

Hydrogenases on Electrodes: Revealing and Elucidating their Complex Chemistry

Fraser A. Armstrong, Natalie Belsey, Sophie Lamle, Alison Parkin, Kylie A. Vincent,

*Department of Chemistry, Inorganic Chemistry Laboratory, Oxford University,
South Parks Road, Oxford, OX1 3QR, England*

Hydrogenases catalyse the rapid interconversions of hydrogen and water in the microbial hydrogen cycle that goes on around us almost unnoticed [1]. These metalloenzymes, the two main classes of which (known as [NiFe] and [FeFe]) have unusual active sites with carbonyl and cyanide ligands, also display remarkably high activity when adsorbed at carbon electrodes, with turnover frequencies far exceeding 1000/sec [2]. Use of advanced voltammetric techniques not only provides a powerful way to control, investigate and unravel the highly complex catalytic properties and redox-coupled chemistries of these enzymes [3-9], but also leads naturally to novel applications and inspirations for developing future hydrogen-based renewable energy technology in which H₂ is the link between electricity and chemical (transportable) fuels [1]. These enzymes convert hydrogen into electricity and electricity into hydrogen, and they perform these tasks very well indeed. A particularly remarkable observation is an example in which hydrogenase electrocatalysis is unaffected by a large excess of carbon monoxide [10].

1. Cammack, R.; Frey, M.; Robson, R., Eds. In *'Hydrogen as a Fuel: Learning from Nature'* Taylor and Francis; London and New York, 2001. **2.** Jones, A. K.; Sillery, E.; Albracht, S.P.J.; Armstrong, F.A.: *Chem. Commun.* 2002, 866-867. **3.** Léger, C.; Jones, A. K.; Roseboom, W.; Albracht, S. P. J.; Armstrong, F. A.: *Biochemistry* 2002, 41, 15736-15746. **4.** Léger, C.; Jones, A. K.; Albracht, S. P. J.; Armstrong, F. A.: *J. Phys. Chem. B.* 2002, 106, 13058-13063. **5.** Lamle, S. E.; Vincent, K. A.; Halliwell, L. M.; Albracht, S. P. J.; Armstrong, F. A.: *J. Chem. Soc. Dalton Trans.* 2003, 4152-4157. **6.** Jones, A. K.; Lamle, S. E.; Pershad, H. R.; Vincent, K.A.; Albracht, S. P. J.; Armstrong, F.A.: *J. Am. Chem. Soc.* 2003, 125, 8505-8514. **7.** Lamle, S. E.; Albracht, S. P. J.; Armstrong, F. A.: *J. Am. Chem. Soc.* 2004, 126, 14899-14909. **8.** Lamle, S. E.; Albracht, S. P. J.; Armstrong, F. A.: *J. Am. Chem. Soc.* 2005, 127, in press. **9.** Vincent, K. A. Parkin, A.; Albracht, S. P. J.; Cammack, R. ; Cavazza, C.; Fontecilla-Camps, J. C.; Lenz, O.; Friedrich B.; Armstrong, F. A.: submitted. **10.** Vincent K. A.; Lenz, O.; Friedrich B.; Armstrong, F. A.: submitted.