

## 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 electron pairs responsible for superconduction and (usually) creation of an energy gap in the density-of-states function around the Fermi level for the remaining normal (unpaired) electrons. These changes are predicted to influence the rate constant for electron transfer between a superconductor and a redox-active species in an adjoining electrolyte,<sup>1–5</sup> because this is directly linked to the density of electronic states in the electrode.<sup>6</sup> For oxocuprate high-temperature superconductors (HTSCs), the effect of superconductivity on the rate constant for electron transfer at the HTSC/electrolyte interface is thus a novel probe of their electronic structure and hence the (as yet unknown) mechanism of their electron pairing and superconduction.<sup>5</sup>

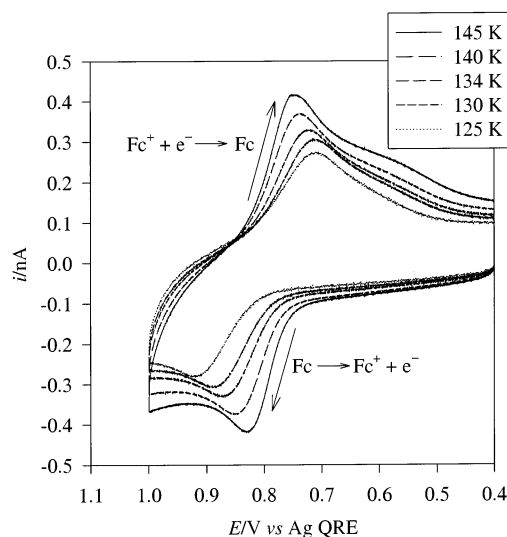
Previously, reactions studied at superconducting HTSC electrodes have been of redox-active species in solid electrolytes,<sup>7–9</sup> frozen glasses,<sup>10</sup> and liquid electrolytes, the last category including freely diffusing species,<sup>11,12</sup> the electrolyte itself,<sup>13</sup> and species tethered to the HTSC via an alkanethiol linker attached to a gold or silver underlayer.<sup>14</sup>

Lorentz et al.<sup>7</sup> reported increases in the electron-transfer rate, localized around  $T_c$ , at HTSC/solid-electrolyte interfaces with Ag/Ag<sup>+</sup> as the redox couple. Their interpretation of this as the participation of electron pairs in the electron-transfer event is, however, by no means certain. Such a response could in theory still arise if only normal electrons were transferred.<sup>4</sup>

The key to resolving this issue and to fully understanding the HTSC/electrolyte interface lies in using liquid rather than solid electrolytes, because liquids allow far greater freedom to select instructive reactions for study, ultimately including the reaction of two-electron acceptors to promote the transfer of electrons that are paired in the HTSC.

Although liquid electrolytes are available for use in the temperature range for HTSC superconductivity (100–135 K), allowing some promising preliminary investigations,<sup>11–14</sup> problems of high solution resistance and reactant insolubility are inevitable at the lowest temperatures. The first problem can be minimized by a combination of low currents, electronic resistance compensation, and the use of the higher  $T_c$  materials based on Tl and Hg. The second problem can be circumvented by attachment of the redox probe to the electrode. An attractive strategy is the self-assembly of alkanethiol monolayers onto HTSCs via an interposing silver or gold layer, thin enough to acquire the superconductivity of the HTSC via the proximity effect; the viability of this method has been demonstrated using Au (40 nm) and Ag (50 nm) films on a Tl-based HTSC ( $T_c = 119$  K).<sup>14</sup>

Here we present sub- $T_c$  electrochemistry of a self-assembled monolayer of CpFeCpCO<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>SH (CpFeCp = ferrocene) on an Hg-based HTSC (Hg<sub>0.8</sub>Re<sub>0.2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>;  $T_c = 134$  K) coated with



**Figure 1.** Temperature dependence of cyclic voltammetry of CpFeCpCO<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>SH/Ag/Hg-based HTSC ( $T_c = 134$  K) in 16:7:1 EtCl/THF/2-MeTHF, containing 0.2 M LiBF<sub>4</sub>; potential sweep rate 5 mV s<sup>-1</sup>.

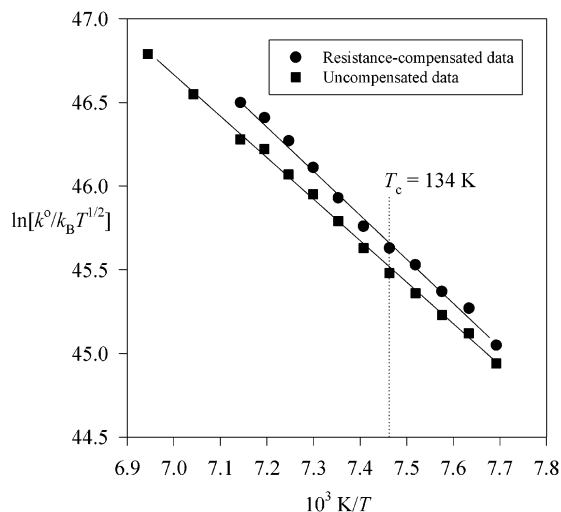
an ultrathin (3.1 nm) Ag layer. This is the first sub- $T_c$  electrochemistry of any kind on this material, which is the highest  $T_c$  superconductor known.

Using a high-vacuum sputter deposition instrument (Kurt J. Lesker Co.), we cleaned the epoxy-mounted HTSC electrode in an Ar plasma for 2 min at 20 W and then sputter coated it with 3.1 nm of Ag at a rate of 0.1 nm s<sup>-1</sup>. The Ag-coated electrode was then immersed for 30 min in a solution, of 1 mM total thiol concentration, composed of CpFeCpCO<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>SH (CpFeCp = ferrocene) diluted 3:1 with *n*-octylmercaptan, in dry ethanol. The resulting monolayer-covered electrode was then rinsed in ethanol, dried in flowing nitrogen, and placed in a purpose built three-electrode cell (Pt counter electrode, Ag quasi-reference electrode) housed within a cryostat (Janis model C21-TR with Lakeshore model 320 temperature controller). A dry, oxygen-free solution of 0.2 M LiBF<sub>4</sub> in 16:7:1 by volume EtCl/THF/2-MeTHF was introduced as the electrolyte, and the voltammetry of the monolayer was then recorded at a series of temperatures using a locally constructed potentiostat, with facility for positive feedback compensation of solution resistance. Figure 1 shows the resulting voltammograms, with well-defined peaks for the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) reaction.

The separation in potential of the anodic and cathodic peaks of the voltammograms depends on the standard heterogeneous rate constant  $k^0$  for the Fc/Fc<sup>+</sup> electron-transfer reaction, which in turn depends on the density of electronic states in the electrode. For the

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**Figure 2.** Arrhenius plot of  $k^\circ$  for Fc/Fc<sup>+</sup> reaction at the interface CpFeCpCO<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>SH/Ag/Hg-based HTSC ( $T_c = 134$  K) in 16:7:1 EtCl/THF/2-MeTHF, containing 0.2 M LiBF<sub>4</sub>.

transfer of a single electron, this is described by the Marcus density-of-states (MDOS) theory<sup>15,16</sup> as

$$k_{\text{red/ox}} = \mu\rho k_B T \int_{-\infty}^{\infty} \frac{\exp\left[-\left(x - \frac{\lambda \pm e_o \eta}{k_B T}\right)^2 \frac{k_B T}{4\lambda}\right]}{1 + \exp(x)} dx$$

where  $\mu$  relates to the strength of electronic coupling between electrode and redox species,  $\rho$  is the density of electronic states in the electrode,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $e_o$  is the electronic charge,  $\eta$  is the applied overpotential (difference between applied potential and formal electrode potential, which when zero gives  $k_{\text{ox}} = k_{\text{red}} = k^\circ$ ),  $\lambda$  is the reorganizational energy and represents the energy necessary to reorganize the solvent dipoles to accommodate the electron transfer, and  $x = \epsilon/k_B T$ , where  $\epsilon$  is the difference in energy between the transferring electron and the Fermi level of the electrode.

A computer simulation program was written (FORTRAN 77) to relate peak separation to  $k^\circ$  according to the MDOS theory and so allow construction of the Arrhenius plots, corrected as  $\ln[k^\circ/k_B T^{1/2}]$  for the effects of solvent dynamics,<sup>16</sup> shown in Figure 2. The results for both resistance-compensated and uncompensated data show no deviation from linearity around  $T_c$ , demonstrating that, for this system, there is no significant effect of superconductivity on the electron-transfer rate constant.

The resistance-compensated data were used to calculate a value of reorganizational energy for the reaction of  $\lambda = 0.92$  eV, plus a value of  $k^\circ(273 \text{ K}) = 357 \text{ s}^{-1}$ . For the same reaction at a bulk Au electrode (comparable to Ag) in a chloroethane/butyronitrile solvent, Richardson et al.<sup>16</sup> report  $\lambda = 0.95$  eV, plus a value of  $k^\circ(273 \text{ K}) = 4.1 \times 10^3 \text{ s}^{-1}$ . The key parameter is thus the value of

$k^\circ(273 \text{ K})$ , which is more than 10-fold lower for HTSC/Ag than for bulk Au. With similar reorganizational energies, this difference in  $k^\circ(273 \text{ K})$  must relate to the nature of the electrode material,<sup>17</sup> the influence of which is thus evident in this experiment, and yet there is no influence of the onset of superconductivity.

If a change at  $T_c$  in the normal electron density-of-states function were to produce a significant change in the rate of transfer of these electrons, then it would be observed for the Fc/Fc<sup>+</sup> reaction, a simple one-electron transfer. Less certain is whether this type of monolayer interface could accommodate the transfer of paired electrons. This is then a significant step in understanding the origin of any effects of superconductivity on related interfaces, suggesting that the rate enhancement noted by Lorentz et al.<sup>7</sup> may indeed be connected with the transfer of paired electrons. Attention must now focus on the creation of HTSC/liquid-electrolyte interfaces incorporating a variety of two-electron acceptors, to probe the transfer of paired electrons. This work, the first sub- $T_c$  electrochemistry on a Hg-based HTSC, shows the relative ease with which such data can be obtained for these very-high  $T_c$  materials.

**Acknowledgment.** We thank Professor R. W. Murray (Kenan Laboratories of Chemistry, University of North Carolina) for generously allowing the use of his laboratory facilities and for supplying all chemicals other than the HTSC itself. We also thank the University of Exeter for funding.

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JA034010M