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# Phd Thesis Defense: Advanced Catalytic Interface Analysis Through In Situ Studies and Automated Experimental Platforms

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September 07, 2026

15:00

ICFO Auditorium

Electrochemical technologies offer a route to decarbonize key industries, such as energy, chemical and fertilizer manufacturing, by converting abundant chemicals like carbon dioxide (CO?) and nitrate into fuels and feedstocks using renewable electricity. Realizing this potential requires electrocatalytic systems that achieve technoeconomic viability, which is linked to performance metrics such as activity, selectivity, and stability. Their deployment is constrained by two coupled challenges: incomplete mechanistic understanding of dynamic electrochemical interfaces and slow manual workflows that cannot efficiently explore the high-dimensional design spaces of catalysts, electrolytes, and operating parameters. In

electrochemical reactions, performance across its many dimensions emerges from the evolving interplay of catalyst structure and local reaction environment at polarized interfaces. Advancing electrocatalytic performance therefore requires tools that can both reveal and enable control over the evolving catalyst-electrolyte interface during operation. This thesis addresses these challenges by combining operando surface-enhanced Raman spectroscopy (SERS), automated data-analysis frameworks, and self-driving laboratory approaches to accelerate electrocatalyst development under technologically relevant conditions for CO? and nitrate electroreduction reactions.

Operando SERS probes acidic CO? electroreduction on copper-based gas diffusion electrodes up to 0.2 A cm?², showing how interfacial species like sulfate, hydroxide, carbo monoxide (CO), and carbon-containing intermediates evolve with potential and pH. Ou findings suggest that strongly adsorbed sulfate blocks active sites and delays CO?E onset a low overpotentials, while co-adsorbed hydroxide and carbon on reconstructed coppe surfaces stabilize *CO coverages that favor C-C coupling and multicarbon product formation These results identify electrolyte anions and local alkalization as key levers for tuning th onset potential, intermediate stabilization, and selectivity in acidic CO? electroreduction opening new strategies for rational system-level design of catalysts and electrolytes.

To handle the complexity of operando experiments, the thesis introduces SERSFlow, a modular framework for structured operando SERS data and reusable analysis pipelines. Implemented as a local-first Python service with a web interface, it combines preprocessing, feature extraction, and multivariate analysis in deterministic workflows that reproduce expert trends while reducing analysis time from hours to minutes. Benchmarking shows that baseline subtraction alone can shift fitted peak areas by 40-100% for weak or overlapping bands, and spatiotemporal mapping reveals micron-scale heterogeneity in adsorbate populations and double-layer structure.

Finally, the Autoammonia platform-a distributed self-driving laboratory for nitrate-to-ammonia reduction-is developed with two active nodes in different institutions. It integrates in situ catalyst electrodeposition, flow-cell nitrate electroreduction, and automated ammonia quantification within a closed-loop workflow managed by orchestration, planning, and safety software. Autonomous campaigns with copper-based catalysts show that self-driving experimentation is feasible in realistic flow-cell architectures and complex electrolytes using accessible hardware and open-source software.

Collectively, the thesis shows that mechanistic operando characterization, reproducible data workflows, and autonomous experimentation are mutually reinforcing components of a coherent strategy for advancing electrocatalysis. The concepts and tools developed here provide a foundation for more systematic, data-rich, and scalable approaches to the design and optimization of electrocatalysts and electrochemical interfaces for sustainable, electrified chemical production.

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