Studies of the Co(II)/Co(III)(dbbip)$_2$ Redox couple as a Mediator for Dye-sensitized Nanocrystalline Solar Cells

Petra Cameron and Laurie Peter

Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom
l.m.Peter@bath.ac.uk Tel. +44 1225 826815 Fax +44 1225 385802

Nusbaumer et al.[1,2] have shown that the well-known iodide/tri-iodide redox relay in dye-sensitized solar cells (DSSC) can be replaced by the Co(II)/Co(III)(dbbip)$_2$ couple (dbbip = 2,6-bis(1’-butylbenzimidazol-2’-yl)pyridine). Bignozzi’s group[3] have also examined a range of cobalt complexes as potential redox mediators for DSSCs. The success of the Co(II)/Co(III)(dbbip)$_2$ system surprised us, because we believed that one of the key requirements fro a redox relay is that it should exhibit facile electron transfer kinetics at the regenerating anode while displaying slow electron transfer kinetics at nanocrystalline TiO_2 (and at the fluorine-doped tin oxide (FTO) substrate in cells without blocking layers). In the case of iodine/tri-iodide, these ‘differential kinetics’ arise from the electrocatalytic properties of the platinum cathode, where dissociative chemisorption of iodine decreases the activation energy for the electrode reaction. By contrast, one-electron outer sphere redox mediators such as ferrocene/ferricinium generally give poor performance as a consequence of rapid electron transfer from the TiO_2 and from the FTO[4]. Our studies of the Co(II)/Co(III)(dbbip)$_2$ couple have shown that the exchange current density does depend on the nature of the substrate, in spite of the fact that we are dealing with an outer sphere reaction. The results of a study using electrochemical and photoelectrochemical methods will be presented and used to show how the factors controlling cell performance can be quantified[5].

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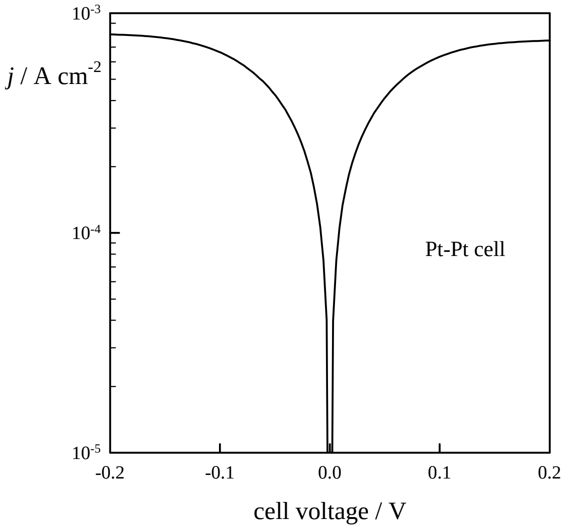
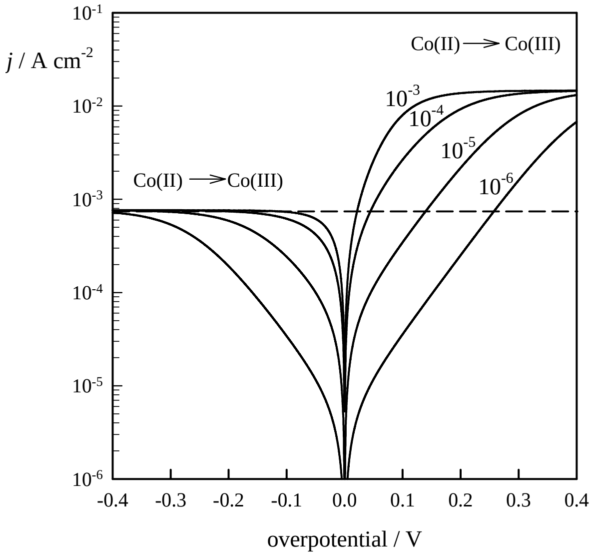
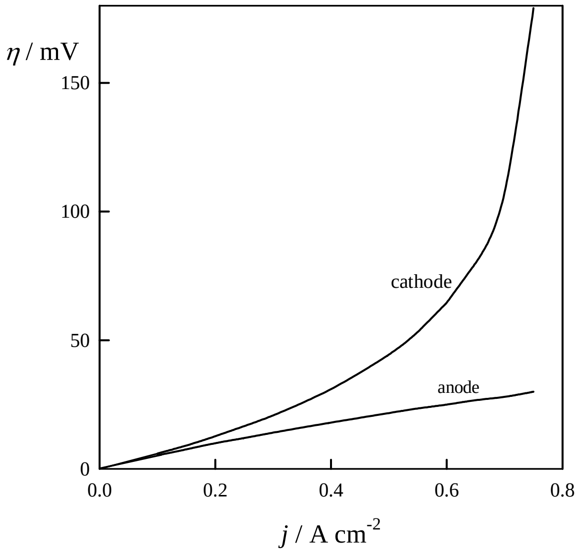


Current voltage characteristics of a thin layer cell with sputtered platinum film electrodes. Inter-electrode spacing 45 µm. Electrolyte: 0.018 M Co(III)(dbbip)$_2$ and 0.162 M Co(II)(dbbip)$_2$.



Current potential characteristics calculated for a one electron redox system such as Co(II)/Co(II)(dbbip)$_2$ with mass transport limits determined by an inter-electrode spacing of 45 µm. The diffusion coefficients of the oxidized and reduced components are 1.1×10^{-6} cm^2 s^{-1} and 1.9×10^{-6}cm^2 s^{1-} respectively. Concentrations of oxidized and reduced components are 0.018 M and 0.162 M. Cathodic transfer coefficient 0.5. Standard heterogeneous rate constant, k^0, as shown. The dashed line shows the mass transport limited current that would be observed in a thin layer cell configuration as a consequence of the fact that the concentration of oxidized species is smaller than that of the reduced species.



Calculated anodic and cathodic overpotentials in the Pt-Pt thin layer cell as a function of current density. Note that the overpotential at the cathode increases rapidly as mass transport limitation sets in. By contrast, the smaller overpotential at the anode is determined by the sluggish electron transfer kinetics as well as mass transport.

References

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