

Realistic Bulk Electrochemistry in Liquid Cell Microscopy

Khim Karki¹, Rui Serra-Maia², Eric Stach², Daan Hein Alsem¹ and Norman Salmon¹

¹Hummingbird Scientific, Lacey, Washington, United States, ²University of Pennsylvania, Philadelphia, Pennsylvania, United States

Transmission electron microscopy (TEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of electrochemical reaction-systems at the nanoscale [1-3]. This has generated strong interests in acquiring more reliable quantitative electroanalytical measurements in realistic reaction environment and has recently been made possible with the advent of *in-situ* liquid environmental cells [1]. This approach has already started to produce new insights on the dynamics and structural changes during processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion [1]. However, the major impediment of these measurements has been their inability to replicate electrochemical data reminiscent of bulk behavior [1]. As a result, it has been challenging to relate resulting chemistry observed *in-situ* in liquid cells to equivalent bulk processes. Here, we present an operando liquid cell TEM/XRM microscopy platform that enables true bulk-electroanalytical measurements mimicking bulk behavior of electrochemical material system.

The studies are performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiN_x membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the bulk level electrochemistry (Figure 1). As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 0.01M CuSO₄ and 20 mM K₃Fe(CN)₆/20 mM K₄Fe(CN)₆ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occur at the working electrode at distinct redox peaks in liquid cell (Figure 2) and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution [4]. In the latter case, the current-potential (I-V) relationship in the *in-situ* cell shows similar Tafel slopes at the same potentials to the RDE setup tests validating the high electrochemical fidelity of the *in-situ* cell. The electrochemical data from *in-situ* bulk liquid cells can be used to correlate the actual bulk behavior of these electrochemical reactions in a true *in-situ/operando* conditions. The work presented here highlights the fact that with suitable hardware system, bulk behavior of the electrochemical processes can be both observed and measured quantitatively [5].

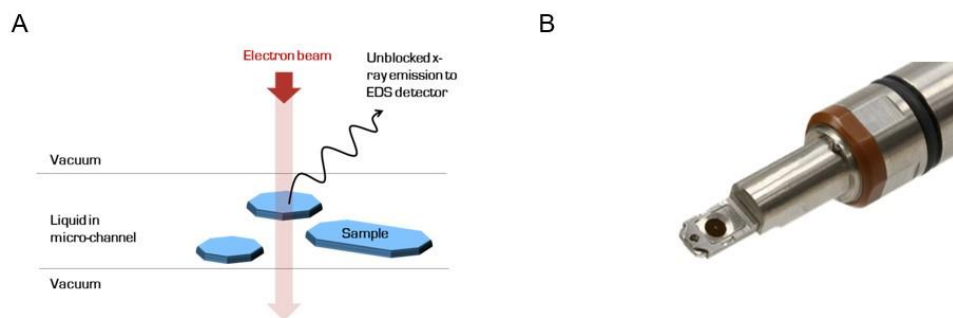


Figure 1. (A) Schematic of assembled liquid cell. (B) Hummingbird bulk electrochemistry TEM holder

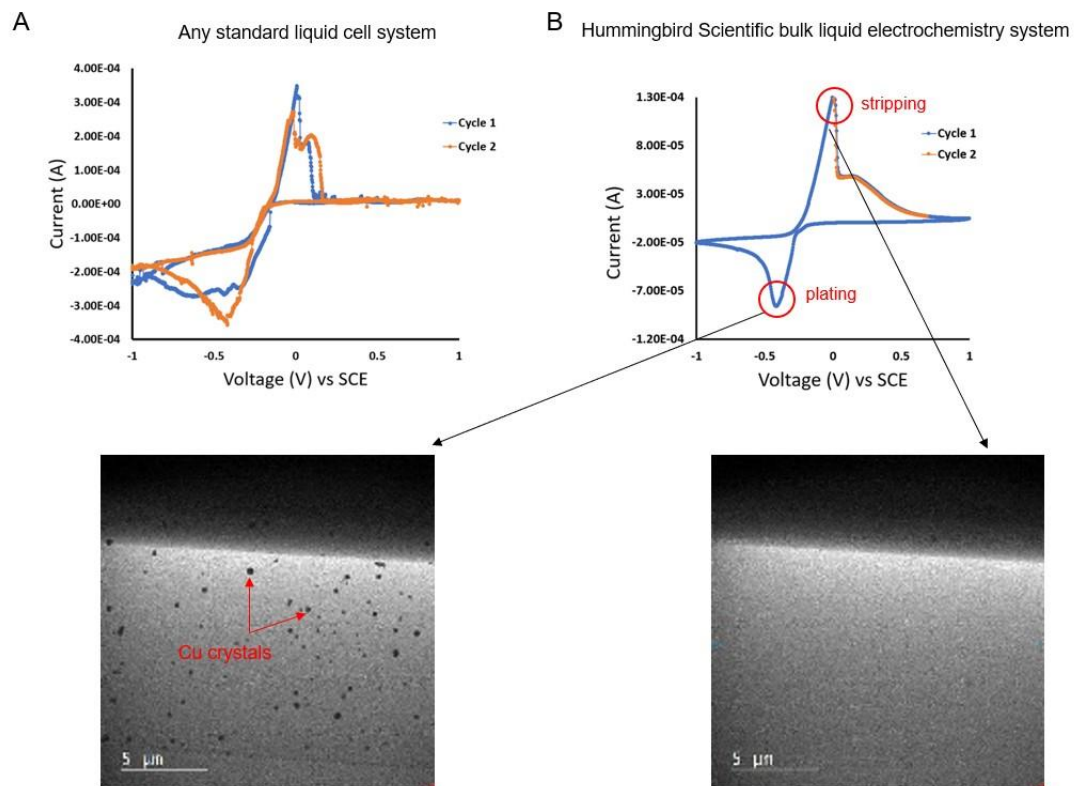


Figure 2.

Cyclic voltammogram (CV) of 0.01M CuSO_4 performed in (C) standard liquid cell TEM system (D) Hummingbird bulk liquid electrochemistry system. The distinct plating peak shows deposition of copper crystals on the WE membrane window. Similarly, the sharp stripping peak shows removal of deposited copper crystals from WE window.

References

- [1] F.M. Ross in *Liquid Cell Electron Microscopy*, Cambridge University Press (2016)
- [2] J. Lim et al, *Science* 353 (2016), p. 566
- [3] E. Fahrenkrug et al, *Journal of Electrochemical Society* 164 (2017), p. H358
- [4] D. Grujicic and B. Pestic, *Electrochimica Acta* 47 (2002), p. 2901
- [5] KK, DHA, and NS acknowledge funding from the Department of Energy, Office of Basic Energy Sciences, SBIR Grant # DE-SC0009573.