

Resolving Electrode-Electrolyte Interfaces in Batteries with Low Dose Cryogenic Transmission Electron Microscopy

Zewen Zhang¹, Yuzhang Li², Weijiang Zhou³, Yanbin Li¹, Wah Chiu^{3,4,5} and Yi Cui^{1,6*}

¹. Department of Materials Science and Engineering, Stanford University, Stanford, CA, United States.

². Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA, United States.

³. Biophysics Program, School of Medicine, Stanford University, Stanford, CA, United States.

⁴. Department of Bioengineering, Stanford University, Stanford, CA, United States.

⁵. Division of CryoEM and Bioimaging, SLAC National Accelerator Laboratory, Menlo Park, CA, United States.

⁶. Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA, United States.

* Corresponding author: yicui@stanford.edu

Solid-liquid interfaces are commonly studied in the absence of the liquid phase due to shortcomings in existing characterization tools to simultaneously access both solid and liquid phases at the nanoscale. This leads to significant gaps in our understanding of structure and chemistry of the key components and interfaces in battery systems, especially the solid-electrolyte interphases (SEI), an interfacial layer formed at the electrode-electrolyte interface due to the electrochemical/chemical decomposition of electrolytes [1]. We adapted and modified a thin film vitrification method [2] to preserve the sensitive interfaces in batteries at native liquid electrolyte environments, where holey carbon grids were coated with evaporated Cu as the current collector in a battery coin cell to host Li metal dendrites deposition and maintain a thin film of liquid electrolyte after blotting.

A series of images of the vitrified electrolyte were taken at various total doses to determine the dose limit for vitrified electrolytes [Fig. 1]. Two types of liquid electrolytes were tested here, 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC) and 1 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME). In carbonate-based electrolytes, small bubbles in the electrolyte appear rapidly at around 50 e⁻/Å². These bubbles were probably hydrogen liberated from the electrolyte solvent molecules [3]. In ether-based electrolytes, there is no apparent bubble formation at the same total dose compared to carbonate-based electrolytes. However, by raising the dose rate to 100 to 200 e⁻/Å²/s, similar bubble formation was observed for ether solvents, too.

High resolution cryo-TEM images were acquired by a Gatan K3 IS camera in the electron-counting mode. One or two short exposure (0.1 s) single-frame shots were taken to estimate the defocus and make it as close as possible to Scherzer defocus. Cryo-EM images were taken with an electron dose rate of around 45 e⁻/Å²/s, a total of 5 frames were taken with 0.1 s per frame for each image. The threshold damage for Li metal and SEI under cryogenic conditions with a 300-kV electron beam should be a lot higher than this [4]. Li metal plated in commercial carbonate electrolyte, 1 M LiPF₆ in EC/DEC, was used as an example to reveal the SEI in the electrolyte [Fig. 2]. Such sample preparation methods and imaging protocols enables the high spatial resolution characterization of these sensitive interfaces in batteries at their native liquid electrolyte environments.

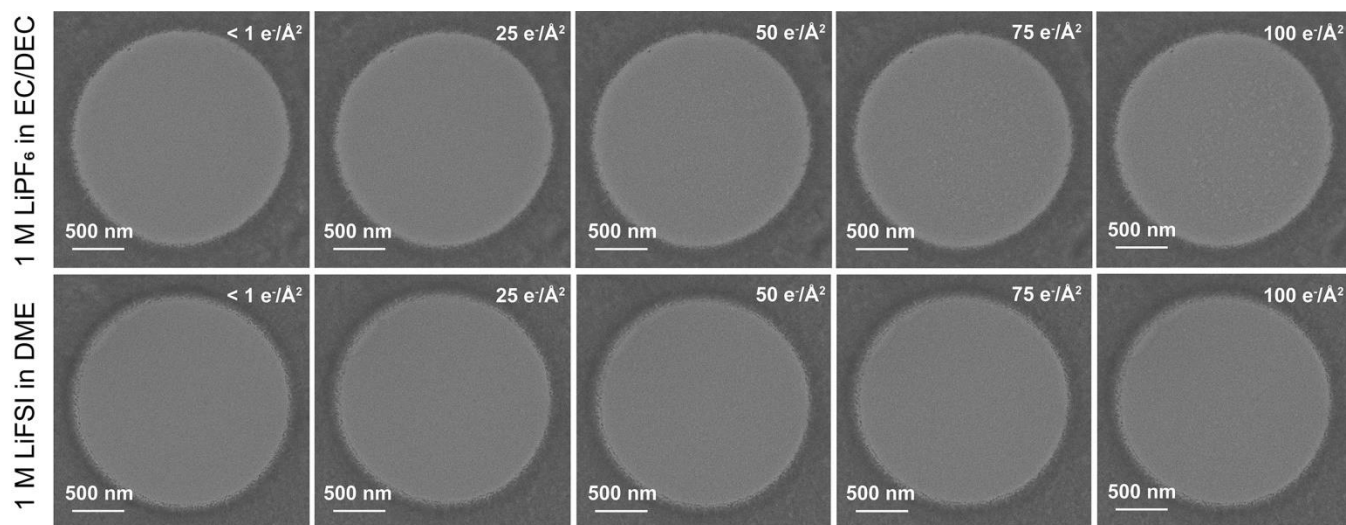


Figure 1. Dose test results for two different liquid electrolyte systems, 1 M LiPF₆ in EC/DEC and 1 M LiFSI in DME.

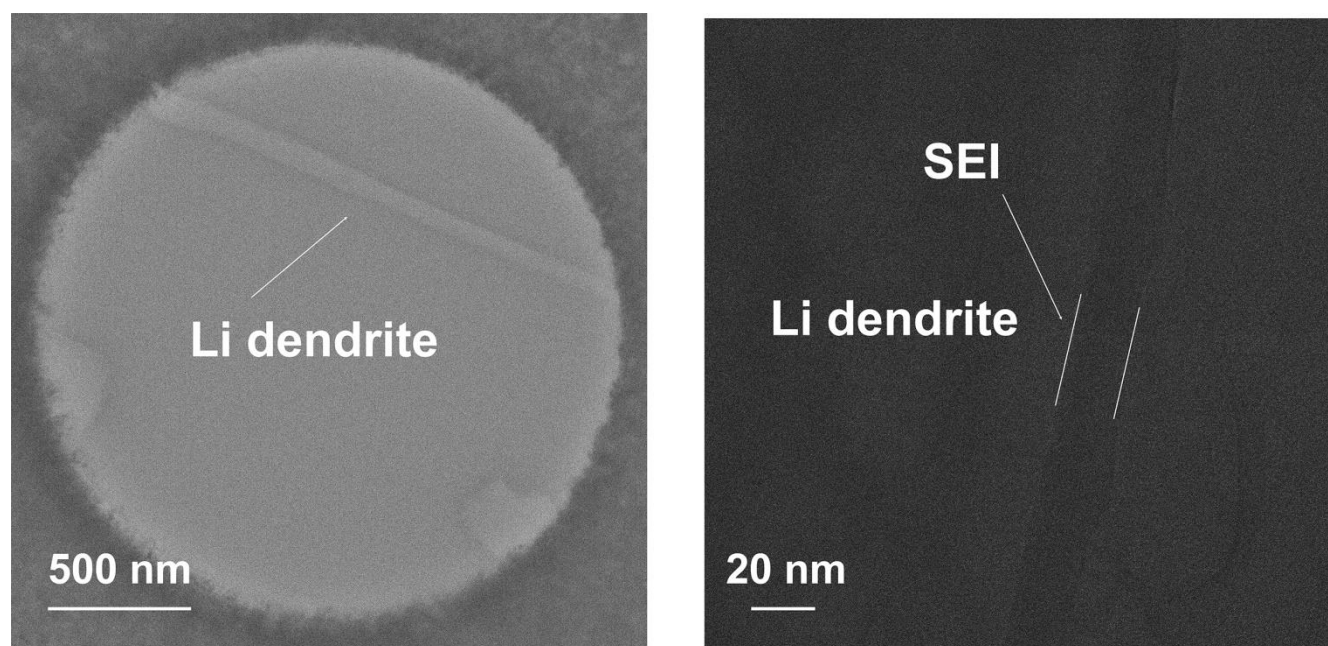


Figure 2. Low resolution and high resolution cryo-TEM images of lithium metal dendrites plated on a Cu evaporated holey carbon grid and embedded in vitrified carbonate electrolyte (1 M LiPF₆ in EC/DEC).

References:

- [1] K Xu, *Chemical Reviews* **114**(23) (2014), p. 11503.
- [2] KA Taylor and RM Glaeser, *Science* **186** (1974), p. 1036.
- [3] RF Egerton, *Micron* **119** (2019), p. 72.
- [4] Y Li et al., *Science* **358** (2017), p. 506.