

Operando Scanning Transmission X-ray Microscopy of Co(OH)₂ Oxygen Evolution Electrocatalysts

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Operando liquid cell microscopy, primarily using transmission electron microscopy (TEM), has enabled the dynamic studies of electrochemical processes in nano-sized materials suitable for various clean energy applications ranging from battery technologies to electrocatalysis [1-6]. We have most recently expanded this approach to the X-ray synchrotron, which is prone to less beam effects compared to electron microscopy for operando electrochemical measurements. The effort has enabled us to understand the underlying mechanism of lithium ion insertion and extraction processes and performances in battery particles [3]. Using this same technique, we have evaluated the electrochemical oxygen evolution reaction (OER) of two-dimensional (2D) cobalt hydroxide (Co(OH)₂) platelet particles as electrocatalyst for the efficient production of clean hydrogen and oxygen. 2D nanomaterials are particularly attractive as electrocatalytic materials because of their large specific surface areas allowing large active sites during the electrochemical reactions [5,6].

We developed and used an operando scanning transmission x-ray microscopy ((STXM) platform at Lawrence Berkeley National Laboratory's (LBNL) Advanced Light Source (ALS) to map the changes in the electronic oxidation state of Co during the electrochemical reaction. Figure 1 shows liquid cell system integrated in beamline 11.0.2 at the ALS. The Co(OH)₂ platelets are dispersed on an x-ray transparent Pt electrode inside the liquid-electrochemical cell and charged/discharged at different rates while simultaneously recording x-ray absorption spectra at the Co L₃-edge with a 50 nm x-ray probe during cycling (Figure 2).

To ensure the accuracy of the operando STXM measurements, same materials using microscopic cell with rotating disk electrode (RDE) was compared against the liquid cell setup in the x-ray. Figure 2a shows the cyclic voltammograms (CV) of 10 mM K₃Fe(CN)₆/10 mM K₄Fe(CN)₆ in 0.1M KOH on a glassy carbon electrode in a macroscopic cell (RDE setup, red) at a scan rate of $v = 10 \text{ mV s}^{-1}$ with no rotation and in the operando STXM cell (blue) at a scan rate of $v = 1 \text{ mV s}^{-1}$ and a flow rate of $10 \mu\text{L min}^{-1}$. The RDE shows the typical “duck-shaped” voltammogram as it was not rotated while the STXM shows a sinusoidal voltammogram due to the slow scan rate and the effective mass transfer due to flow. $E_{1/2}$ is centered at the reversible redox potential for both cells showing the high electrochemical fidelity of the operando STXM cell. Similarly, we also compared oxygen evolution (Figure 2b) on $50 \mu\text{g cm}^{-2}_{\text{geom}}$ Co(OH)₂ on glassy carbon in a macroscopic RDE cell (red) at a rotation rate of $\omega = 1600 \text{ rpm}$ and a scan rate of $v = 10 \text{ mV s}^{-1}$ and in the operando STXM cell with Co(OH)₂ on Pt (blue) at a scan rate of $v = 10 \text{ mV s}^{-1}$ and a flow rate of $10 \mu\text{L min}^{-1}$. The current-potential relationship in the operando STXM cell shows similar Tafel slopes at the same potentials to the RDE tests validating the high electrochemical fidelity of the operando STXM cell. This work highlights the importance and potentials of liquid cell x-ray microscopy in understanding the electrochemical activities of individual

nanomaterials with higher spatial and chemical resolution. The liquid-electrochemistry hardware developed for this work can also be used for cross-correlative imaging using TEM, SEM and X-ray microscopes [7].

References:

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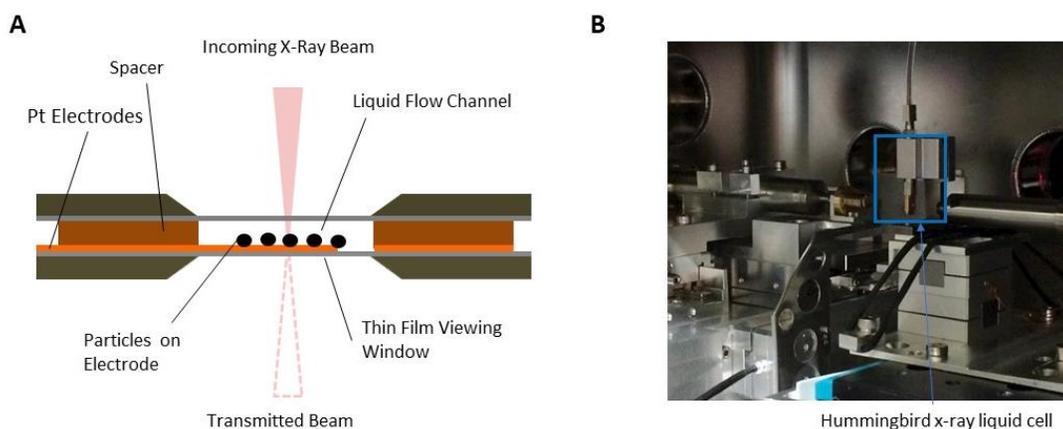


Figure 1. (A) Schematic of assembled liquid cell. (B) STXM Beamline 11.0.2 at the ALS, LBNL.

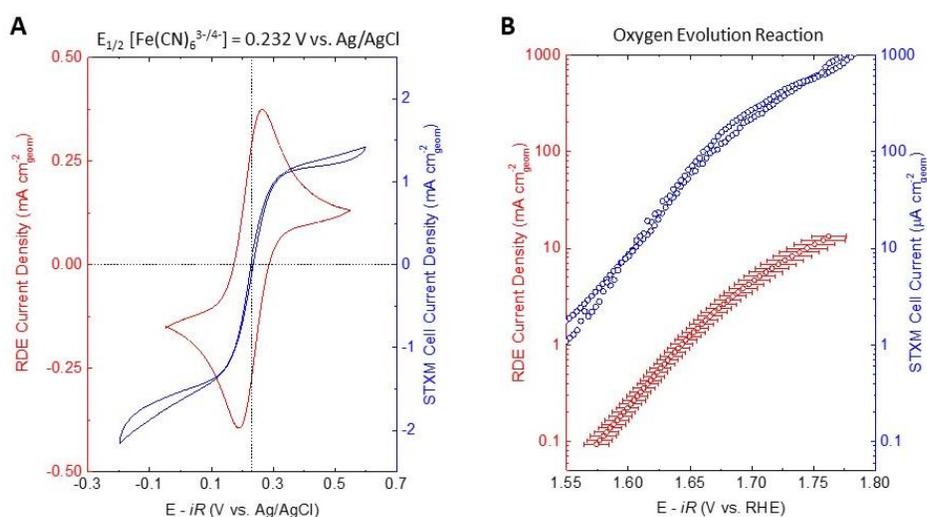


Figure 2. Electrochemistry in the Operando STXM cell (A) CV of 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ /10 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1M KOH in RDE and liquid cell. (B) OER of $\text{Co}(\text{OH})_2$ in RDE and liquid cell.