Using Vibrational Spectroscopy and Electrochemical Stress Measurements to Interrogate Metal Electrode Surfaces

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This talk will report on our use of spectroscopic and electrochemical strain methods to examine metal electrode surfaces. We report on work involving the oxygen reduction reaction, nitrate reduction, and lithiation of Sn electrodes. In the area of nitrate reduction – performed on Cu single crystal surfaces -- characterization techniques reveal the interplay between the surface structure and reactivity. In particular, access to surface oxides yields a high performing catalyst, while inhibition of surface oxide formation leads to diminished activity and a completely different set of products relative to the oxide accessible case.

Spectroscopy also plays an import role in interrogating the oxygen reduction reaction. We use graphene modified electrodes to provide a spectroscopic platform with which to interrogate porphyrin and pthalocyanin-modified electrodes for the ORR. The understanding derived from the mechanistic work provides directions for synthesis of advanced catalysts. In particular, we have synthesized a series of bio-inspired metal coordination polymers exhibiting oxygen reduction activity and developed a series of correlations between the structure of these materials and their activity. Interestingly, we find that the ligands used for the oxygen reduction reaction also enhance CO_2 reduction to CO when exposed to Ag surfaces. The origin of this enhanced CO production likely relates to inhibition of specific CO binding sites on these surfaces.

Finally, we report on our use of electrochemical strain methods to interrogate Sn electrode lithiation. In the presence of oxide, strain methods show conversion of compressive to tensile strain concomitant with oxide reduction. However, in the absence of surface oxide, Sn lithiation yields compressive strain only, the magnitude of which is modified by the formation of the solid electrolyte interphase.