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In-situ and *Operando* Studies with Soft X-Ray Transmission Spectromicroscopy

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Soft X-ray scanning transmission microscopy (STXM) [1] is a powerful tool for nanoscale materials analysis. Ptychography [2-4], which can be measured using soft X-ray STXMs equipped with a suitable X-ray camera, provides a spatial resolution 3-10 times better than conventional STXM with the same spot size. Recently soft X-ray ptychography has been implemented in STXMs at the Canadian Light Source (CLS) and at Synchrotron Soleil. *In situ* and *operando* studies of energy conversion systems have been carried out with soft X-ray STXM [5-7] and soft X-ray ptychography [2,8-10].

Over the past decade, my group has collaborated with researchers from industry (the Automotive Fuel Cell Co-operation (AFCC) and Ballard Power) to develop and apply STXM and ptychography to characterize polymer electrolyte membrane fuel cell (PEM-FC) electrodes and materials. We have measured the distribution of the persulfonic acid ionomer in the cathodes of PEM-FC under *in situ* variable humidity and temperature conditions [5]. We also developed an *operando* system in which the electrochemical state of a material is changed with real time control of the applied potential, type of electrolyte, and the electrolyte flow rate [11]. The latter system has been used to study electrodeposition of Cu on Au from a $Cu(SO_4)$ solution, and electro-stripping of the deposited Cu.

Recently a major improvement in the *in situ* flow electrochemical apparatus has been made [12]. Figure 1 presents a schematic of that improved apparatus. When compared to the device reported in 2018, the new device is much more reliable with respect to fluid leaks and electrical connections. It also features two inlet and two outlet flow channels which facilitates changing the electrolyte in minutes rather than hours and is very useful for removing air or gaseous product bubbles.

Figure 2 reports preliminary results from studies of Cu electrocatalysis of the CO_2 reduction (CO_2R) reaction, which is actively under investigation to find an economic way of turning CO_2 from point sources (*e.g.* cement production) or direct air capture into C_1 and C_2 chemical feedstocks and fuels. First a mixed Cu(0), Cu(1) catalyst layer was *in situ* electrodeposited from a $Cu(SO_4)_{aq}$ solution on to the thin part of the Au working electrode (Fig. 1e). After changing the electrolyte to a 0.1 M $NaHCO_3(aq)$ solution, STXM stacks at the Cu 2p edge were measured at several potentials in order to follow the evolution of the oxidation state distribution of the Cu through several electrochemical cycles (CV) in which, first the Cu was partially oxidized, then, at the lowest potential (-0.5 V wrt SHE) of the CV scan, dissolved CO_2 from the saturated $NaHCO_3(aq)$ electrolyte solution was reduced.

I will also present results from *ex situ* Ni L-edge studies of Ni-N-C single atom electrocatalysts being explored for CO_2R [13]. We have already used STXM and product yield testing to show that excess Ni in these types of catalyst is detrimental, leading to water splitting to form H_2 rather than the more desirable CO or C_2 products. We plan to use the improved flow electrochemical apparatus for *in situ* studies of CO_2 reduction by Cu nanoparticles [14], Ag-doped Cu [15], and Ni-N-C [16] electrocatalysts, in order to obtain mechanistic insights that may help further optimize these electrocatalysts [17].

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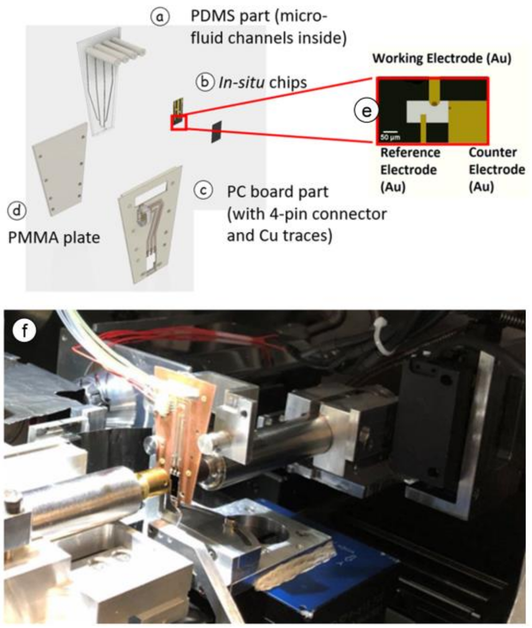

Figure 1. Microfluidic – based flow electrochemical cell for *in situ* and *operando* electrocatalysis studies [12]. (a-e) Details of the cell. The SiNx window area is 240 µm wide and 100 µm high. The active measurement area (dark circle on the WE) is 20 µm diameter, and has a ~10 nm Au thickness (plus 100 nm SiNx, and 2-3 nm Cr). (f) Photo of the cell inside the CLS ambient STXM.

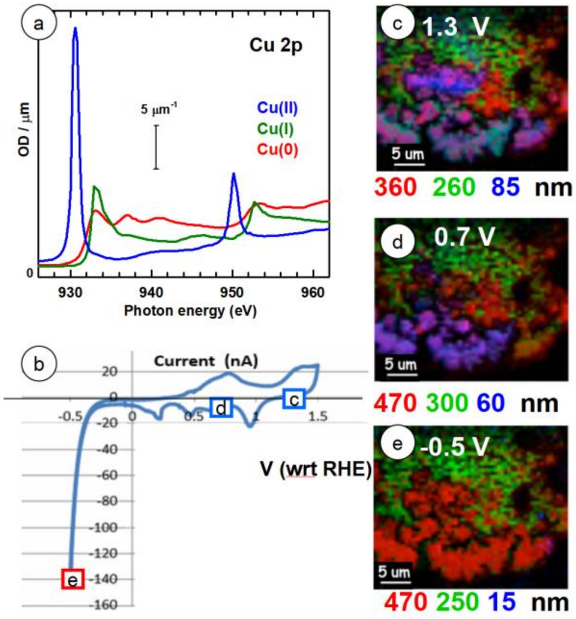

Figure 2. *In-situ* CO_2 reduction on *in situ* electro-deposited Cu. (a) Quantitative (OD1) Cu 2p reference X-ray absorption spectra used to map oxidation states. (b) *in-situ* CV recorded after changing electrolyte from 5 mM $CuSO_4$/25 mM $(NH_4)_2SO_4$ to 0.1 M $NaHCO_3$. (c – e) Cu oxidation state maps at 1.3 V, 0.7 V and -0.5 V w.r.t. RHE. The numbers below each map are maximum thickness in nm of **Cu(0)**, **Cu(1)** and **Cu(2)** derived from fitting a Cu 2p stack to the reference spectra in (a).