

Beam Effects During In Situ Potential Cycling and Imaging of Sulfuric Acid and Platinum Electrodes

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A new class of transmission-electron-microscope (TEM) compatible cells has been developed and now allow the *in situ* and *operando* observation of numerous electrochemical reactions on the nanoscale.[1] This then requires a quantitative characterization of an electron beam's effect on an actively electrochemically cycled system. Previous research has included beam-precipitated formation of metal nanocrystals directly formed from metal-salt solution,[2, 3] as well as for the imaging of highly reactive Li-based electrochemical systems using both wet and dry electrolytes.[4, 5] These studies span the expected electron dose rate range from highly intense beams (1000s $e^-/\text{\AA}^2\cdot\text{s}$) designed to force crystallization to the smallest possible beam strengths (fractions of $e^-/\text{\AA}^2\cdot\text{s}$) for the minimally invasive imaging of electrochemical systems.

To understand beam effects, we use a model system of platinum electrodes and sulfuric acid to investigate how the presence of an intermediate-to-low intensity electron beam ($\sim 1 e^-/\text{\AA}^2\cdot\text{s}$) affects cyclic voltammograms (CVs), and how the CVs change with time following beam exposure in a flowing electrolyte. Figure 1 shows the unchanging platinum electrode in a flowing-electrolyte style electrochemical cell. Here, we are using the largest field-of-view and smallest beam intensity for the 'standard' viewing conditions (2000x, intermediate condenser aperture, which is visible in image) in our TEM (JEM2200FS). Figure 2 shows the effect of turning the beam on and off *during* potential cycling. Here, we note a small increase in current when the beam is applied, with a $\sim 1\text{nA}$ difference between the different CVs at -0.33 V , which is to be expected if the irradiated electrode collects all current from the primary electron beam. More importantly, a static potential shift to one of the 'beam on' cycles (applied *ex post facto* by simple subtraction) puts the beam back on a very similar curve to the 'beam off' CV. Finally, we see that 'beam off' CVs can be reproduced following application of the beam (not shown) after a brief period of leaving the beam off, which indicates the flow of liquid through the cell allows for replenished electrolyte to replace the irradiated portions such that the original, beam-off CV is recovered. We will present these and other results using electrochemical impedance spectroscopy on this canonical electrochemical system, and discuss their impact on *in situ* TEM.

References

1. Zheng, H., Y.S. Meng, and Y. Zhu, MRS Bulletin, 2015. **40**(01): p. 12-18.
2. Chen, X., et al., Acta Materialia, 2012. **60**(1): p. 192-198.
3. Zheng, H., et al., Science, 2009. **324**(5932): p. 1309-1312.
4. Zeng, Z., et al., Faraday Discussions, 2014.
5. Liu, X.H., et al., Advanced Energy Materials, 2012. **2**(7): p. 722-741.

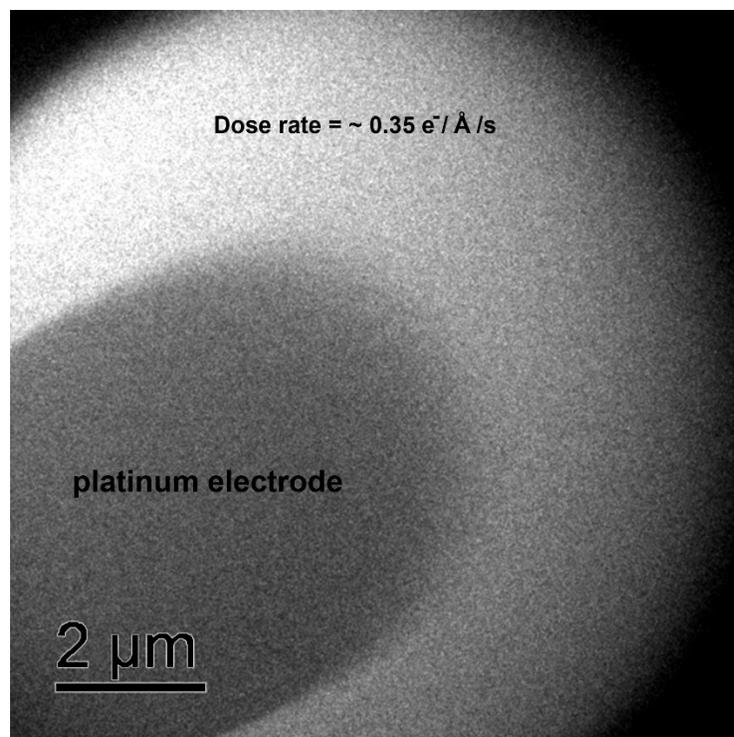


Figure 1: Bright-field transmission electron micrograph (Mag = 2000x) of commercial electrochemical cell with platinum electrodes and flowing 0.2M sulfuric acid. during cycles shown in Fig. 2. Electrode is not seen to change during cyclic voltammogram, nor are bubbles formed.

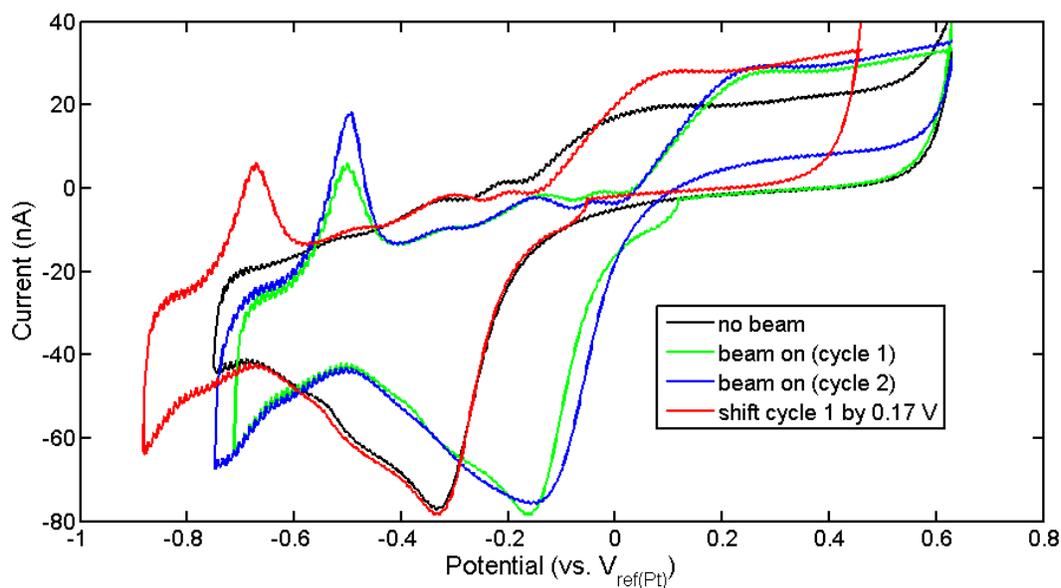


Figure 2: Cyclic voltammograms of entire cell during imaging of electrode in Fig. 1. Sweep rate is 100mV/sec.