in situ Spectroscopic and Computational Study of Electrocatalytic CO_2 Reduction on Cu Electrodes

Jinhui Meng, Chaoyu Li, Tianquan Lian,
Department of Chemistry, Emory University, Atlanta, GA 30322

Hongsen Wang, Héctor D. Abruña
Department of Chemistry and Chemical Bioloy, Cornell University, Ithaca, New York 14853-1301

Jessica G. Freeze and Victor S. Batista
Department of Chemistry and Energy Sciences Institute, Yale University, New Haven, CT 06520

Adam P. Willard
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139-4307

Many electrocatalytic reactions involve potential dependent changes of both reactive surface intermediates and the electrode surface itself. For example, surface oxides and hydroxides on copper have been proposed to play key roles in lowering the energy barriers for carbon-carbon coupling, and CO_2 activation process, during CO_2 reduction to C_{2+} products on Cu surfaces. Many experiments have reported that CO_2 reduction rates and product distribution depend on the identity of the electrolyte ions, suggesting their active roles in the reaction. However, identifying the nature of surface and surface adsorbed molecular species, and probing their roles in electrocatalytic reactions remain elusive and challenging. To gain molecular level insights of such catalytic reactions, we have adopted a multi-modal approach that aims at *in situ* molecular spectroscopic probing of surface and solution species. To provide an *in situ* spectroscopic probe of such key surface intermediates on well-defined single crystal electrode surfaces, we have applied *in-situ* SHell-Isolated Nanoparticle Enhanced Raman Spectroscopy (SHINERS) to the study of CO_2 reduction on Cu. The observed spectral signatures are assigned with the help of advanced quantum chemical calculations. Furthermore, the evolution of products, in bulk solution, are measured simultaneously by *in situ* electrochemical DEMS. With this multimodal approach, we have identified the electrochemical window for CO_2 activation to surface adsorbed COO^- and the formation of CO. Accompanying these conversions, the potential dependent evolution of Cu(poly) surface oxide and hydroxide species as well as competitive adsorption of CO_3^{2-} with COO^- and CO on Cu electrode have also been observed. Detailed reaction mechanisms, informed by the direct observation of adsorbed intermediates, are being developed with computational modelling and will be discussed in this presentation.