

Electrons provide the bonding between the atoms in any material, so it is not surprising that electrolysis can bring about dramatic and precise chemical changes. We have developed a conceptual approach to exploring molecular electronic structure and reactivity that combines electrochemical and spectroscopic methods as explained below. Redox processes in simple coordination complexes may turn out to be mainly metal-centred, or truly delocalised or mainly ligand-centred, as with bipyridyls. In bimetallic clusters, intensely coloured *mixed-valence* states can arise. In all these examples, electrosynthesis offers a logical route to the unusual oxidation states, once these have been identified by voltammetry. In particular, *in-situ* optical spectro-electrochemistry enables quite elusive species to be studied readily without the need for isolation. The resulting spectral data are usually elegant and very informative. We regard electrochemistry as a powerful ally for bench chemists, rather than an end in itself, though computational simulation of electrode response is now a vitally important aspect of validating the interpretation of redox behaviour.



Dr Heath and Dr Otieno-Alego lectured by invitation in May at "Conservation Science 2002" in Edinburgh. Dr Heath also taught an optical spectrometry course to trainees in the national Laboratory Technician scheme at Canberra Institute of Technology. Dr Mahon remains a consultant with cap-XX Pty Ltd and Dr Webster (QEII Fellow, 2001) retains his association with the group. Nicholas Perkins was awarded his PhD and his thesis highly commended. Alexandra Pavli (Narrabundah College) was our CSIRO student researcher for 2002, supervised by Stephen Lee.

Convulsive Modelling of Redox Processes at Disk Electrodes

The reliable construction of electro-analytical electrodes with disk geometry ensures the continued popularity of this design. However, the discontinuity at the perimeter between the active conducting surface and insulating annulus is a great obstacle to solving the complex differential equations. Previous mathematical treatments relied on one or other alternative simplifications appropriate to the short and long time limits. A hybrid analytical-numerical procedure known as the Integral Equation Method has been used to extend the short-time expression so that this mathematical description can be used throughout. Convulsive Modelling is then applied to this description in order to predict the response of the disk electrode under either current or potential control. (with P.J. Mahon, and D.K. Cope [North Dakota State U., USA], K.B. Oldham [Trent U., Ontario Canada])

Development of a Nonlinear Electrochemical Dummy Cell

The use of small-amplitude alternating signals is a very powerful tool in voltammetry and for this reason the acV method has been incorporated into a bipotentiostat built in the RSC electronics workshop. A difficulty in testing these circuits is that the passive components in ordinary hard-wired dummy cells are linear and so they fail to simulate the real solution-cell electrochemical response to alternating modulation. However, in a dummy cell with two opposed diodes connected in series, the reverse bias current of one diode or the other is active whatever the direction of the applied voltage. We find that, with suitably chosen elements, the response simulates pseudo-electrochemical behaviour over a frequency range, and that a dummy cell of this configuration enables effective and convenient testing of electrochemical instruments with alternating signal modes. (*with P.J. Mahon*)

Mixed Valency in Binuclear, Trinuclear and Tetranuclear Clusters

Metal cluster compounds are of enduring importance in transition metal chemistry. We have a long-standing interest in confacial bimetallic complexes of the form $L_3M(\mu-X)_3ML_3$. Dr Nick Perkins devised a strategy for constructing extended confacial arrays by attaching two RuL_3 fragments to an MX_6 or M_2X_9 core. For example, linear tetrametallics of the type $[(R_3P)_3Ru(\mu-X)_3Os(\mu-X)_3Os(\mu-X)_3Ru(PR_3)_3]^+$ with a II, III, III, II resting state show two Os-centred reductions and two Ru-centred oxidations. The pattern of metal-metal bonding is predicted to change systematically as a function of oxidation level, in accord with spectro-electrochemical data spanning five oxidation states. (*with C. Barlow[‡], L. Dubicki[‡], A. J. Edwards, M. Gupta, D. L. Kay, S. B. Lee, N. E. Perkins, R. D. Webster, A. C. Willis*)

Development of NMR Spectro-electrochemistry

Marriage of electrolysis with potentially incompatible NMR spectroscopy has largely eluded chemists, despite the attractions of high-field NMR spectroscopy as a structurally informative solution-phase technique. In 2000, we reported a successful electrogenerative cell for practicable in-situ NMR detection. This assembly fits in a normal spinning sample tube in a standard multinuclear, FT spectrometer. Refinement of the Bramley/Prenzler in-situ electrochemical NMR cell has been taken up by Dr Richard Webster as part of his QEII Fellowship program (see elsewhere). Promising targets for complementary NMR/EPR characterisation include the reversible $[Co(dtc)_3]^{0/+}$ couple, and a family of $Ru(acac)_2L_2$ complexes in oxidation states II to IV. (*with R. Bramley, M. A. Keniry, R. D. Webster*)

Porphyrin Dimers Linked by Conjugated Poly-Alkyne Bridges

Meso-linked 'Arnold bisporphyrins' have an extended poly-alkynyl bridge of the form MOEP-X-MOEP where X = C₄, C₆, or even C₈. The conjugated dimer anions are accessed by chilled in-situ spectro-electrochemistry. Mixed-valence [P₂]¹⁻ and doubly reduced [P₂]²⁻ have very intense NIR absorption bands beyond 1000 nm. These distinctive spectra in three oxidation states are well fitted by a generic 'two-porphyrin eight-orbital' scheme, initially containing 8, then 9, then 10 electrons.

In a long-sought advance, the new generation of sterically protected Arnold bisporphyrins can be reversibly oxidised as well as reduced. The stable, EPR-active p-radical ions [P₂]¹⁺ and [P₂]¹⁻ of tri-aryl [Zn(tr-ArP)]-C₄-[Zn(tr-ArP)] reveal almost superimposable two-band near-IR spectra. The eye-catching homology between 7- and 9-electron cases was actually predicted by the original MO scheme [New J. Chem. 1998]. (D. P. Arnold^{*}, R. D. Hartnell [Queensland U. Technology], and G.A. Heath, D. L. Kay, R.D. Webster)

Redox Activation of the Iron-Molybdenum Cofactor of Nitrogenase

The remarkable mechanism of biological nitrogen fixation is being elucidated by direct electro-modulation of the catalytic Fe/Mo/S cluster, extruded intact from its protein. This collaboration involves ferrying the precious material from the UK Nitrogen Fixation Laboratory for spectro-electrochemistry in Melbourne (FTIR) and later at ANU (EPR, UV-NIR). (with S. P. Best [Melbourne U.], L. L. Martin [Flinders U.], C. J. Pickett [John Innes Centre, Norwich, UK])

Corrosion Studies

This collaborative activity is concerned with the deterioration of metals and other materials (i.e., with deleterious redox processes). We are concerned with the scientific conservation of historic items, as well as technological problems such as pitting corrosion of dairy equipment and unwelcome inorganic deposits in internal combustion engines. Surfaces are studied by many methods, including Raman imaging microscopy, X-ray single-crystal and powder diffraction, and impedance spectroscopy. Further studies of aero-engine combustion deposits were commissioned by the Australian Transport Safety Bureau (ATSB). (with A.J. Edwards, S. B. Lee, P.J. Mahon, L. Norén, R. D. Webster, and M. Sterns, [Chemistry, ANU], G. L. Bailey [Australian War Memorial], D. C. Creagh, V. Otieno-Alego [U. Canberra], D. L. Hallam, R. Tait [National Museum of Australia], A. Romeyn [Commonwealth Dept of Transport and Regional Services, Canberra])