In-Situ Structures for Nanoscale Electrochemistry

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Motivation—Dramatic improvements in electrical energy storage are required in order to meet our nation's goals for energy efficiency and environmental management. Li-ion batteries offer great promise for achieving these goals, but there are issues with limited energy storage and long-term performance and reliability. To overcome these issues, we need fundamental understanding of electrochemical processes in real-time with atomic to nanoscale spatial resolution. In this work, we describe the development of novel *in-situ* platforms to probe battery electrochemistry at the nanoscale. These platforms are designed to isolate individual nanoparticle battery components and permit their characterization during electrochemical cycling inside a high resolution transmission electron microscope (HRTEM).

Accomplishment—We have developed a silicon micromachined platform to encapsulate Li-ion battery materials and electrolytes between a narrow gap created between two thin, electron transparent windows. The platform has been designed to enable – for the first time – HRTEM measurements of the structural and chemical changes that occur in Li-ion battery cathodes and anodes during charge and discharge cycling. Specifically, we will image the processes of lithium insertion and de-insertion in intercalation and conversion anode and cathode materials, such as graphitic anodes, represented as multi-wall carbon nanotubes, and oxide cathodes, represented as $Li_xMn_2O_4$ nanowires. In addition, we will image the chemical processes that result in loss of battery capacity with cycling, specifically the mechanism and morphology of solid electrolyte interphase (SEI) formation. The mechanisms of Li insertion and capacity loss during cycling represent some of the most important areas where deeper understanding is required in order to develop higher capacity and longer lifetime batteries.

A schematic of our *in-situ* platform is shown in Figure 1(a). The platform is created by bonding two chips using a flip-chip approach, with the bottom chip containing a dense array of buried electrical interconnects that permit electrical contact to battery materials. Figure 1(b) shows the bottom chip and a close-up of the electrical interconnect structure. The interconnect structure was designed to permit the assembly of nanoparticles and nanowires across a narrow electron-transparent aperture using the process of dielectrophoresis.

Dielectrophoresis (DEP) is a technique that enables the assembly of individual nanoparticles and nanowires spanning narrow electrode gaps by a process of applying AC electric fields in solutions containing suspended nanoparticles. We have designed special structures for DEP that permit the assembly of battery electrode materials on electron transparent membranes. Figure 2(a) shows a HRTEM image of a multi-wall CNT, and Figure 2(b) shows a scanning electron microscopy image of a MnO_2 nanowire assembled using DEP. These structures isolate battery-relevant nanoscale materials, enabling HRTEM studies of electrochemistry at the nanoscale.

Significance—Many research reviews have cited that the greatest need for battery research is to understand the mechanisms of energy storage and degradation with atomic-scale resolution during real-time electrochemical cycling. The platforms that we are developing will enable these studies for the first time. New understanding will enable the development of new materials and architectures with greatly improved performance compared to today's Li-ion storage cells.

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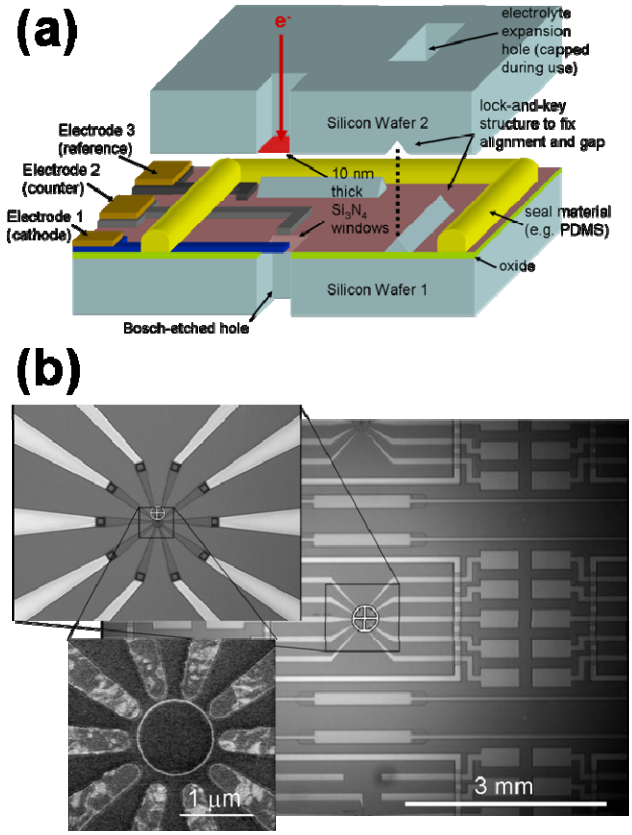

Figure 1. (a) A schematic of the *in-situ* electrochemistry platform for HRTEM studies of battery electrochemical processes. The platform is constructed using a flip-chip approach combing two MEMS chips that encapsulate a thin layer of electrolyte between electron-transparent windows. (b) Images of the lower chip of the platform showing the dense array of closely-spaced electrodes. This electrode geometry enables DEP of nanoscale battery materials.

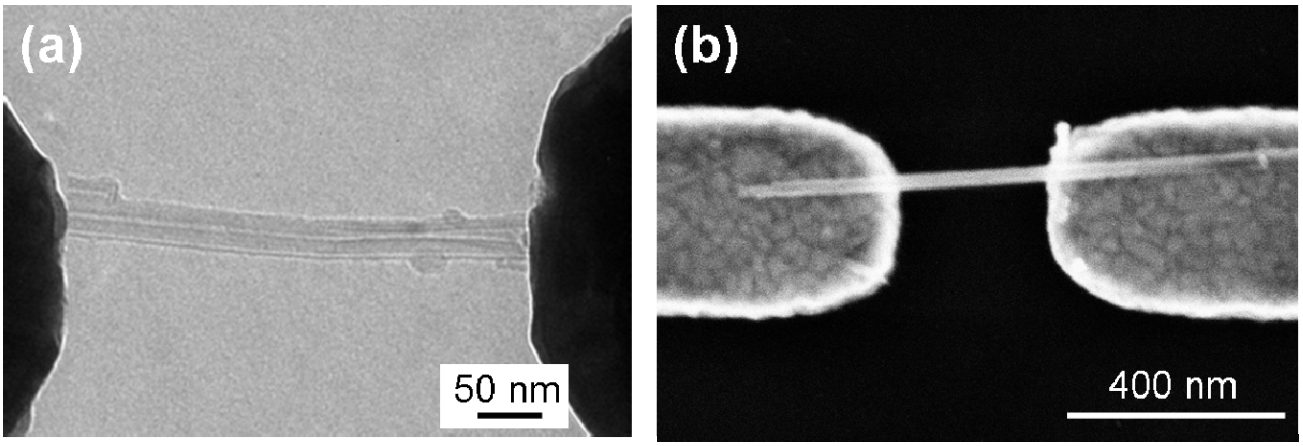

Figure 2. Examples of our work using DEP to assemble battery electrode materials. (a) A multi-wall carbon nanotube was assembled across a silicon nitride electron-transparent membrane using DEP. This image was taken using a HRTEM. (b) A scanning electron microscope image of a MnO_2 nanowire assembled using DEP. When reacted with Li, MnO_2 is a common Li-ion cathode material.