Sub-T_c Electron Transfer At The Hg-HTSC/Liquid-Electrolyte Interface

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The onset of superconductivity at a critical temperature T_c is accompanied by the formation of superconducting electron pairs and (usually) the creation of an energy gap in the density-of-states function for the remaining unpaired electrons. For oxocuprate high-temperature superconductors (HTSCs), the mechanisms associated with these changes remain under discussion in the literature.

The rate of electron transfer between an electrode and a redox-active species in an adjoining electrolyte is directly linked to the density of electronic states in the electrode and is thus a novel probe of the superconducting state.

Lorentz *et al.*[1] report increases in electron-transfer rate, localized around T_c, at HTSC/solid-electrolyte interfaces, with Ag/Ag^+ as the redox couple. Their interpretation of this as participation of electron pairs in the electron-transfer event is by no means certain. Indeed, it has been shown that such a response could arise from single electron transfer and, significantly, that the effect of HTSC superconductivity on electron-transfer rate should depend upon the HTSC conduction mechanism to a discernable extent.[2]

The flexibility to pick electrode reactions to favour or disfavour pair transfer (for example spacing electron acceptors close to the correlation length of the HTSC would favour pair transfer) to at least resolve the pair *vs.* normal question requires the use of liquid electrolytes.

The use of liquid electrolytes in the temperature range for HTSC superconductivity (100 – 135 K) is plagued by high uncompensated solution resistance and reactant insolubility, though we have shown previously that voltammetry is possible with freely-diffusing redox species.[3] The solubility problem is obviated by tethering redox species as self-assembled monolayers (SAMs) and, while direct attachment to HTSCs is difficult, there is the possibility of proximity effect superconduction through an intervening silver layer.[4] The problem of solution resistance is minimized by using the highest T_c material available.

In the present study, a SAM of ferrocene thiol $CpCO_2Cp(CH_2)_8SH$ (CpFeCp = ferrocene), diluted with *n*-octylmercaptan, was prepared on the surface of a Hg-based HTSC (T_c = 134 K), sputter coated with a silver layer of *ca*. 30 Å thickness. The cyclic voltammetry of this interface, immersed in a liquid electrolyte, was recorded at temperatures above and below T_c, as shown in Figure 1. The peak separations of these voltammograms were used to provide, through fitting to Marcus density-of-states theory, values of the standard heterogeneous rate constant k^o for the Fc/Fc^+ electron-transfer reaction. The results for both resistance-compensated and uncompensated data have been used to create Arrhenius plots, corrected for the effects of solvent dynamics, which show no deviation from linearity through T_c.

The resistance-compensated data were used to calculate a value of reorganizational energy for the reaction of λ = 0.92 eV, plus a value of $k^o_{273\,K} = 357\ s^{-1}$. For the same reaction at a bulk Au electrode in a chloroethane/butyronitrile solvent, Murray *et al.*[5] report λ = 0.95 eV, plus a value of $k^o_{273\,K} = 4.1 \times 10^3\ s^{-1}$. The key parameter is thus the value of $k^o_{273\,K}$, which is more than 10-fold lower for HTSC/Ag than for bulk Au. The influence of the underlying electrode material is thus evident and yet there is no influence of the onset of superconductivity. It is therefore tempting to conclude that previous observations of rate increases around T_c for solid electrolyte systems are indeed due to pair transfer, which, as Lorentz points out,[1] would be less likely in a liquid electrolyte because of the associated higher reorganizational energy.

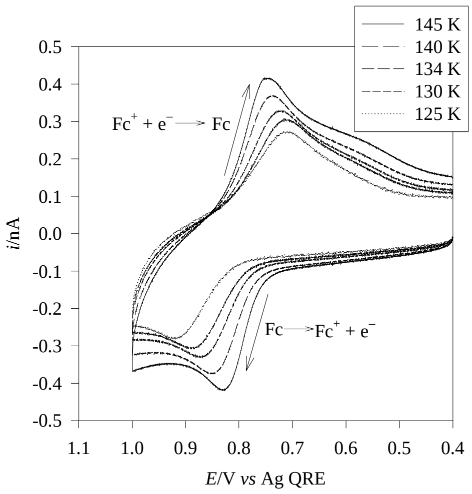

Figure 1 Temperature dependence of cyclic voltammetry of $CpCO_2Cp(CH_2)_8SH/Ag$ (30 Å) /Hg-based HTSC (T_c = 134 K) in 16:7:1 EtCl/THF/2-MeTHF, plus 0.2 M $LiBF_4$; sweep rate 5 mV s^{-1}.

This work is the first sub-T_c electrochemistry on a Hg-based HTSC, and shows the relative ease with which rate data can be obtained for these very-high T_c materials. Similar experiments using different electroactives, particularly 2-electron acceptors, should yield valuable information on the electronic properties of these materials.

References

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