

## Modelling the Voltammetric Behaviour of Electroactive Self Assembled Monolayers

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Electrodes coated with a monolayer of redox-active groups are commonly used for probing and understanding electron transfer kinetics.<sup>1</sup> Changing parameters of the self-assembled monolayer (SAM) such as the length and functionality of the bridging group as well as properties of the supporting electrolyte can be used to influence the electron transfer behaviour.<sup>2</sup>

When classically treated to ignore the electrostatic interactions between charged redox groups the voltammetric wave for a redox couple like ferrocene/ferrocenium is predicted to have symmetric shape. The peak current is also found at the standard redox potential ( $E^0$ ) and a full width at half maximum (FWHM) equal to  $90.6/n$  mV. The FWHM should not change with the surface coverage of head groups introduced. Experimentally both deviations in the peak potential from  $E^0$  and broadening of the FWHM are seen especially at high surface coverages.<sup>3</sup> This non-classical behaviour can be described by modelling the interfacial potential distribution across the system.<sup>4</sup> This method accounts for the interaction between neighbouring charged redox groups, described experimentally as the interaction factor. The interfacial potential distribution of SAMs containing reversible redox head groups has been described analytically. Here an electrostatic approach was used quantitatively represent interactions between redox groups and the structure of the double-layer described using Gouy-Chapman theory. Whilst this method was able to qualitatively describe the experimental behaviour, the analytical expressions were limited to conditions where electron transfer kinetics at the redox head group is fast for the time scales used.

In this work COMSOL Multiphysics, a commercial finite element modelling package is used to model this system under non-equilibrium conditions. The Nernst Planck Poisson equation is solved to describe the time-dependent coupling of electrostatic fields and mass transport in solution. This approach enables the interfacial potential across the system as well as changes in the concentration distribution of the electric double layer to be modelled. It also provides a starting point for incorporating more complex phenomena such as a stern layer to account for the discret size of the electrolyte ions and ion-pairing.<sup>5,6</sup>

### References

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