

Liquid Electrochemical Cell for *in-situ* TEM Studies of Batteries

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Real-time tracking of the physical and chemical changes that occur in the battery during operation is critical for understanding how the electrodes function and why they fail. In a complex composite electrode, bulk and interfacial changes occur at all length scales, from nano-scale in primary nanoparticles to micron-scale in secondary particles and agglomerates. Typically, *in-situ* X-ray techniques have been employed for studying structural changes in the bulk electrodes. However, the poor spatial resolution limits their ability to probe nano-scale changes in individual particles and at interfaces. The recent advancements in *in-situ* transmission electron microscopy (TEM) techniques have opened a new avenue to study various battery processes within the nano-scale regime at high temporal and spatial resolution. However, these nano-electrochemical cells build on the open-cell configuration are limited in the choice of electrolytes – either use solid or ionic liquids [1, 2]. Herein, we demonstrate the utility of the liquid-cell technique for *in-situ* TEM studies of batteries, with an advantage of being flexible of using standard liquid electrolyte, to observe electrochemical reaction within individual particles under real electrochemical conditions.

The liquid-cell platform (designed by Hummingbird Scientific) consists of silicon microchip devices with a three-electrode cell configuration (top chip) for electrochemical measurements, and an integrated microfluidic channel (bottom chip) for liquid flow path (Figure 1a, b). The electrode materials are directly loaded onto a patterned chip, and are further assembled into a liquid cell. Standard liquid electrolytes (e.g. 1M LiPF₆ salt in ethylene carbonate and dimethyl carbonate) are sealed within the thin membranes (50 nm or below) of the top and the bottom chips in a cell. We have studied two different types of cathodes materials, Cu_xV₂O₅ and FeF₂ as model systems. They are promising cathode materials because of their ability to accommodate more than one electron per transition metal, thus resulting in higher specific capacities (>500 mAh/g) [2, 3].

We performed *in-situ* TEM studies of lithium electrochemical reactions with individual Cu_xV₂O₅ and FeF₂ nanorods, directly visualizing such electrochemical process during phase nucleation and transformation in the bulk, as well as related interfacial phenomena. A spatial resolution down to nano-scale is achieved under optimized imaging conditions. As shown in Figure 1c, d, reasonably good contrast of nanoparticles in the liquid electrolyte is obtained by annual bright-field STEM imaging. A further careful characterization is currently underway, to gain more details on the liquid-solid interactions within individual particles. In addition, it is critical to study the facet-dependent evolution and phase transformation in single-crystalline Cu-V-O and FeF₂ nanorods during lithiation and delithiation. Details from *in-situ* TEM studies, including complex reactions in the electrode-electrolyte interface, along with lithium transport kinetics and morphological evolution in individual electrodes will be discussed [4].

References:

- [1] Huang et al., In situ observation of the electrochemical lithiation of a single SnO₂ nanowire electrode. *Science* **330**, 1515 (2010).
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- [3] Wang, F. *et al.*, Conversion reaction mechanism in lithium ion batteries: study of the binary metal fluoride electrodes. *J. Am. Chem. Soc.* **133**, 18828-18836 (2011).
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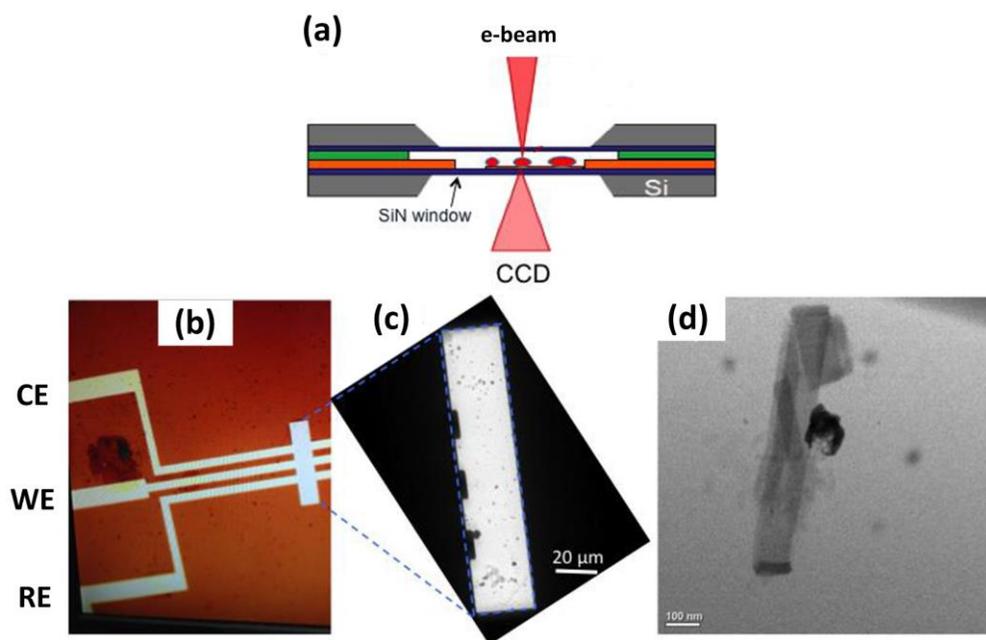


Figure 1. Liquid electrochemical cell for *in-situ* TEM studies of batteries. (a) A schematic illustration of *in-situ* liquid cell for use in the TEM. (b) Optical image of a patterned chip, with integrated counter (CE), working (WE), and reference (RF) electrodes. (c, d) Bright-field TEM images of Cu_xV₂O₅ nanorods in the presence of liquid electrolyte.