

The electrochemical control of oxidation and reduction processes in organic and inorganic systems is an area of extensive research in both academia and industry. Electrochemical techniques are extremely useful in generating interesting species in unusual oxidation states, or for producing reactive intermediates (as, for example in the reductive dimerization of vinyl cyanide in the Monsanto manufacture of Nylon 66), but provide little intrinsic structural information. To overcome this limitation, spectroscopic methods have frequently been used in conjunction with electrochemical methods in order to monitor the progress of a reaction and to obtain more detailed structural and mechanistic information. The *in situ* alliance of electrochemistry/spectroscopy is particularly valuable in situations where the species undergoing the redox process would not survive the transfer from an electrochemical to a spectroscopic cell, or in situations where it is essential that the spectroscopic analysis occur concurrently to the electrochemical generation, such as in kinetic studies. The focus of this research is developing and utilising spectroscopic techniques (including EPR, UV-VIS, FTIR and NMR) to study processes involving electron transfer, primarily in organic systems. Resources and expertise are shared with the *Coordination Chemistry and Spectro-electrochemistry Group*.



***In situ* Electrochemical-NMR Spectroscopy**

NMR spectroscopy has capacity for the structural identification of solution-phase species. However, despite widespread interest in both NMR spectroscopy and voltammetry, the compatibility problems that exist between the two procedures have made it extremely difficult to achieve an *in situ* combination, with few published attempts. The principal difficulty is the requirement that a metal electrode be located within the magnet of a NMR spectrometer, with the current flowing simultaneously to spectral acquisition. The purpose of the present study is to design a versatile and robust *in situ* electrochemical-NMR spectroscopy cell, capable of operation in a number of different NMR spectrometers under variable temperature and anaerobic conditions. The cell is presently undergoing a process of refinement using the technical expertise of the RSC mechanical, electrical and glass workshops. The finished cell will be applied to studying a number of challenging redox systems where important information regarding the structure, identity or kinetic behaviour of participating reactants and/or intermediates has not been achievable with the use of other spectroscopic methods.

ATR-FTIR Spectroscopy of Solution Phase Radicals

The School recently purchased a FTIR spectrometer (the ReactIR™) that utilises an attenuated total reflectance (ATR) probe in order to monitor the progress of chemical reactions and obtain kinetic data from solution phase reactions. It was thought that such a technique could be useful for obtaining the IR spectra of species that are too unstable to survive being transferred to a conventional FTIR cell. After some initial teething problems that required the instrument being returned to America for repair, successful experiments were carried out this year where the probe was used to obtain the IR spectra of reactive carboxylate radical anions and 2,4,6-substituted phenoxyl radicals. The radicals were prepared by electrolysis of the neutral compounds in a specially built electrochemical cell constructed in the RSC glassblowing workshop. Future studies will focus on improving the performance of the electrochemical cell with the aim of obtaining

IR spectra of species that are considerably less stable, such as α -tocopheroxyl (the vitamin E radical) and other biologically important phenoxyls.

EPR Spectroscopy of Organic and Transition Metal Species

Work continues on obtaining the EPR spectra of organic and inorganic radicals that require special conditions to be stabilised, such as low temperatures or exotic media. Cyclic voltammetric and controlled potential electrolysis experiments performed at -40°C in CH_2Cl_2 have indicated that tethered arene-ruthenium(II) complexes can be oxidised by one-electron to form moderately stable compounds. EPR experiments confirmed that the oxidation occurred at the metal centre to form the Ru^{III} complexes. At temperatures below $\sim -20^{\circ}\text{C}$, the oxidised species remain stable for long periods of time, but at higher temperatures quickly decompose to other Ru^{II} compounds. A combination of electrochemistry and EPR spectroscopy helped to establish the optimal conditions with which to synthesise and isolate the tethered arene-ruthenium(III) compounds. (*with J.R. Adams, M.A. Bennett*)

Processed wood surfaces exposed outdoors are rapidly degraded because lignin strongly absorbs UV light, which leads to radical-induced depolymerisation of lignin and cellulose, the major structural constituents of wood. We have used EPR spectroscopy to monitor the concentration of free radicals in wood and to assess the feasibility of using chemical modifying agents to reduce photo destabilisation. (*with P.D. Evans [Dept. Wood Science, U. British Columbia, Canada]*)

Copper Corrosion

Passive films formed on copper electrodes in neutral or basic solutions have a duplex structure with an outer layer of CuO or $\text{Cu}(\text{OH})_2$ and an inner layer of Cu_2O . It is because of the formation of these thermodynamically and kinetically stable passive films in approximately neutral pH media that copper tubes are a widely used and generally reliable conduit for domestic water supplies. However, one source of pitting corrosion of copper is the presence of aggressive anions such as Cl^- and SO_4^{2-} , which accelerate the breakdown of the passive layers. We have developed a procedure for studying the corrosive nature of the aforementioned anions in the concentration range typically found in potable water supplies (20–200 ppm) using artificial copper pits that are prepared by voltammetrically forcing dissolution of 60 or 80 mm copper wires embedded in an epoxy matrix. The morphology and chemical composition of the pit caps are examined by Raman spectroscopy, optical microscopy, scanning electrode microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Raman spectroscopy is particularly useful for *in situ* studies because H_2O scatters only weakly between $3100\text{--}150\text{ cm}^{-1}$, thus the samples do not need to be dried (such as they do for SEM, EDX and XPS analysis) thereby reducing the probability of alteration of the corrosion products prior to spectroscopic analysis. (*with A. Lowe, M. Stoll [Engineering, FEIT, ANU], V. Otieno-Alego [U. Canberra]*)

<http://rsc.anu.edu.au/research/webster.php>