

## ***In Situ* Electrochemical Cell TEM for Battery and Fuel Cell Systems**

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Significant progress has been made towards liquid *in situ* transmission electron microscopy (TEM) for material systems [1]. TEM provides atomic to micron scale morphological and compositional information, which, when combined with *in situ* techniques, enables observation of dynamics at high spatial resolution. Incorporating electrodes allows *in situ* electrochemical experiments to be performed for batteries [2,3] and fuel cells [4]. The further development of these systems requires nanoscale insight into the fundamental mechanisms of operation and degradation. Here we discuss critical factors behind chip performance and *in situ* techniques for fuel cell and lithium ion battery materials.

The *in situ* chip we designed reproduces the performance of a traditional electrochemical cell. The working electrode is on the silicon nitride viewing membrane to enable imaging of the electrochemical process (Fig 1a). We use an electron-transparent, glassy carbon working electrode that has a featureless background signal originating from the capacitive response of the liquid (Fig 1b). Classical test cases for electrochemistry are reproduced *in situ*, as shown by cyclic voltammetry of platinum nanoparticles on Vulcan in 0.1M NaOH measured in the TEM (Fig 1b). This is a rigorous electrochemical test case, since the features are surface effects, including hydrogen adsorption and desorption on the platinum surface, that are sensitive to contaminants at the sub-monolayer level. [3]

This optimized electrochemical cell chip enables studies of processes for energy conversion and storage. We study platinum nanoparticles on high surface area carbon in 0.1 M H<sub>2</sub>SO<sub>4</sub> (Fig 2), a common fuel cell catalyst that can also perform electrolysis. At sufficiently low or high potentials, water is split to form hydrogen or oxygen gas as verified by EELS (Fig 2b,c). In the STEM images (Fig 2a), the Pt-C aggregates initially have low contrast, indicating thick liquid. After a low potential is applied, a hydrogen bubble is formed near the particles (region with dark background), which dissipates 20-30 s after the potential is returned to open circuit. At high potentials, an oxygen bubble is formed. One factor impacting the electrochemistry is a shift in the potentials due to hydrogen diffusing to the Pt pseudoreference electrode, changing the reference to a hydrogen couple (H<sub>2</sub>/H<sup>+</sup>) rather than (Pt/PtO).

Combining spectroscopy with *in situ* imaging enables chemical identification during processes such as the charging and discharging of a battery [3]. In Fig 3, we charge and discharge the battery cathode material LiFePO<sub>4</sub>. We track the state of lithiation by imaging regions of the material that have lost 5 eV in energy filtered TEM (EFTEM) mode. The 5 eV signal indicates delithiated FePO<sub>4</sub>, and we see more delithiated regions appear and disappear reversibly on charge and discharge. This is a promising method for electrochemical energy storage and conversion materials, since they undergo energy changes on the order of a few eV during cycling, as long as the energy resolution is sufficient. [5]

### References:

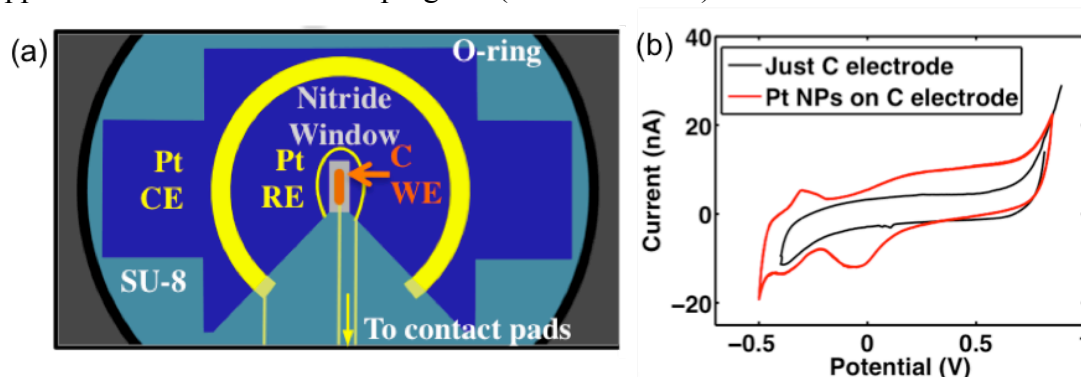
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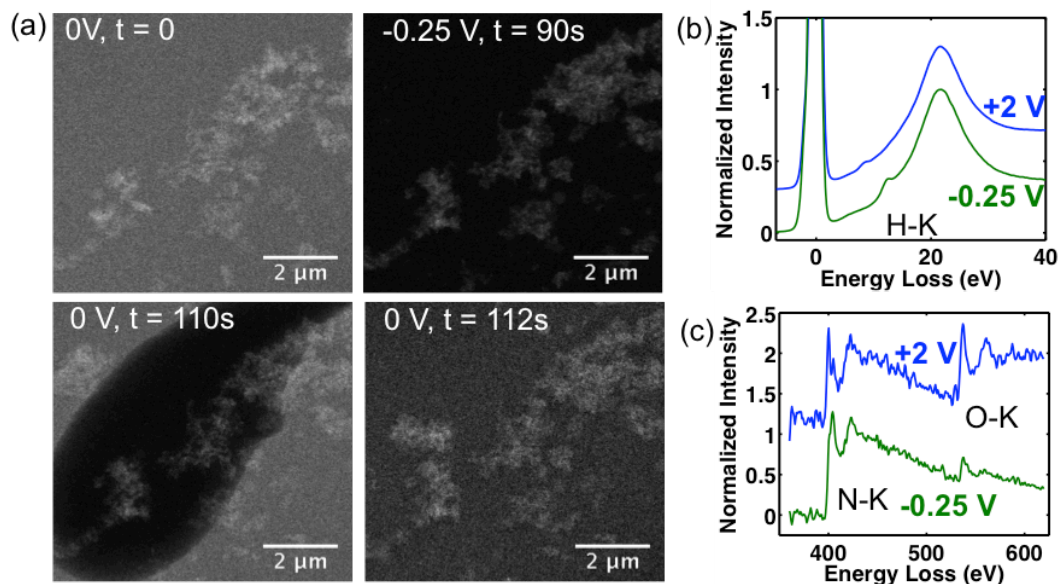
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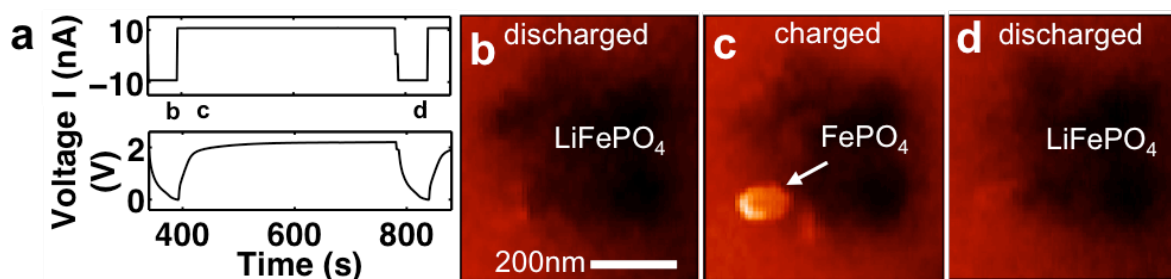
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**Figure 1.** In situ electrochemistry holder and electrochemical data. (a) Schematic of the top chip, with a C working electrode on the membrane, Pt reference and counter electrodes. (b) Pt nanoparticle cyclic voltammetry (CV), while the chip alone (no Pt deposited) shows a minimal electrochemical response.



**Figure 2.** Electrochemical generation of gas in the electrochemical cell. (a) HAADF STEM images show hydrogen bubble formation near Pt at negative potentials, that disappears upon returning to open circuit potential. Negative potential turned on at  $t=0$  and held for 90 s. (b) EELS finds hydrogen bubbles at low potentials (peak near 13 eV) and (c) oxygen bubbles at high potentials.



**Figure 3.** (a) Charge/discharge of the battery cathode material  $\text{LiFePO}_4$ . 5 eV EFTEM images of the lithiated (b,d) and delithiated (c)  $\text{LiFePO}_4$ , highlighting regions of  $\text{FePO}_4$ , at the times marked in (a).