Sub-T_c electron transfer at the HTSC/polymer interface

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The first kinetic measurements for electron transfer (ferrocene/ferricinium reaction) at the interface between an HTSC (Tl,Pb$_{1223}$) and a redox polymer (ferrocene-tagged polypyrrole) show that superconductivity affects electron transfer rate, which thus offers a novel probe of the superconducting state.

At the superconducting transition temperature, T_c, formation of the paired electrons responsible for superconduction is usually accompanied by the opening of an energy gap around the Fermi level in the density-of-states function for the remaining unpaired (normal) electrons. In theory, these changes should influence the rate of electron transfer between a superconductor and a redox-active species in an adjoining electrolyte,[1–5] since this rate is partly determined by the density of electronic states in the electrode.[6] The effect of superconductivity on the rate of electron transfer at the interface between an electrolyte and a high-temperature superconductor (HTSC) thus offers a novel probe of the electronic structure and hence the (as yet unknown) mechanism of electron pairing and superconduction in these materials.[5]

Reactions studied at superconducting HTSC electrodes have thus far been of redox-active species in solid electrolytes,[7–9] frozen glasses,[10] and liquid electrolytes, the last class including the reaction of freely-diffusing species,[11,12] the electrolyte itself[13] and species tethered to the HTSC *via* an alkanethiol linker attached to a gold or silver underlayer.[14]

Lorentz *et al.*[7] reported an approximate doubling at T_c of the current associated with the Ag/Ag$^+$ electron transfer reaction at HTSC/solid-electrolyte interfaces. This current peak they interpreted as evidence for the participation of electron pairs in the electron transfer event, though such a response could in theory still arise if only single electrons were transferred.[4]

Full understanding of the HTSC/electrolyte interface, and hence its utilization as a probe of superconductivity, lies in using liquid rather than solid electrolytes since, unlike solids, liquids allow essentially limitless choice of reactions for study. For example, to discern whether electrons that are paired in the HTSC may be transferred to an electrolyte species, the transfer should be favoured by choosing appropriate 2-electron acceptors.

Although liquid electrolytes are available for use in the temperature range for HTSC superconductivity (100–135 K), allowing some promising preliminary investigations,[11–14] high solution resistance and reactant insolubility are inevitable problems at the lowest temperatures. The first problem is reduced by using the highest T_c materials available, based on Tl and Hg. The second problem is avoided by attaching the redox probe to the electrode, either as a self-assembled monolayer[14] or as a polymer.[15]

Here we present sub-T_c electrochemistry of the ferrocene unit of pyrrole **1**, electropolymerized as an amorphous and hence liquid-like polymer onto a Tl$_{0.5}$Pb$_{0.5}$Sr$_2$Ca$_2$Cu$_3$O$_9$ (Tl,Pb$_{1223}$) electrode (T_c = 122 K). This is the first investigation of the effect of superconductivity on electron transfer at an HTSC/polymer interface.

At room temperature, in an electrolyte of 0.1 M NBu$_4$ClO$_4$ in dry, oxygen-free dichloromethane, polymer-coated Tl,Pb$_{1223}$

electrodes gave well-defined voltammetry for the ferrocene/ferricinium (Fc/Fc$^+$) reaction.† Linear dependence of peak current on the square root of the potential sweep rate was taken to indicate current-limiting diffusion of the counter ion through the polymer film.[16]

pyrrole 1
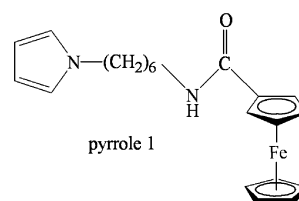
The HTSC electrode area was approximately 0.01 cm^2 (porosity prevents accurate determination). Voltammetry of polymer films formed by the same procedure on Au electrodes (of accurately known area) indicated a coverage of 6.2×10^{-8} mol cm^{-2} of ferrocene. Taking the monomer volume of 0.346 nm^3 (calculated using MacSpartan Pro® 2.0) as a simple cube then leads to an upper estimate of the typical film thickness of 0.13 μm (around 180 monomer layers).

The voltammogram (Fig. 1) of such a polymer-coated HTSC electrode at 122 K (T_c) in dry, oxygen-free butyronitrile/chloroethane (2:1 by volume), containing 0.1 M NBu$_4$ClO$_4$, shows peaks for the Fc/Fc$^+$ reaction and is typical for the temperature range 130 to 110 K.‡

The cathodic peak current, i_{pc}, and the separation between cathodic peak potential, E_{pc}, and the formal potential, $E°'$, for Fc/Fc$^+$ were measured as indicative of electron transfer rate. The formal potential, taken to be midway between the anodic and cathodic peaks, was measured at the point of minimum separation between the anodic and cathodic currents. This procedure, justified by the symmetry of the central region of the voltammograms, proved superior to estimating the potential of the poorly defined anodic peak. The resulting values established
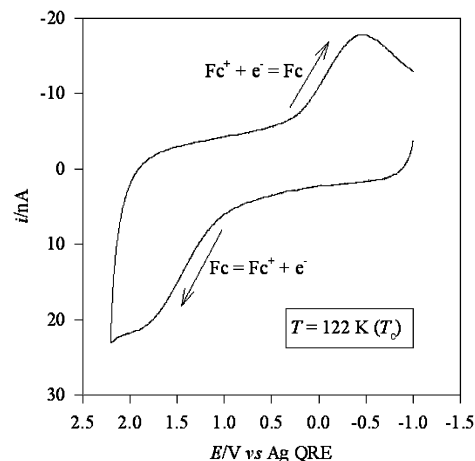

Fig. 1 Cyclic voltammogram of an electropolymerized film of pyrrole **1** on Tl,Pb$_{1223}$ in 2:1 chloroethane/butyronitrile, containing 0.1 M NBu$_4$BF$_4$, at 122 K (T_c); potential sweep rate 0.02 V s^{-1}.

the linear relationship between $E^{\mathrm{o}\prime}$ and temperature, hence allowing the calculation of $E_{\mathrm{pc}} - E^{\mathrm{o}\prime}$.

The apparently smooth variation (Fig. 2) through T_{c}, of both i_{pc} and $E_{\mathrm{pc}} - E^{\mathrm{o}\prime}$, shows that there is certainly no change in electron transfer rate at T_{c} comparable to that reported by Lorentz et al.[7] The two separate curves drawn for i_{pc} vs T, intersecting at 119 K, are attributed to a coincident, marked increase in the uncompensated solution resistance, as observed separately by ac impedance at a gold electrode.
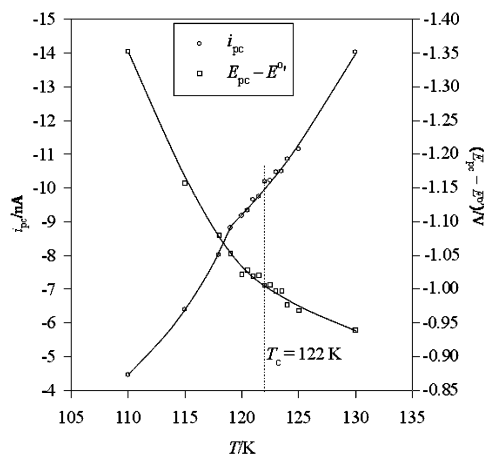
Fig. 2 Temperature dependence of i_{pc} and $E_{\mathrm{pc}} - E^{\mathrm{o}\prime}$.

However, the Arrhenius-type plot§ (Fig. 3) of $\ln[-i_{\mathrm{pc}}/\exp(E_{\mathrm{pc}} - E^{\mathrm{o}\prime})]$ vs 10^3 K/T provides tentative evidence for a more modest effect of superconductivity for this system. Digital simulation (DigiSim® 2.1, Bioanalytical Systems, Inc.) of voltammograms for 1-electron transfer at a metal electrode establishes that such a plot is in that case linear if the rates of both diffusion and electron transfer are assumed to be governed by equations of Arrhenius form, with constant pre-exponential and activation energy values. For the HTSC–polymer interface there is a definite change in slope at T_{c} (see figure inset) indicating a change in electron transfer rate and inviting further, more quantitative study. The discontinuity around 119 K is attributed to the previously mentioned increase in solution resistance.
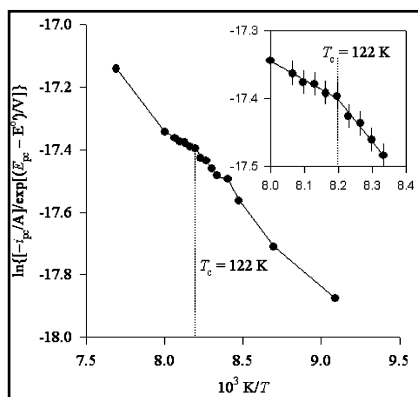

Fig. 3 Arrhenius-type plot of $\ln[-i_{\mathrm{pc}}/\exp(E_{\mathrm{pc}} - E^{\mathrm{o}\prime})]$; inset shows detail (with error bars) of region around T_{c}.

This is the first attempt at even semi-quantitative analysis of sub-T_{c} electron transfer at the interface between an HTSC and a redox-tagged polymer in a liquid electrolyte. If, at T_{c}, changes in the normal electron density-of-states function produce a change in the rate of transfer of these electrons, then this is the likely explanation of our observations for the Fc/Fc$^+$ reaction, since this is a simple 1-electron transfer. It is rather less certain whether this type of reaction at a polymer interface could accommodate the transfer of paired electrons, which may indeed then account for the rather larger effects observed by Lorentz et al.[7] Attention must now focus on the creation of further HTSC/polymer and other liquid–electrolyte interfaces incorporating a variety of 2-electron acceptors, in order to probe for the transfer of paired electrons.

Notes and references

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