

IN SITU STUDIES OF ELECTROCHEMICAL REACTIONS USING VIBRATIONAL SUM FREQUENCY GENERATION

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Electrochemical reactions play important roles in chemical energy conversion. However, the surface reactions that govern these processes are not well understood because of the difficulties associated with accessing the electrode/electrolyte interface and making chemically specific measurements with interface sensitivity. Vibrational spectroscopy offers the required chemical specificity and can be used to elucidate reaction pathways based on the formation of key functional groups along a reaction coordinate. However, the challenge is to implement infrared spectroscopy as a surface sensitive probe at the electrode/electrolyte interface. Vibrational sum frequency generation spectroscopy is an inherently interface specific technique, but most people who study electrode/electrolyte interfaces employ a thin film of electrolyte which leads to wavelength-dependent attenuation of the infrared field and also presents mass transport limitations when seeking to probe electrocatalytic reaction kinetics. We present a method to overcome these limitations with high signal quality and under conditions that are compatible with electrocatalysis at high current densities. Under these conditions we study CO₂ reduction on polycrystalline gold thin films and gold nanoparticles which show faradaic efficiencies for carbon monoxide of 20% and 60% respectively. We identify possible reasons for the observed difference in selectivity.