has been recognized has the holy grail for metallic anode material due to its ultra-high theoretical capacity (3860 mAh/g) and low reduction potential (~3.014 V vs. SHE). However, severe dendrite formation and dead-Li formation during the cycling of Li metal anode greatly hinder its practical application due to the fact of potential safety hazard caused by penetration of dendrite. Thus, understanding the mechanisms relating to Li growth is in desperate need such as nucleation growth, dendrite formation, dead-Li formation, and SEI formation. Herein, *in-operando* Transmission X-ray Microscopy (TXM) is used to visualize the above mentioned growing phenomena in real-time with different additives in commercialized Li-ion battery electrolyte. The additives studied in this work include fluoroethylene carbonate (FEC), $LiPF_2O_2$ (LPF), lithium difluoro(oxalato)borate (LiDFOB). Different morphologies of plated Li are observed with quite different growing behavior. The *in-operando* TXM technique established in this work can serve as a great platform evaluate the effects of additives, surface modification, or electrolyte formulation for metal dendrite suppression in various metal batteries such as sodium metal battery and zinc metal battery.

Keywords- Lithium growth, dendrite, dead-Li, in-operando TXM.

Introduction

Lithium metal, with an ultrahigh theoretical specific capacity (3,860 mAh g^{-1}) and extremely low redox potential (-3.040 V vs. standard hydrogen electrode), has already been extensively investigated over the four decades. However, lithium metal batteries (LMB) still suffer from several barriers and yet to be commercialized. More specifically, the safety issues induced by Li dendrite growth and internal short-circuit (ISC), poor efficiency attributed to the formation of high surface area lithium (HSAL, dendrite) and dead Li, and severe electrolyte decomposition at the negative electrode leading to electrolyte dry-up and the formation of thick solid electrolyte interphase (SEI) that increases the internal resistance and consumes the electrolytes.

To overcome the above-mentioned hurdles, several approaches have been reported such as electrolyte formulation, surface modification, and additives to mitigate the dendrite formation and dead-Li formation. Apart from evaluating the electrochemical performance of different approaches, it is still not enough to understand the Li growth, dendrite/dead-Li formation mechanism within different electrolyte systems.

From our previous work, we have successfully visualized the dead-Li formation and dendrite growth using *in-operando* TXM within a plastic Li||Cu cell[1]. In this work, we modified the cell set-up with a confined reaction area to control the current density, and directly visualized the effects of different additives on dendrite suppression and promoting uniform Li plating/stripping.

Experiments

The *in-operando* TXM measurements are conducted at the BL01B1 beamline in National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The incident X-ray with photon energy of 8 keV transmits the as-assembled in-situ plastic Li/Li cell upon Li plating/stripping processes, goes through a zone

plate and phase ring to generate phase contrast images. Each of the image with the frame size of 15×15 μm is acquired by 20 seconds of exposure time to gain a satisfactory image quality.[1] The mosaic image is obtained by assembling various single images with the size of 30(W)×75(H) μm. In addition, a blank image at the region with only plastic bag and electrolyte was taken and used as the background subtraction for each acquired image. During measurement, the electrochemical Li plating process is simultaneously conducted using a portable potentiostat (AutoLab M101, Metrohm) to apply a constant current of -0.2 mA cm^{-2} for an hour based on the area of Li foil.

Results

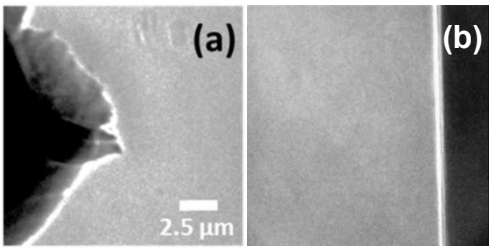

Figure 1. Surface roughness comparison between (a)previous set-up[1] and (b)modified set-up.

With the modified cell set-up, we perform *in-operando* TXM measurement using the conventional carbonate-based electrolyte (1M $LiPF_6$ in EC:DEC) to serve as a reference for the study of Li plating/stripping mechanism. From *Figure 2a*, it can be observed that dendritic Li (high surface area Li, HSAL) severely grown after the plating process with the mossy structure, which has a rather loose integrity. This could lead to continuous SEI fracture upon cycling, consumption of electrolyte, and safety hazard. Meanwhile, during the stripping process, the dendrite starts dissolving from the region of the deposited Li where is closer to the surface of Cu wire. This can be explained by the higher charge transfer resistance at the farther end of the deposited Li from Cu surface. Thus, the disconnection of the dendrite causes the formation of dead-Li, which then results in low coulombic efficiency and fast capacity fading in anode-free Li metal battery.

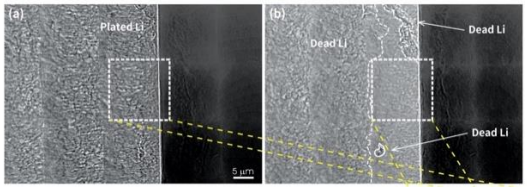

Figure 2. In-operando TXM measurement for Li plating/stripping. Mosaic images of the Cu surface (a) after Li deposition and (b) Li stripping under the current density of 2 mA cm^{-2} with 1M $LiPF_6$ in EC:DEC as the electrolyte.

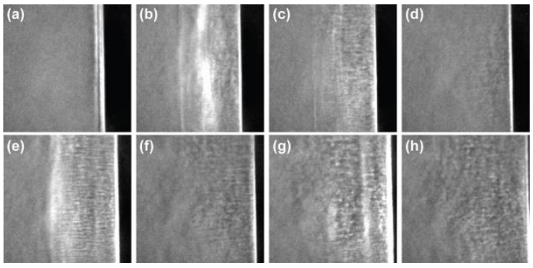

Figure 3. in-operando TXM observation of Li growth under the current density of 2 mA cm^{-2} with 1M $LiPF_6$ in EC:DEC with 1 wt% of LPF as the electrolyte.

We further applied the modified cell set-up different electrolyte configuration, the effect of LPF as an additive for dendrite suppression is shown in *Figure 3.* It can be seen that LPF significantly suppressed the dendrite formation and dead-Li formation. Which can potentially lead to higher coulombic efficiency of LMB and AFLMB and extend the cycle life of the batteries.

Discussion

The *in-operando* TXM experiments successfully visualized the formation of dendrite and dead-Li during charge/discharge processes. The platform can be applied in different electrolyte systems and serve as a protocol evaluating the effect of dendrite suppression by additives or surface modification, which shows great potential and advantage on the development of next generation high energy density and safety AFLMBs.

References

1. Cheng, J.-H., et al., Visualization of Lithium Plating and Stripping via in Operando Transmission X-ray Microscopy. The Journal of Physical Chemistry C **2017**, 121 (14), 7761-7766.