Bioelectrochemical systems investigated using neutron reflectometry

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Biophotovoltaic devices (BPVs) that use photosynthetic bacteria to harvest light energy by growing a biofilm directly onto the electrode are currently limited by low power outputs due to slow electron transfer between the biofilm and electrode[1]. The reasons for this remain unclear—although there has been significant progress towards improving device efficiency (e.g. via electrode engineering or genetic modification of the photosynthetic bacteria), details of the fundamental molecular behaviour at this interface are largely unexplored.

Here, we present the characterisation of small biologically relevant redox species such as nicotinamide adenine dinucleotide (NADH) at the electrode/electrolyte interface, using specialised surface study techniques that allow us to monitor these systems *in situ*[2],[3]. Neutron reflectometry (NR) is a particularly powerful technique that allows angstrom-level resolution of changes in interfacial structure perpendicular to the surface plane. By using a custom-designed electrochemical NR cell, we were able to monitor the reversible adsorption of NADH from a carbon electrode as a function of applied potential, and reveal some interesting behaviour when comparing the adsorption behaviour of two different flavins. Complementary techniques such as depletion isotherms allowed us to extract thermodynamic parameters for these systems and give an overall picture of their interactions with electrode surfaces. We are now using this methodology to increase the complexity of the systems being studied to proteins and model cell membranes, with the aim of better characterising electron transfer mechanisms within bioelectronic devices such as BPVs.

[1] McCormick, A. J.; Bombelli, P.; Bradley, R. W.; Thorne, R.; Wenzel, T.; Howe, C. J. *Energy Environ. Sci.* **2015**, *8*, 1092.

[2] Wood, M. H.; Humphreys, E. K.; Welbourn, R. J. L. *Langmuir*, **2019**, *35*, 6055.

[3] Wood, M. H.; Rubio-Lara, J.; Welbourn, R. J. L. *In Prep.* **2021**.