

JCAP-Caltech Surface Science Lab: ECSSA Journey from Whiteboard to Installation to Experiments

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Abstract:

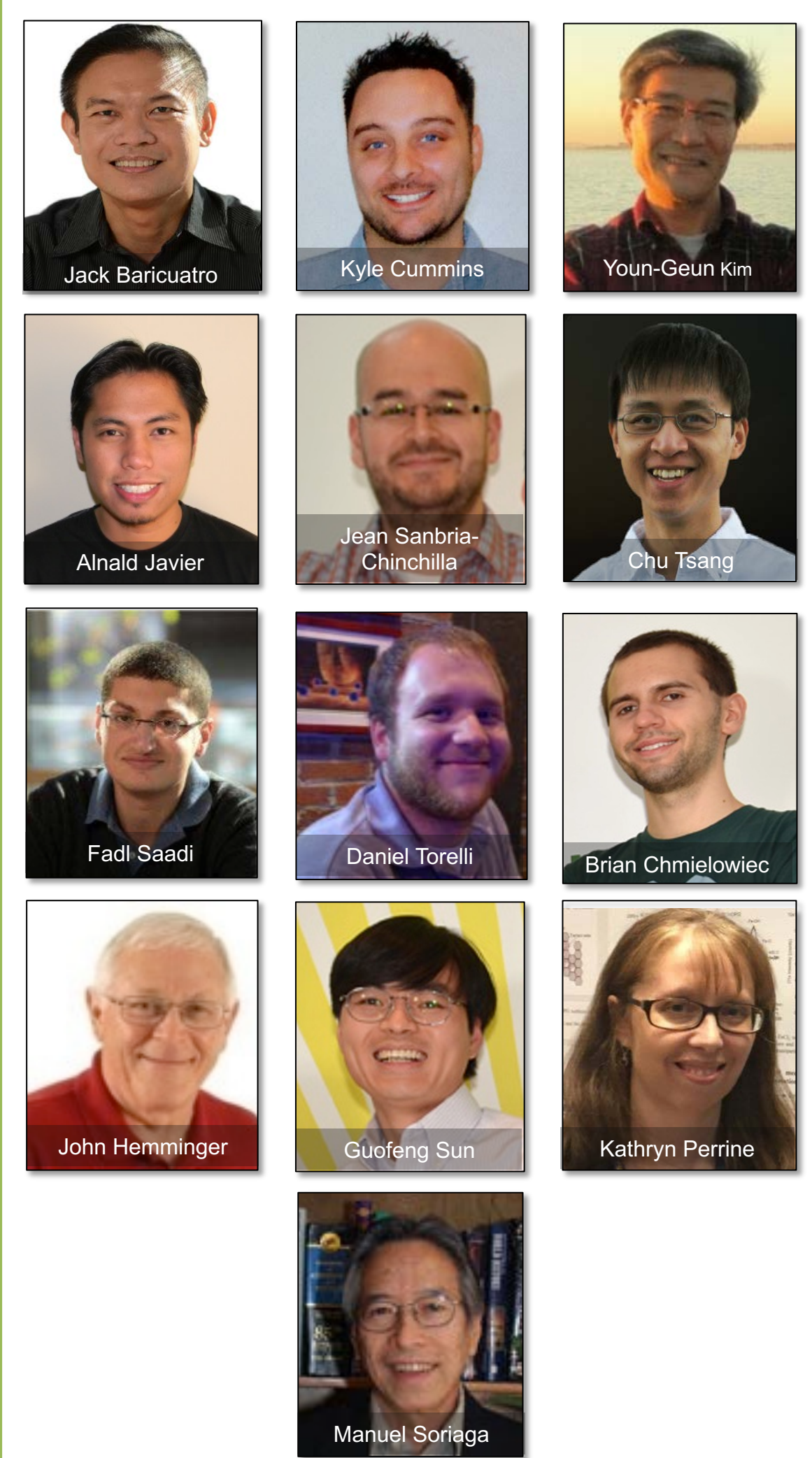
The design, assembly, and operational considerations of a multi-technique interfacial physics instrument are described, highlighting the integration of traditional electrochemical methods with modern surface spectroscopic and preparative techniques. The instrument, referred to as ECSSA (Electrochemical Surface Science Apparatus), is a central tool in the experimental approach of the surface science laboratory at JCAP-Caltech. The principal function of the ECSSA is to provide a platform for the non-traditional, atomic-level approach to the study of CO₂R heterogeneous electrocatalysts. The interrogation protocol is based on the detailed examination of well-defined model catalyst systems before, during, and after precisely controlled reaction conditions. The complementarity of EC-CSA with the seriatim module of operando tools developed separately bridges the pressure and materials gap in the investigation of model and "real world" electrocatalysts.

Introduction

A typical experiment on the ECSSA starts with catalyst preparation (via the PVD or EC chamber) followed by transfer into the distribution chamber (DC). The catalyst is then transferred to the surface analysis chamber for initial-state characterization of the surface prior to electrocatalysis. The sample is later moved to the gate-valve-isolable EC chamber for catalysis-related experiments. At selected stages of the reaction, the electrode is emersed from solution and returned to the analysis chamber to scrutinize any reaction-induced changes in the surface structure and composition. This analysis-catalysis-analysis iteration is repeated quite a few times to establish important interfacial relationships. Nowhere in the experimental protocol is the sample exposed to uncontrolled environments. The surface analytical techniques accessible within ECSSA include XPS, AES, UPS, LEED, HREELS, LEISS and TPD.

A case study is presented which aims to test CH₄ production from Fe monolayer (ML)-modified WC(pc). Theoretical treatments of transition metal carbides (TMCs) revealed TMML/TMC as a class of materials capable of disrupting linear scaling relationships of surface-bound C, H, and O intermediates that limit the use of pure transition metals for CO₂R. Experiments showed that ultrathin films of Fe on WC was capable of enhancing selectivity for CH₄.

Team 2012-2020

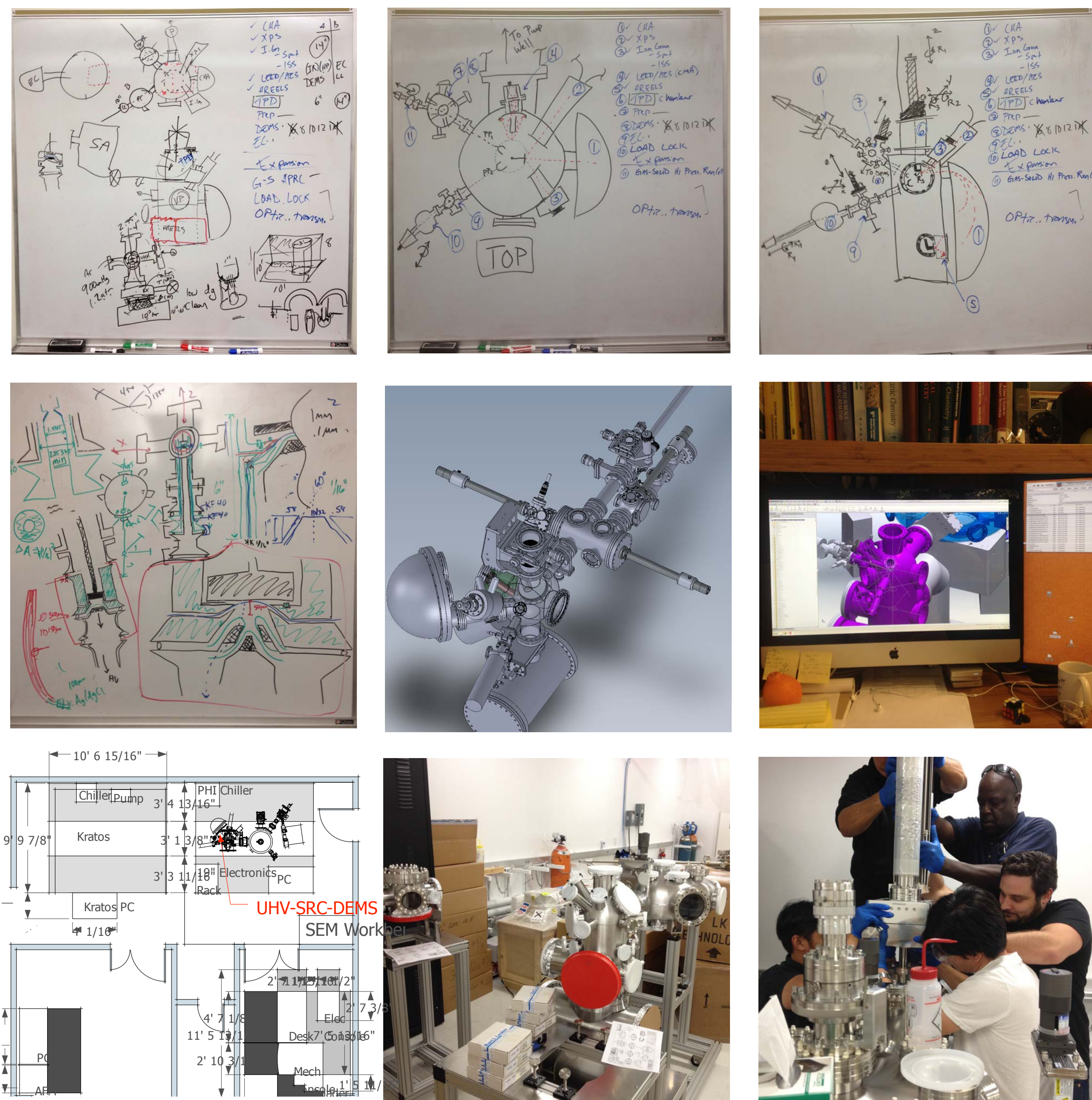


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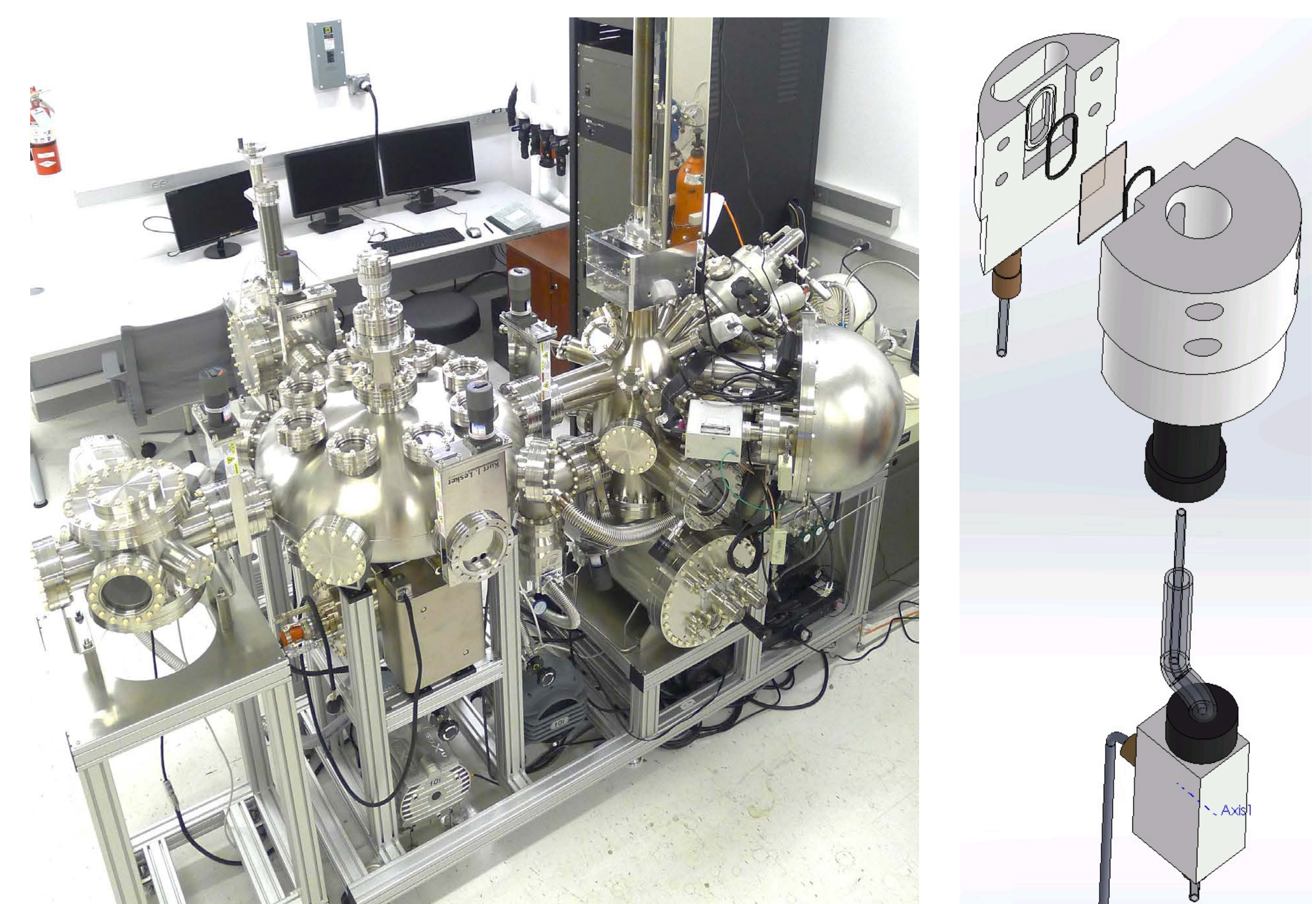
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Research Activities: Highlights

Early Days of the Surface Science Lab



Apparatus for Surface Science Investigations of CO₂R Catalysts

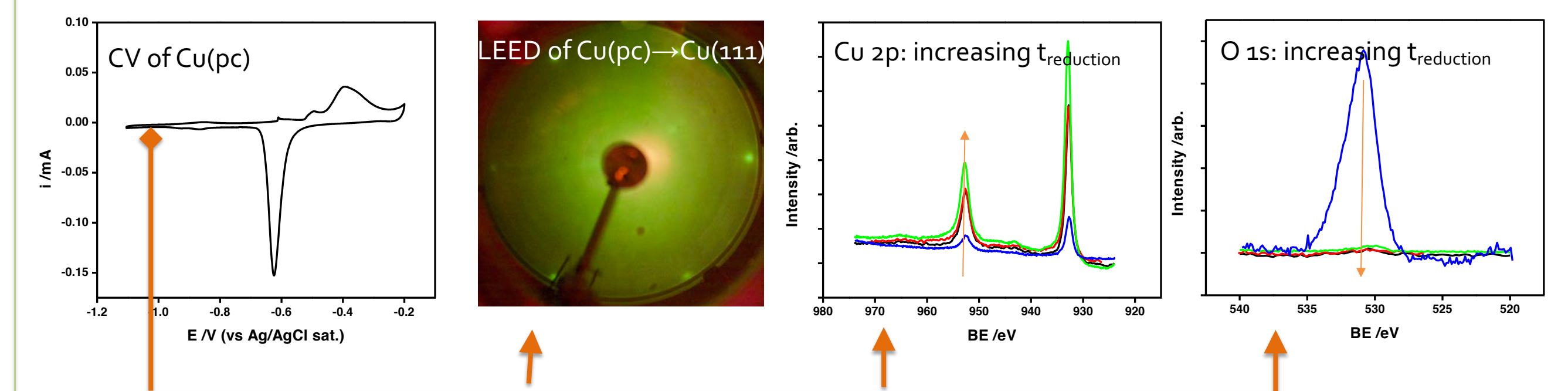


Tandem UHV-EC apparatus. Installed surface analytical capabilities include:

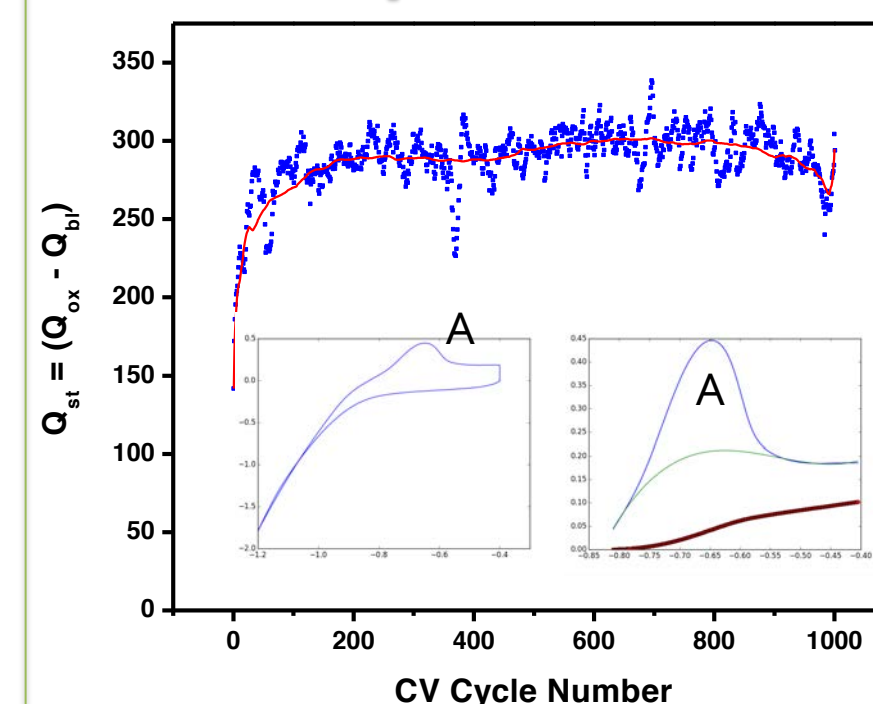
SURFACE COMPOSITION	SURFACE STRUCTURE AND SPECIATION
Low-energy Ion Scattering Spectroscopy (LEISS)	Low-energy Electron Diffraction (LEED)
Auger Electron Spectroscopy (AES)	Temperature-Programmed Desorption (TPD)
X-ray Photoelectron Spectroscopy (XPS)	Electron Energy Loss Spectroscopy (HREELS)

Complementary to its surface science capabilities, the apparatus includes a gate valve-isolable reaction chamber, where reactive gas dosing and Electrochemistry (EC) experiments are performed. The conventional cell employed for routine EC excursions features an ion-selective membrane-isolated counter electrode compartment. Additional custom designs for the reaction chamber include a cell which interfaces to a Differential Electrochemical Mass Spectrometer (DEMS) and direct gas sampling of the headspace to a Quadrupole Mass Spectrometer (QMS) to allow potential-dependent product distribution analysis.

Approach: Emersion Potential/Structure/Composition Correlates

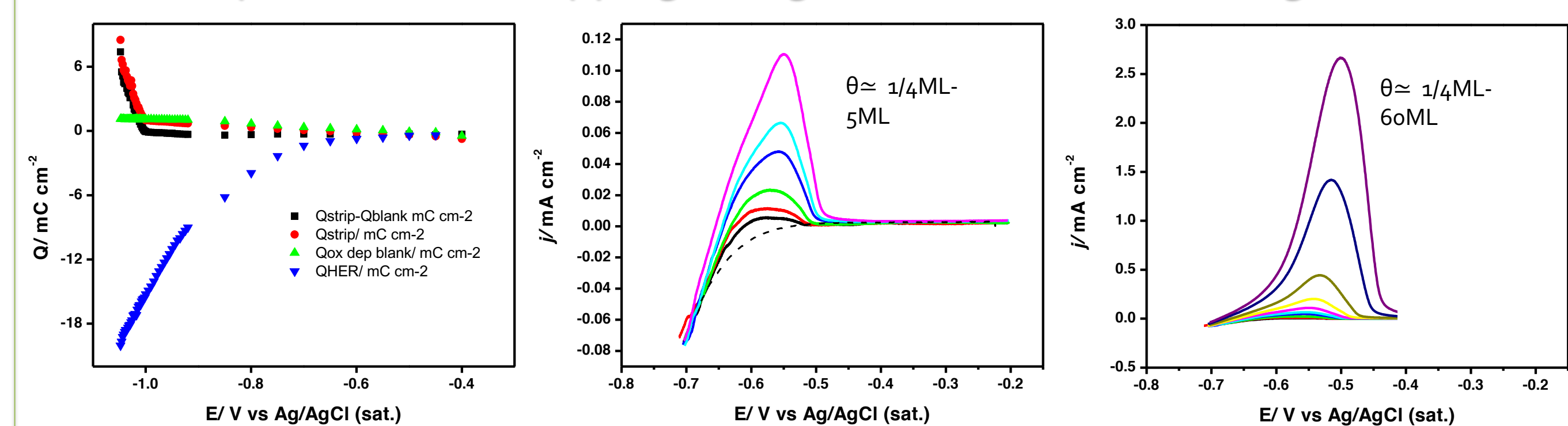


Example Work: Electrochemical Deposition of Fe/WC(pc) Thin-Films



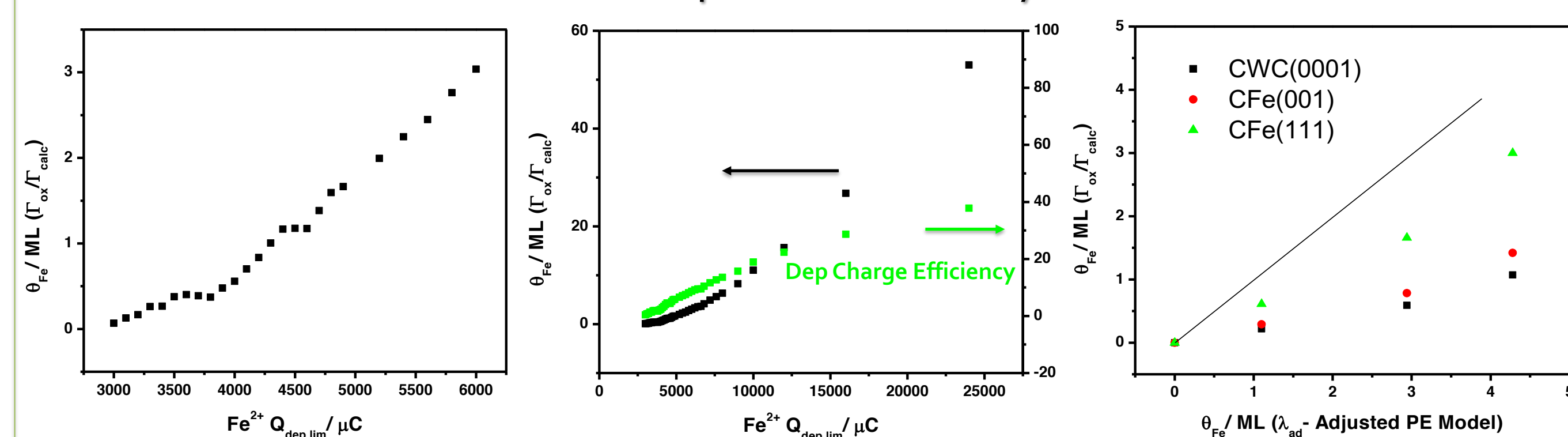
10,000 cycles of Fe deposition are carried out to calibrate ML amounts of Fe-coverage on WC. Depositions are performed in a 10 mM (NH₄)₂Fe(SO₄)₂·6H₂O solution with 100mM (NH₄)₂SO₄ supporting electrolyte, adjusted to pH=4 using 100 mM H₂SO₄. The depositions are performed cathodically by potentiodynamic excursions between -0.90 and -1.2 V vs. Ag/AgCl (Sat). Deposition amount is determined by integration (baseline subtracted) of the anodic Fe→Fe²⁺ dissolution peak (A). Past 100 cycles, any given deposition/stripping cycle gives Q_{avg}=292.7 μC (%σ= 4.7).

Dependence of Stripping Charge on Potential and Charge-limits



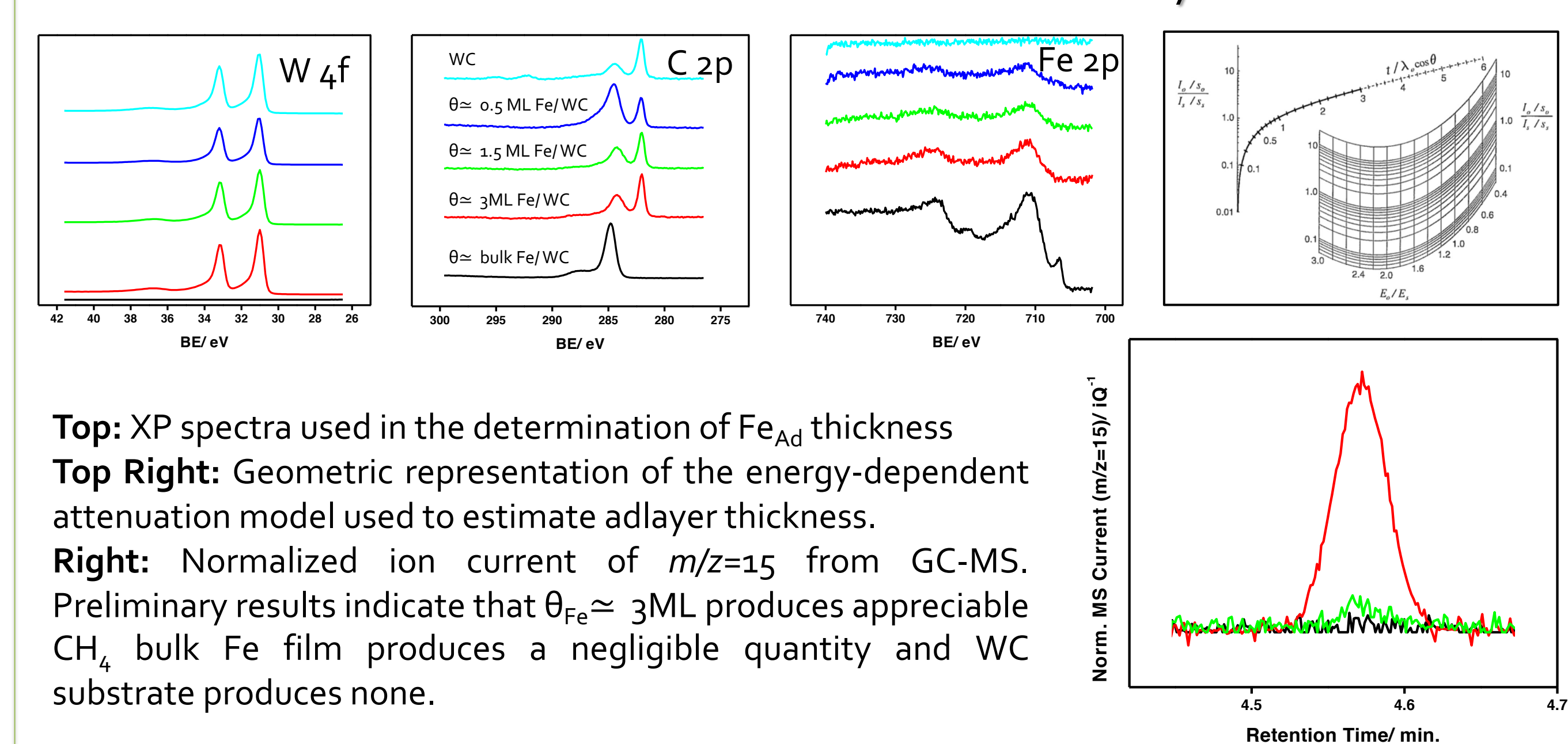
Left: Coulopotentiogram depicting the effect of holding potential (30 s) on stripping charge.
Middle: Potentiodynamic stripping of Fe MLs after increasing Q_{red} limits at -0.9V.
Right: Potentiodynamic stripping of bulk Fe after increasing Q_{red} limits at -0.9V.

Calibration of As-Deposited Fe-Adlayer Thickness



Left: Dependence of calculated fractional Fe coverage (ML regime) on Q_{red} limit.
Middle: Dependence of calculated fractional Fe coverage (bulk regime) on Q_{red} limit.
Right: Fitness of three different packing models based on coverage determination from XPS.

Surface Characterization and Product Analysis



Top: XP spectra used in the determination of Fe_{Ad} thickness
Top Right: Geometric representation of the energy-dependent attenuation model used to estimate adlayer thickness.
Right: Normalized ion current of m/z=15 from GC-MS. Preliminary results indicate that θ_{Fe} ≈ 3ML produces appreciable CH₄ bulk Fe film produces a negligible quantity and WC substrate produces none.

Conclusions

1. Electrochemical surface science protocols have been developed for the reproducible electrodeposition and characterization of Fe films, with monolayer to bulk coverages, on WC(pc).
2. The surface packing density of Fe adatoms on WC may be controlled by a loosely-packed Miller index of the Fe-bcc structure.
3. Monolayer coverages of Fe on WC(pc) enhance the selectivity of CO₂R in bicarbonate solution toward CH₄ production.