**New Electrochemical Methods for Understanding Biological Redox Chemistry**

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Biology produces many inspirational catalysts that ‘activate’ small, inert, molecules such as protons, N2 and H2O via redox chemistry catalysed at transition metal active sites. Such enzymes are used in novel clean-energy technologies such as enzyme fuel cells and solar water-splitting devices. The Parkin group is developing protein film Fourier Transform Voltammetry (PF-FTacV) as a tool to study these bio-catalysts in collaboration with Prof Alan Bond (Monash).1,2 This talk will showcase recent work carried out on [NiFe]-hydrogenases. Although an “O2-tolerant” subset of enzymes offer the tantalizing ability to remain catalytically active at oxidizing H2 in air, they are unfortunately very poor H2 production (H+ reduction, 2H+ + 2e- ⭢ H2) catalysts.3 By combining electrochemistry, molecular biology and structural studies we have been able to prove that it is the electron-transfer relay of iron-sulfur centres, not the active site ligands, which play a vital role in controlling O2 inhibition and catalytic bias.4,5 We are now exploring why this happens using PF-FTacV and unpublished results will demonstrate our progress in probing electron transfer centres that are invisible via all previous experiments using electron paramagnetic resonance and “traditional” direct current protein film voltammetry. New advances in electrode surface modifications are also described.6



**Figure 1.** Overview of the technique of protein film Fourier transform alternating current voltammetry, PF-FTacV.

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