

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

Adam P. Hitchcock,<sup>1</sup> Chunyang Zhang,<sup>2</sup> Haytham Eraky,<sup>1</sup> Ladan Shahcheraghi,<sup>2</sup> Fatma Ismail<sup>2</sup> and Drew Higgins<sup>2</sup>

<sup>1</sup> Dept. of Chemistry & Chemical Biology, McMaster University, Hamilton, Canada.

<sup>2</sup> Dept of Chemical Engineering, McMaster University, Hamilton, Canada.

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<sub>4</sub>) 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<sub>2</sub> reduction (CO<sub>2</sub>R) reaction, which is actively under investigation to find an economic way of turning CO<sub>2</sub> from point sources (e.g. cement production) or direct air capture into C<sub>1</sub> and C<sub>2</sub> chemical feedstocks and fuels. First a mixed Cu(0), Cu(1) catalyst layer was *in situ* electrodeposited from a Cu(SO<sub>4</sub>)<sub>aq</sub> solution on to the thin part of the Au working electrode (Fig. 1e). After changing the electrolyte to a 0.1 M NaHCO<sub>3</sub>(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<sub>2</sub> from the saturated NaHCO<sub>3</sub>(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<sub>2</sub>R [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<sub>2</sub> rather than the more desirable CO or C<sub>2</sub> products. We plan to use the improved flow electrochemical apparatus for *in situ* studies of CO<sub>2</sub> 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].

## References:

- [1] AP Hitchcock, *J. Electron Spectrosc. Rel. Phen.* **200** (2015), p. 49.  
 [2] DA Shapiro *et al*, *Nat. Photonics* **8** (2014), p. 765.  
 [3] XH Zhu *et al*, *Proc. Nat. Acad. Sci.* **113** (2016), E8219.  
 [4] H Yuan *et al*, *ACS Applied Nanomaterials* **4** (2021), p. 621.  
 [5] AP Hitchcock *et al*, *Microscopy & Microanalysis* **20** S3 (2014), p.1532.  
 [6] J Lim *et al*, *Science* **353** (2016), p. 566.  
 [7] C Gosse *et al*, *Lab on a Chip* **20** (2020), p. 3213.  
 [8] YS Yu *et al*, *Nano Letters* **15** (2015), p. 4282.  
 [9] B Bozzini *et al*, *J. Electron. Spectrosc. Rel. Phen.* **220** (2017), p. 147.  
 [10] DA Shapiro *et al*, *Science Advances.* **6** (2020), eabc4904.  
 [11] V Prabu *et al*, *Rev. Sci. Instr.* **89** (2018), p. 063702.  
 [12] P Ingino *et al*, *Rev. Sci. Instr.*, in preparation.  
 [13] CY Zhang *et al*, *ACS Catalysis*, in preparation.  
 [14] RM Arán-Ais *et al*, *Nature Energy* **5** (2020), p. 317; *Nature Comm.* **11** (2020), p. 3489.  
 [15] TTH Hoang *et al*, *J. Am. Chem. Soc.* **140** (2018), p. 5791.  
 [16] MM Millet *et al*, *Angewandte Chemie Int. Ed.* **59** (2020), p. 21613  
 [17] STXM and ptychography was performed at the CLS, which is supported by the Canada Foundation for Innovation. We thank Dr. Martin Obst and Pablo Ingino for sharing their improved flow electrochemical cell design.

