Handout: SECM for Advanced Electrocatalysis Research

Introduction: Beyond Bulk Measurements

Scanning Electrochemical Microscopy (SECM) is a transformative technique for catalysis research, enabling the direct visualization and quantification of reaction rates at the micro- and nanoscale. Unlike traditional electrochemical methods that measure an average response over an entire electrode, SECM uses a mobile ultramicroelectrode (UME) to map local activity with high spatial resolution. This provides unprecedented insight into catalyst performance, identifying active sites, defects, and compositional hotspots that govern overall efficiency.

Core Application: High-Throughput Catalyst Screening

SECM is exceptionally well-suited for the rapid screening of combinatorial catalyst libraries. By arranging hundreds of different material compositions in a microarray on a single substrate, SECM can quickly identify the most promising candidates for a target reaction.

- **Method**: The SECM probe is scanned across the array in "Generation/Collection" mode. The substrate (catalyst spots) is biased to drive the reaction (e.g., Oxygen Evolution Reaction - OER), generating a product (O_2). The probe is biased to detect this product.
- **Output**: The resulting current map provides a direct, quantitative visualization of catalytic activity. High current at the probe corresponds to a highly active catalyst spot on the substrate.

Case Study 1: Identifying Optimal OER Catalysts in a Pt-Ag Alloy Library

Objective: To rapidly identify the most active composition for the Oxygen Evolution Reaction (OER) within a Platinum-Silver (Pt-Ag) alloy gradient.

SECM in Action: An SECM area scan was performed over the Pt-Ag library. The probe current, corresponding to the detection of evolved oxygen, was recorded at each point. The resulting 2D map, as shown in the presentation, uses a color scale to represent activity.

Key Finding: The map immediately revealed distinct “hotspots” of high current. These bright red and yellow areas correspond to the specific Pt-Ag compositions with the highest intrinsic activity for OER. This allows for the direct identification of the optimal alloy ratio without the need for laborious, serial testing of individual materials.

Case Study 2: Quantifying Single Pt Nanoparticle Activity for HER

Objective: To measure the intrinsic activity of individual Platinum (Pt) nanoparticles for the Hydrogen Evolution Reaction (HER) and understand performance variations at the single-particle level.

SECM in Action: The SECM probe was precisely positioned over individual nanoparticles. Using feedback mode and advanced kinetic analysis of the approach curve, the heterogeneous electron transfer rate constant (k) was extracted for each particle.

Key Finding: SECM revealed a significant distribution in activity among nanoparticles that appeared identical under microscopy. This demonstrates that catalytic performance is not uniform across a particle ensemble. By quantifying these differences, SECM enables a deeper understanding of how factors like nanoparticle size, faceting, and local defects influence catalytic efficiency, guiding the synthesis of more uniformly active catalysts.

Summary of Advantages

- **High Spatial Resolution**: Resolve activity at the micrometer and nanometer scale.

- **Rapid Screening**: Quickly evaluate entire libraries of materials in a single experiment.
- **Quantitative Analysis**: Extract kinetic parameters (e.g., reaction rate constants) for local features.
- **Direct Visualization**: Generate intuitive, color-coded maps of electrochemical activity.