Coordination Chemistry and Spectro-electro Chemistry

Dr Graham Heath

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 that combines electrochemical and spectroscopic methods as explained below. Computational simulation of electrode response is also a vital aspect of validating the interpretation of redox behaviour. Redox processes in simple coordination complexes may turn out to be mainly metal-centred, 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 in depth without isolation.

Dr Heath made two research visits to the *Photon Factory* synchrotron in Tsukuba, Japan, accompanied the second time by Dr Mahon. Dr Mahon has taken up operation of the UC Raman Microscope Facility, and remains a consultant with cap-XX Pty Ltd. Maria Kubik has joined the group to pursue her doctoral studies on artists' materials. Professor Creagh (U. Canberra) and Dr Otieno-Alego (AFP Forensic Criminalistics) were awarded RSC Visiting Fellowships, attached to the group. Dr Webster (QEII Fellow, 2001–) also retains his association with the group. Jennifer Zampese (U. Canterbury) was our summer scholar for 2002/03, closely assisted by Stephen Lee. Ms Sushilla Knottenbelt and Dr John McGrady (U. York, UK) visited our laboratory between January and March to continue collaboration on redox-active clusters.

Convolutive Modelling of Redox Processes at Disk Electrodes

For popular electro-analytical electrodes with disk geometry, the discontinuity at the perimeter between the active conducting surface and insulating annulus is a great obstacle to solving the complex differential equations. Previous treatments relied on alternative simplifications appropriate to only the short or long time limits. A hybrid analytical-numerical procedure known as the Integral Equation Method has been used to sufficiently extend the short-time expression. Convolutive Modelling is then applied 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 Non-linear Electrochemical Dummy Cell

A difficulty in testing apparatus for a.c. voltammetry is that the passive components in normal hard-wired dummy cells are linear and so they fail to simulate the real solution-cell electrochemical response to a.c. 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 sign of the applied voltage. With suitably chosen elements, the response simulates a pseudo wet-cell over a frequency range. This device enables effective and convenient testing of versatile electrochemical instruments with alternating signal detection modes. *(with P.J. Mahon)*

Mixed Valency in Bi-, Tri- and Tetra-nuclear 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 $L_3M(\mu\text{-}X)_3ML_3$. Dr Nick Perkins built extended confacial arrays by attaching two RuL_3 fragments to an MX_6 or M_2X_9 core. Linear tetrametallics of type $[(R_3P)_3Ru(\mu\text{-}X)_3Os(\mu\text{-}X)_3Os(\mu\text{-}X)_3Ru(PR_3)_3]^+$ with a II,III,III,II resting state show two Os-centred reductions and two Ru-centred oxidations. The pattern of metal-metal bonding changes over the five oxidation states, in accord with the spectro-electrochemical data. *(with L. Dubicki, A.J. Edwards, S.B. Lee, P.J. Mahon, N.E. Perkins, R.D. Webster, and S.Z. Knottenbelt, J.E. McGrady [U. York, UK])*

Technical Developments in Spectro-electrochemistry

Marriage of electrolysis with supposedly incompatible NMR spectroscopy had largely eluded chemists until 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. Redevelopment 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). In a separate development, collaboration with Melbourne colleagues has given us access to an advanced electrolytic flow-cell for redox-modulated EXAFS measurements on our metal clusters at the Australian Beamline Facility in Tsukuba. *(with R. Bramley, M.A. Keniry, R.D. Webster, and separately with S.P. Best, M. Bondin, A. Moreno [U. Melbourne])*

Redox-active Organometallic Complexes

Parallelling our in-house research in redox-active inorganic complexes and linear metal arrays is a long-standing interaction with Dr Mark Humphrey and his colleagues on the instrumental characterization of the extended library of organometallic compounds developed under his leadership for application as non-linear optical materials. This has led to a practicable electro-generative non-linear-optical cell, and to systematic correlations linking the optical and redox behaviour of these systems with trends in their molecular and electronic structure. *(with S.B. Lee, A.Y. Park, and M.P. Cifuentes, M.G. Humphrey, S.K. Hurst, J.P. Morrall, C.E. Powell, M. Samoc, R. Stranger [Chemistry, ANU])*

Corrosion and Conservation Studies

We are concerned with the scientific conservation of historic items and works of art, as well as technological corrosion in equipment and unwelcome inorganic deposits in internal combustion engines. The Merlin engines of Lancaster bomber *G-for-George* required such scrutiny before the aircraft's recent return to public display. Surfaces and pigments are studied by many methods, including diffuse reflectance, Raman imaging microscopy, X-ray single-crystal and powder diffraction, and impedance spectroscopy. Particular attention is presently being given to paintings from the *'Angry Penguins'* group and other significant works, with the collaboration of the National Gallery of Australia *(with A.J. Edwards, M.E. Kubik, S.B. Lee, P.J. Mahon, R.D. Webster, and R. Maxwell [Art History, ANU], 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])*

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