## Realistic electrochemistry in liquid cell microscopy

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The utilization of microfluidic cell in transmission electron microcopy (TEM) and X-ray microscopy (XRM) has enabled dynamic observation of materials behavior in their native reaction environment with higher spatial-and-temporal resolution [1, 2]. This approach has been instrumental in advancing broader research areas, particularly, in the field of electrochemistry photocatalysis, and other energy related devices [1]. However, the inability to acquire realistic quantitative information in TEM/XRM, mimicking bulk behavior, has prevented researchers from interpreting data accurately and reliably. First, the hardware components are not best optimized to perform in the reduced scale environment of the TEM/XRM [3]. Second, the chips configurations such as sizes and aspect ratios of different electrodes suitable for various electroanalytical measurements are poorly designed. Here, we present an *operando* liquid cell TEM/XRM microscopy platform demonstrating the capability to acquire realistic electroanalytical measurements and mimicking bulk behavior.

The operando liquid cell platform shown in Figure 1A and 1B typically consists of two microfabricated chips sandwiched with electron transparent SiNx membranes for encapsulating liquid and viewing in the microscope. We integrated a newly developed electrochemical cell with an advanced hardware system and optimized electrochemistry chips with a specialized configuration of working electrode (WE), counter electrode (CE) and reference electrode (RE) around the cell. This new configuration allows true quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. To illustrate the capability, we present cyclic voltammetry (CV) studies using some model compounds such as 01.M $CuSO_4$ and 20 mM $K_3Fe(CN)_6$/20 mM $K_4Fe(CN)_6$ in 0.1M KCl solutions. In the case of 0.1M $CuSO_4$, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell (Figure 1C) and the result mimics the bulk electrochemical cells (Figure 1D) with large electrode areas and larger volume of electrolyte solution [4]. This work highlights the fact that with suitable hardware integration and with better layout of the patterned chips configuration, bulk behavior of the electrochemical processes can be both observed and measured quantitatively. These electroanalytical measurements made in the small volume and limited diffusion cell geometries showing bulk-level behavior can be extended to other broader electrochemical systems including photocatalysis using optical TEM system, as will be discussed [5].

References:

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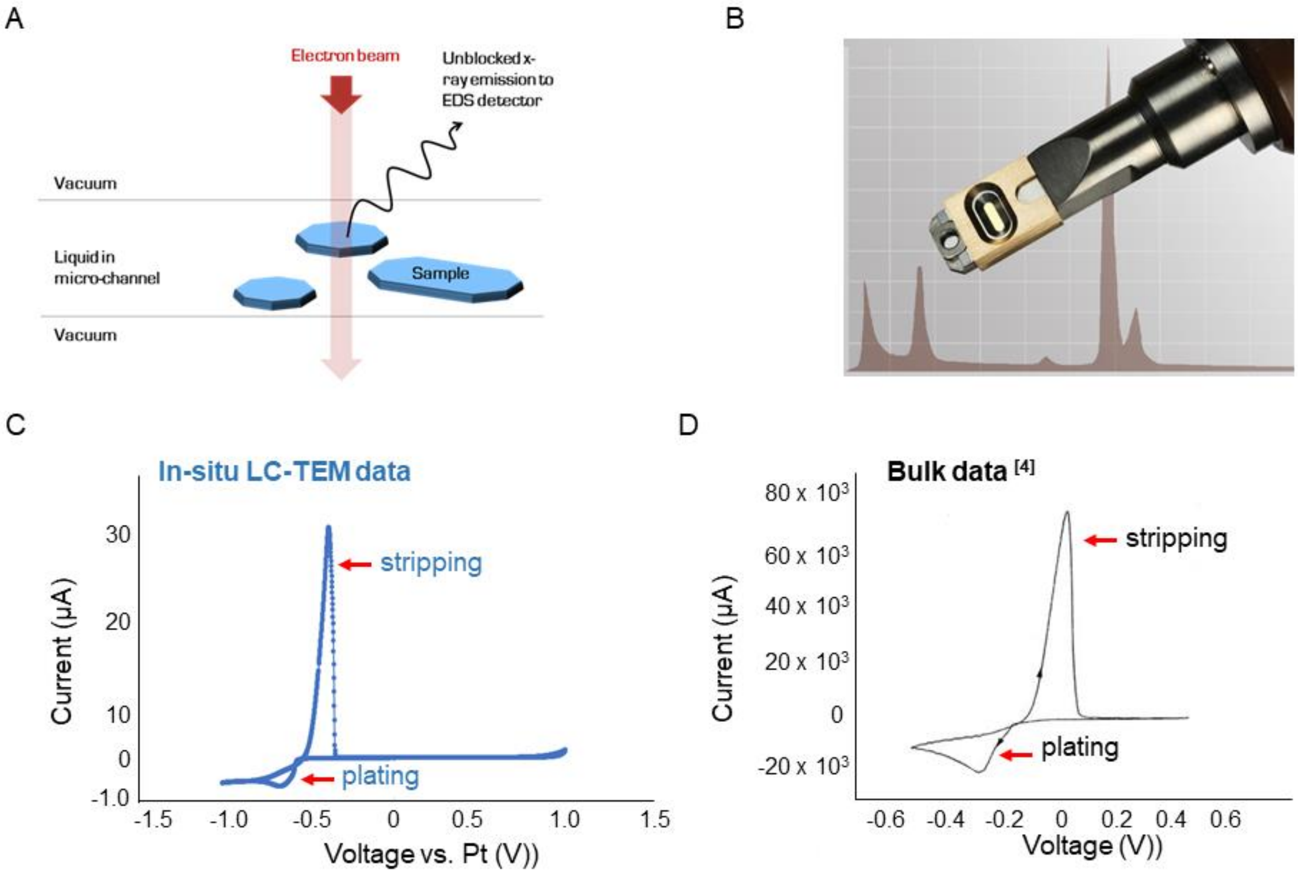


Figure 1. (A) Schematic of assembled liquid cell. (B) Liquid cell tip with EDS compatibility. (C) A CV curve of 0.1M CuSO4 performed in (C) in-situ LC-TEM, and (D) bulk cell extracted from Ref 4.