Correlative Electrochemical Multi-Microscopy: Building an Understanding of Electrochemical Interfaces From Local to Global

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Electrodes used in electrochemistry, with applications in electrocatalysis, energy storage, sensor technologies and corrosion, are heterogeneous and complex on a range of lengthscales. We advocate new approaches to study electrochemical and electrocatalytic phenomena, whereby the activity of an electrode is visualized by electrochemical microscopy in the form of "activity maps" and "potentiodynamic movies". These quantitative data are then correlated to co-located electrode structure from complementary high-resolution microscopy and spectroscopy techniques. This *correlative electrochemical multi-microscopy* approach relates electrode structure to activity clearly and unambiguously. In our work, scanning electrochemical cell microscopy (SECCM) and scanning ion conductance microscopy (SICM) are key techniques that are used for the acquisition of both electrochemical activity maps/movies and topography – *synchronously* and with nanoscale spatial resolution. These techniques use nanopipette electrochemical (half) cells as probes that can be made easily in a variety of formats, characterised in detail, and modelled. By overlaying data from these measurements with images from *e.g.* electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy, we obtain a deep view of electrochemical interfaces and processes.

This is a general approach for investigating electrochemical interfaces, and illustrative examples of this approach will be described, including the study of: layered materials, structurally and/or compositionally heterogeneous surfaces such as polycrystalline metals, screen printed electrodes and conducting polymers, and ensemble electrodes comprising of nanoparticles on an electrode support surface, with applications in electrocatalysis and energy storage (batteries). We will also touch on how SECCM and SICM can be used for *controlled delivery* and to *pattern* and *fabricate structures* at interfaces.

A key thesis of our work is that complex electrode surfaces can be broken down and studied as set of simpler "single entities" (e.g., individual steps, terraces, defects, crystal facets, grain boundaries, single particles). The resulting nanoscale understanding of electrochemical reactivity can then be used to create scalable models for electrochemical interfaces that will ultimately facilitate the rational design of functional (electro)materials.

Many talented people at Warwick and elsewhere have contributed enormously to our work in this area over the past decade. I am indebted to them for their significant contributions and they will be acknowledged throughout.