Voltammetry of Self-Assembled Ferroceneoctanethiol Monolayers on Metal-Coated High-Temperature Superconductor Electrodes at Sub-T_c Temperatures

Stephen R. Peck,[†,‖] Larry S. Curtin,[‡,‖] Leonard M. Tender,[§,‖] Michael T. Carter,[‖] Roger H. Terrill,[‖] Royce W. Murray,*,[‖] James P. Collman,[⊥] William A. Little,[⊥] H. M. Duan,[▽] C. Dong,[▽] and A. M. Hermann[▽]

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, Department of Chemistry and Physics, Stanford University, Stanford, California 94305, and Department of Physics, University of Colorado, Boulder, Colorado 80309-0390

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Abstract: A scheme is described for measuring electron transfer kinetics between a surface-immobilized redox monolayer and a high temperature superconductor (HTSC) electrode at temperatures above and below the superconductor transition temperature T_c. The scheme depends on coating the HTSC electrode with an ultrathin metal film (Au, Ag) onto which redox monolayers of ferroceneoctanethiol with octanethiol diluent are co-chemisorbed by self-assembly. The ferrocene redox moiety is separated from the metal film/HTSC by an alkane chain tunneling barrier. Cyclic voltammetry and potential step electron transfer rate measurements are given for monolayer coated HTSC/Au film and HTSC/Ag film electrodes at temperatures above and below the 119 K T_c of the $Tl_2Ba_2CaCu_2O_8$ (Tl_{2212}) superconductor employed as the HTSC/metal electrode. The ferrocene monolayers display well-defined voltammetry down to 105 K. While the electron transfer rate measurements are estimates only, the voltammetry and rate measurements are the first of their kind for a molecular monolayer on an electrode in the superconducting state. The results will guide adjustment of the alkane chain tunneling barrier to a length appropriate for slower and more accurate electron transfer rate measurements, even at applied overpotentials large enough to reduce the electron transfer barrier to values smaller than the electron-pairing energy.

Following the discoveries[1,2] of high-temperature superconductor (HTSC) materials, several laboratories[3−6] have explored chemical aspects of HTSC interfaces with chemical materials

that are in the "normal" conducting state. Lorenz and co-workers[3] have observed changes in the electrochemical reaction impedance of the Ag^+/Ag couple at a solid electrolyte/HTSC electrode interface as the experimental temperature crosses the superconducting transition temperature T_c. McDevitt et al.[4] have observed T_c-related effects in optical absorptions of dye-coated HTSC films and in their contact resistances with conducting polymers. Our own research has produced a binary fluid electrolyte solution,[5] ethyl chloride and butyronitrile (EtCl/PrCN) containing Bu_4NClO_4, in which voltammetry at a metal microband electrode was conducted at temperatures down to 88 K. Using this fluid electrolyte, we observed[6] T_c-correlated changes in the electrochemical double layer capacitance of two different HTSC electrode compositions and less well T_c-correlated changes in solvent reduction electrode kinetics. Observation[6] of the T_c-correlated double-layer capacitance effect and of an unchanged (*ex situ*) T_c following electrochemical experimentation demonstrated that the superconducting property of the HTSC was not destroyed upon contact with the electrolyte solution or by use as an electrode. More recently, Green et al[7] have described sub-T_c cyclic voltammetry in an ethyl chloride/tetrahydrofuran fluid electrolyte solution of ferrocene at HTSC electrodes. While no kinetic assessment was made, a plot of voltammetric peak currents *vs* temperature revealed no special effect at T_c. No other electrochemical observations[6,7] at

‖ University of North Carolina.

⊥ Stanford University.

▽ University of Colorado.

† Present address: E. I. du Pont de Nemours & Co., P.O. Box 1217, Parkersburg, WV 26102.

‡ Present address: Department of Chemistry, Temple University, Philadelphia, PA 19122.

§ Present address: Department of Chemistry, Stanford University, Stanford, CA 94305.

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superconducting electrodes contacting fluid molecular media are available.

This report presents a scheme that will facilitate quantitative measurements of electron transfer kinetics at HTSC electrodes in fluid electrolytes for temperatures crossing T_c. The objective is to open a way to explore whether electron transfer kinetics involving delivery of electrons from a superconducting electrode exhibit any special features, such as involvement of *paired* electrons in electron transfer reactions. The initial but essential aspect of any electrode kinetic scheme suitable for sub-T_c experimentation is to identify a reaction with a rate amenable to practical, quantitative measurements at low temperatures. The constraints are substantial: (a) Low-temperature fluid electrolytes,[5,7] including the EtCl/PrCN system, are ionically resistive, a property which is incompatible with accurate measurement of very fast electrode kinetics. The selected reactions must exhibit slow rates, which must furthermore remain slow enough to be measurable even when large overpotentials (*vide infra*) are applied. (b) Guiding data on metal electrode kinetics at the necessary temperatures (e.g., 110—130 K) do not exist, nor do (c) data on solubilities and diffusivity of electroactive solutes at such temperatures.

The present work offers a solution to this needle-in-a-haystack problem by using monolayers of electroactive species chemisorbed or tethered at the HTSC interface. Immobilizing the reactant removes uncertainties of the temperature dependencies of its solubility and diffusivity. Secondly, the scheme imposes a tunneling barrier between the HTSC electrode and attached reactant. By adjusting the size of the tunneling barrier (by the design of the chemisorbed molecule, such as the length of an alkane chain barrier) the electron transfer rate can be slowed into a range of values that are conveniently measurable in spite of the resistive nature of the electrolyte medium.

Two approaches to tethering electron donor/acceptor groups at HTSC electrode surfaces are illustrated in Figure 1. In Figure 1A, the electroactive moiety is covalently attached directly to the ceramic copper oxide superconductor surface, using oxide-reactive chemistry, such as siloxane, metal—oxo, or phosphate linkages.[9] This approach requires that the chemical modification involve only the outermost HTSC oxide layer and that the superconducting properties of the electrode are preserved out to its surface. This scheme has not yet been explored.

The second scheme, Figure 1B, is illustrated in this paper. This scheme was inspired by recent descriptions by Chidsey[10] and Finklea et al.[11] of the electron transfer kinetics of electroactive alkanethiol monolayers on gold electrodes in aqueous media at near-ambient temperatures. We recognized that the alkane chain length would serve as an adjustable tunneling barrier (*vide supra*) and accordingly launched an investigation[12] of the low-temperature voltammetry of ferrocenealkanethiols chemisorbed on gold and silver metal electrodes and of the

A

B

M = Au, Ag, Cu
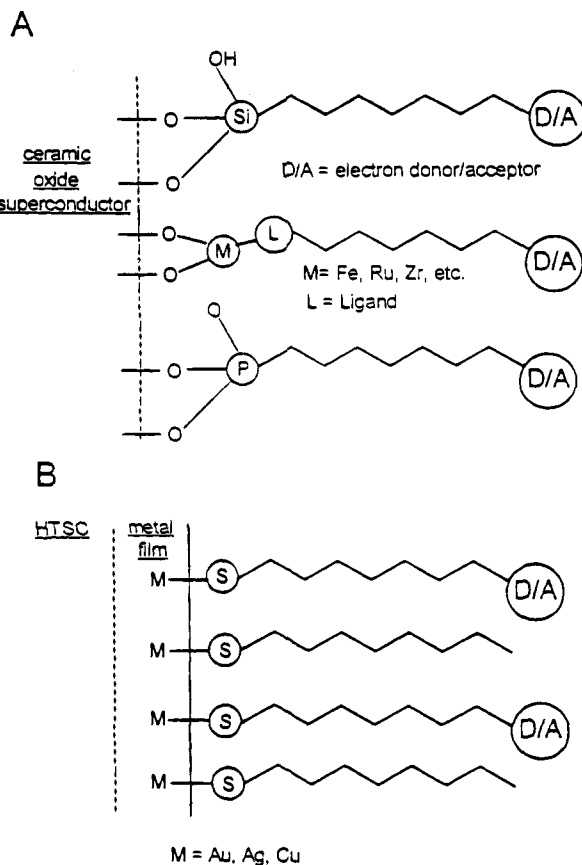
Figure 1. Strategies for tethering electron donor/acceptor species to the surfaces of HTSC electrodes. (A) Derivatization of the oxide surface with siloxane, metal—oxo, and phosphate. (B) Chemisorption of self-assembled monolayer of D/A—alkanethiol, diluted with alkanethiol, to the thin Ag or Au film that coats the HTSC.

techniques and data analysis[13] needed to obtain reliable ferrocene[+/0] electron transfer rate constants ($k°$) in the face of large solvent resistivities. Reorganizational barrier energies close to classical dielectric continuum model predictions were obtained[13] from the temperature dependencies of $k°$ for C-8, C-12, and C-16 ferrocene alkanethiols, and $k°$ varied exponentially[13] with alkane chain length as expected. Ferrocenealkanethiol monolayers appear to have the hoped-for characteristics of a readily adjustable tunneling barrier in the low-temperature organic solvent. In the present paper, we explore the scheme of Figure 1B in the fluid electrolyte[5] 2:1 v/v EtCl/PrCN/0.075 M Bu₄NPF₆ with Tl₂Ba₂CaCu₂O₈ (Tl₂₂₁₂) super-conductor[14] electrodes ($T_c = 119$ K) coated with thin gold and silver films, on which are chemisorbed self-assembled mixed[13b,15] monolayers of octanethiol and ferroceneoctanethiol (e.g., $CH_3(CH_2)_7SH/CpFeCp(CH_2)_8SH$). We will describe cyclic voltammetry and estimates of electron transfer rates of the ferroceneoctanethiol monolayers at temperatures above and below (down to 105 K) the 119 K T_c of the metal-coated superconductor. Neither the chain length of the C-8 alkanethiol

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barrier selected nor the experimental protocol to avoid solution resistance effects proved to be optimal, so the $k°$ measurements are estimates only. The primary intent was to introduce the tunneling scheme of Figure 1B and to demonstrate the general feasibility of measuring electron transfer rate constants for electroactive monolayers on metal-coated HTSC electrodes.

An important aspect of the scheme in Figure 1B involves what is known as the proximity effect. For a "conventional" (low-temperature) superconductor in good electrical contact with a metallic conductor, the leakage of electron pairs from the superconductor to the normal conductor results in the acquisition[16] of superconductor properties by the non-superconducting phase. This superconductor "proximity effect" has been investigated[17] for (high-temperature) ceramic copper oxide superconductors as well. The scheme of Figure 1B aims at invoking the proximity effect through an ultrathin Au or Ag layer and through the self-assembled, molecular tunneling layer. This part of the scheme is not demonstrated in this paper and remains for future experiments to explore. In particular, the transmission of electron pairs should be most effective for very thin metal films.[17] However, no attempt was made to minimize metal film thickness in the present work.

Yet another aspect of using the tunneling barrier of the scheme of Figure 1B appears in view of a recent theoretical analysis[8] suggesting that paired-electron transfers at superconducting electrode surfaces may be very inefficient. Among the conceptual difficulties in sub-T_c electrochemistry is thermalizing of the electron pair in crossing an activation barrier of energy that is much greater than the electron pairing energy. In this light, study of the reaction as an *activationless* process is a useful situation. An activationless reaction is achieved by application of an overpotential equal to or larger than the reaction's reorganizational barrier.[10,11] Ordinarily, the use of such large overpotentials would increase the rate of a facile (outer-sphere) electrode reaction to inaccessibly large values; the presence of an appropriately chosen tunneling barrier, however, should retard the rates of even such high overpotential experiments into experimentally measurable ranges.

Experimental Section

Chemicals. A sintered pellet whose X-ray diffraction pattern indicated roughly equal proportions of $Tl_2Ba_2CaCu_2O_8$ (Tl_{2212}) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl_{2223}) phases was prepared at the University of Colorado by a literature method.[14] Four-point probe resistivity measurements gave a zero-resistance T_c of 119 K. For simplicity we label this sample as Tl_{2212}. $CpFeCp(CH_2)_8SH$, a generous gift,[18] octanethiol (Aldrich, >97%), butyronitrile (PrCN, Aldrich, 99+%), absolute ethanol (AAPER Alcohol and Chemical Co.), and silver trifluoromethanesulfonate (Fluka, Purum grade) were used as received. Tetra-*n*-Butylammonium hexafluorophosphate (Bu_4NPF_6, Fluka, Puriss grade) was recrystallized twice from methanol. Chloroethane (EtCl, Linde) was condensed into a Schlenk tube and stored at room temperature. Water was purified ($R > 18$ MΩ) via a Barnstead NANOpure system. Gold (99.99%) and silver shot (99.9999%) were used as sources for the vapor-deposited thin metal films. Acetonitrile (Burdick and Jackson) was stored over 4 Å molecular sieves.

Electrode Fabrication. Working electrodes were prepared by cleaving a sintered pellet of Tl_{2212} into *ca.* 2 mm blocks with a razor blade. A Teflon-shrouded silver-coated copper wire was attached to the HTSC block via a *ca.* 0.3 μm thick evaporated (Key Vacuum Products, Model KV-301) silver pad with silver solder (Kester), reinforced with a bead of silver epoxy (Epoxy Technology Inc., epo-Tek H2OE) and cured overnight at 70 °C. The superconductor working electrode and a 0.5 mm diameter silver wire (quasi-reference electrode) were potted in an evacuated cylindrical mold with an insulating epoxy (Shell EPON 828, *m*-phenylenediamine curing agent, cured overnight at 70 °C). The end of the 6 mm diameter, *ca.* 5 cm long epoxy-encapsulated electrode assembly was sanded (Buehler 600 grit) to expose the superconductor working and Ag reference electrodes. Four-point resistivity measurements have shown[6] that performing electrochemical measurements with HTSC electrodes prepared in this manner does not alter their zero-resistance T_c values.

Metal Film/HTSC Electrode Preparation. The Tl_{2212} electrodes were metal-coated by two different methods. In one, the exposed superconductor was sanded (Buehler 600 grit) and sonicated in acetone for 1 min, and its surface was cleaved by a razor blade immediately prior to evaporation of 150−500 Å of Au or Ag at *ca.* 1 Å/s on the electrode face. Alternatively, a 190 nm thick (average) Ag film was electrodeposited at −0.5 V *vs* Ag wire from a degassed 1 mM $AgCF_3$-SO_3 solution in CH_3CN (0.1 M Bu_4NPF_6) onto a freshly sanded (Buehler 2000 grit) Tl_{2212} electrode. The electrode was removed from solution and rinsed with degassed ethanol before disconnection from the potentiostat. The electrodeposited Ag film was found to be highly dendritic by optical microscopy, indicating a strongly crystalline structure.

Chemisorbed Monolayer Preparation. Stock solutions (1 mM in ethanol) of ferroceneoctanethiol and *n*-octanethiol were mixed[15] in 1:1 or 1:5 v/v ratios to produce the coating solutions. For evaporated gold coated HTSC electrodes, monolayers were formed by exposing the electrode assembly to a stirred coating solution for *ca.* 15 h; silver coated electrodes were exposed for 30 min for electrodeposited silver and 16 h for evaporated films.[19] All thiol chemisorptions were done immediately after metal film deposition. After thorough rinsing with ethanol, the thiol-coated evaporated gold or silver film was carefully scraped from the Ag reference electrode and the epoxy surrounding the HTSC working electrode, and the electrode assembly was rinsed with butyronitrile before being placed it in the electrochemical cell.

Electrochemical Measurements. The HTSC/metal film and reference electrode assembly was fitted into a stainless steel cylinder, the bottom of which served as the counter electrode separated by *ca.* 0.5 mm from the HTSC working electrode to minimize uncompensated solution resistance. The cylinder was placed in the chilled electrolyte solution (0.075−0.15 M Bu_4NPF_6 in 2:1 (v/v) EtCl/PrCN, prepared as previously described)[5,6] in the electrochemical cell and brought to the desired temperature (±0.5 K) in a liquid nitrogen cryostat (Janis Model 6CND-NVT, Lakeshore Model 805 temperature controller). Cyclic voltammetry and chronoamperometry were performed with a potentiostat of local construction and a PAR Model 175 universal programmer. Transient currents were captured with a digital storage oscilloscope (Nicolet Model 310); a digital filter[20] of local design removed 60 Hz (and higher-order harmonic) noise. The quantity of electroactive ferrocene in the monolayer was measured by integration of the reduction branch of a slow potential scan cyclic voltammogram taken at low temperature.

Typically, the cell was cooled to below *ca.* 180 K before voltammetric scans were initiated because we know[12] that ferrocenealkanethiol monolayers are exceptionally stable at this and lower temperatures. Electrode kinetics were estimated by comparing experimental ΔE_{peak} values to calculations of cyclic voltammogram properties based on Marcus theory, as described elsewhere.[21] Electrode kinetics were in some cases estimated using potential steps initiated at $E°$; the current

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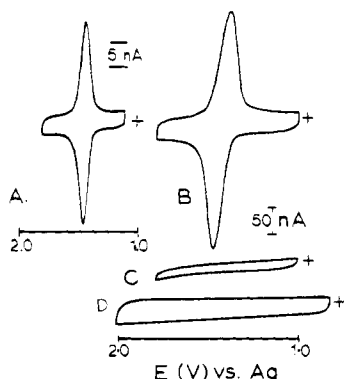
Figure 2. Curve A (5 mV/s; ΔE_{peak} = 20 mV) and curve B (50 mV/s; ΔE_{peak} = 100 mV): cyclic voltammetry at 140 K of a ferroceneoctanethiol monolayer (Γ = 9.8 × 10^{-11} mol/cm²) chemisorbed on 400 Å Au film on a Tl₂₂₁₂ HTSC electrode in 2:1 v/v EtCl/PrCN/0.075 M Bu₄NPF₆. Chemisorption from 0.17 mM ferroceneoctanethiol, 0.83 mM octanethiol in ethanol, 14 h. Curve C (control experiment): cyclic voltammetry (50 mV/s, 140 K) of a HTSC electrode prepared in the same manner but lacking the Au film. Curve D: cyclic voltammetry of a freshly cleaved HTSC electrode (140 K).

vs time transients were of 10−20 s duration and were corrected for background currents using potential steps in the featureless double-layer region at potentials more negative than the ferrocene$^{+/0}$ couple. As discussed below, the electrode kinetic measurements should be regarded as estimates only because of uncompensated resistance effects.

Results and Discussion

Voltammetry at Gold-Coated Tl₂₂₁₂ Electrodes. Octanethiol-diluted ferroceneoctanethiol chemisorbed on a gold-coated Tl₂₂₁₂ electrode exhibits at 140 K voltammetry typical of a surface-immobilized species, Figure 2A,B. At small potential scan rates the peak currents are linearly proportional to scan rates. Qualitatively, the voltammograms are comparable to those previously reported for self-assembled[10−13,15] monolayers and are well-defined, even though the surface of the cleaved, somewhat porous HTSC, with its evaporated Au layer, is macroscopically rough.[6,22] Voltammetry like that in Figure 2A,B can be observed for many hours, with a stability comparable to that seen on bulk Au metal electrodes.[12,13] No significance should be attached to the positive value of the apparent potential since the Ag wire pseudo reference potential shifts upon cooling, as we reported before.[12]

Figure 2C shows voltammetry of another Tl₂₂₁₂ electrode, freshly cleaved but *not* coated with evaporated Au, after exposure to a ferroceneoctanethiol coating solution. The absence of a ferrocene response and the appearance of only double layer charging current show that voltammetry like that in Figure 2A is attributable only to gold-chemisorbed ferrocene. That the ferrocene-tagged alkanethiol does not stably chemisorb on a naked HTSC surface means that, ultimately, extremely thin evaporated or electrodeposited metal films and islands can be employed without concern about complete coverage of the HTSC surface by the metal film. Figure 2D shows voltammetry of a naked, freshly cleaved Tl₂₂₁₂ electrode, which is also featureless, with somewhat larger capacitive currents.

Figure 3 shows voltammograms for another ferroceneoctanethiol monolayer on a 400 Å gold-coated Tl₂₂₁₂ electrode at temperatures spanning the 119 K superconducting transition
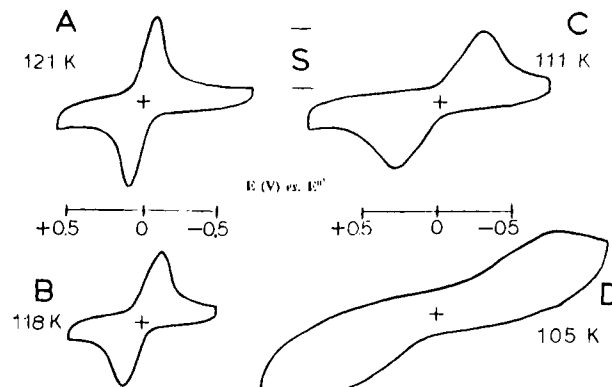
Figure 3. Curve A (121 K; ΔE_{peak} = 156 mV; 5 mV/s; S = 10 nA), curve B (118; ΔE_{peak} = 252 mV; 5 mV/s; S = 10 nA), curve C (111 K; ΔE_{peak} = 564 mV; 2 mV/s; S = 2 nA), and curve D (105 K; ΔE_{peak} = 1.62V; 2 mV/s; S = 0.5 nA): cyclic voltammetry of a ferroceneoctanethiol monolayer (Γ = 9.8 × 10^{-11} mol/cm² from charge under wave at 140 K) on 400 Å Au film on a Tl₂₂₁₂ HTSC electrode in 2:1 v/v EtCl/PrCN/0.075 M Bu₄NPF₆.

temperature T_c of the Tl₂₂₁₂ electrode. The peaks for ferrocene oxidation and reduction become progressively separated and broadened as the temperature is lowered, but a faradaic current can still be discerned above background at temperatures as low as 105 K. *These results show that surface-confined voltammetry can be observed at temperatures sufficiently low that the HTSC electrode underlying the metal film is in the superconducting state.* They also represent the lowest temperature at which voltammetry has been achieved for any molecular monolayer.

The peak potential separations (ΔE_{peak}) in the voltammetry of Figures 2 and 3 can be used to estimate the standard rate constants (k°) for electron transfers between the HTSC/Au electrode and the ferrocene sites. The ΔE_{peak} values increase with decreasing temperature and with increasing potential scan rates, as would be expected for control by slow electron transfer kinetics.[23,24] ΔE_{peak} increases can also originate, on the other hand, from potentiostatically uncompensated resistance in the electrolyte solution (iR_{unc}). Therefore the rate constants (k°) must be regarded as only lower limit estimates, with uncertainties as noted below.

k° values were estimated with theory based on the Marcus equation[25] with consideration of the distribution of electronic states in the electrode about the Fermi level. Voltammograms were simulated from this theory, more fully described elsewhere,[21] to produce working plots of ΔE_{peak} values as functions of k°. The calculations are analogous to theory presented by Chidsey[10] and Finklea et al.[11] for potential step experiments, and, for the case of overpotentials that are small in relation to the reorganizational energy, are identical to the Butler−Volmer-based theory of Laviron.[24] For the data in Figures 2 and 3 and another experiment at 124 K (not shown, ΔE_{peak} = 100 mV at 5 mV/s), the estimates[26] at the indicated temperatures are as follows: k° = 0.35 s^{-1} (140 K); 0.025 s^{-1} (124 K); 0.007 s^{-1} (121 K); 0.0008 s^{-1} (118 K). Other experiments[13b] in this laboratory with ferroceneoctanethiol chemisorbed on etched bulk electrodes, when using no other tools than those mentioned

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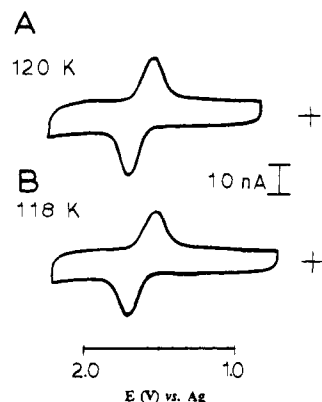
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Figure 4. Curve A (120 K; ΔE_{peak} = 164 mV; 10 mV/s) and curve B (118 K; ΔE_{peak} = 192 mV; 10 mV/s): cyclic voltammetry of a ferroceneoctanethiol monolayer (Γ = 0.45 × 10^{-11} mol/cm²) on evaporated 500 Å Ag film on a Tl$_{2212}$ HTSC electrode in 2:1 v/v EtCl/PrCN/0.15 M Bu$_4$NPF$_6$. Chemisorption from 0.5 mM ferroceneoctanethiol, 0.5 mM octanethiol in ethanol, 16 h. Unlike this result, long chemisorption times often produce poorly defined voltammetry, probably owing to Ag film corrosion.

above (relatively small electrodes, slow potential scan rates, and a small cell spacing) to suppress iR_{unc} effects, produce[13b] similar rate constants, $k°$ = 0.4—0.8 s^{-1} at 140 K and 0.03 s^{-1} at 124 K; but when instrumental positive feedback[23,27] was used to suppress iR_{unc}, larger values were produced[13b], $k°$ = 2 s^{-1} (140 K) and 0.2 s^{-1} (125 K) which we believe to be little affected by uncompensated resistance. It appears that the iR_{unc} effect depresses $k°$ values at 140 K and 124 K by *ca.* 3- and 7-fold, respectively, on bulk Au electrodes; so the above results on the HTSC/Au electrodes are almost certainly too small by similar factors at 140 and 124 K, and by larger factors at lower temperatures. These rate data, while the first of their kind, must be regarded as rough lower limit estimates only.

Voltammetry and Potential Steps at Silver-Coated Tl$_{2212}$ Electrodes. We have also investigated the electrochemistry of octanethiol-diluted ferroceneoctanethiol monolayers on silver-coated Tl$_{2212}$ electrodes. Silver films also offer the possibility of a superconductor proximity effect, as exemplified by the work of Holcomb et al.[17b,e]

Cyclic voltammetry of ferroceneoctanethiol chemisorbed on Ag-coated Tl$_{2212}$ electrodes is as well-defined as that on Au/HTSC, including voltammetry at sub-T_c temperatures. Figure 4 shows voltammetry at 120 and 118 K, just above and below T_c.[28]

Potential step experiments can also be used for determination of electron transfer rate constants of self-assembled electroactive monolayers, as described by Chidsey[10] and Finklea et al.,[11] by plotting the current—time transients as first—order reactions, i.e.,

(27) (a) Positive feedback compensation is a well-known technique[23] to electronically compensate for the ohmic potential loss not compensated for by the three-electrode potentiostat (iR_{unc}). It can be expected that the electronic compensation is always less than 100% of R_{unc}, and this technique is not regarded as efficacious in measuring $k°$ on fast time scales for nearly reversible couples.[28b] In the referred-to experiments,[13] R_{unc} is large, typically between 1 × 10⁶ to 1 × 10⁵ ohms for T = 125—150 K as measured by AC impedance and instrumentally during positive feedback compensation experiments. With monolayer quantities of reactants and at low temperatures, however, the currents flowing are quite small, and the electron transfer rates are so slow that cyclic voltammetric ΔE_{peak} values are large even at modest potential scan rates (i.e., Figure 3). The result is that the portion of iR_{unc} that is not electronically compensated by the positive feedback is small or insignificant in comparison to the kinetically induced ΔE_{peak} value, and values of $k°$ deduced[21] from experimental ΔE_{peak} values are constant over a range of potential sweep rates, which is a classical signal that iR_{unc} effects are not important. (b) Milner, D.; Weaver, M. J. *J. Electroanal. Chem.* **1985**, *191*, 411.
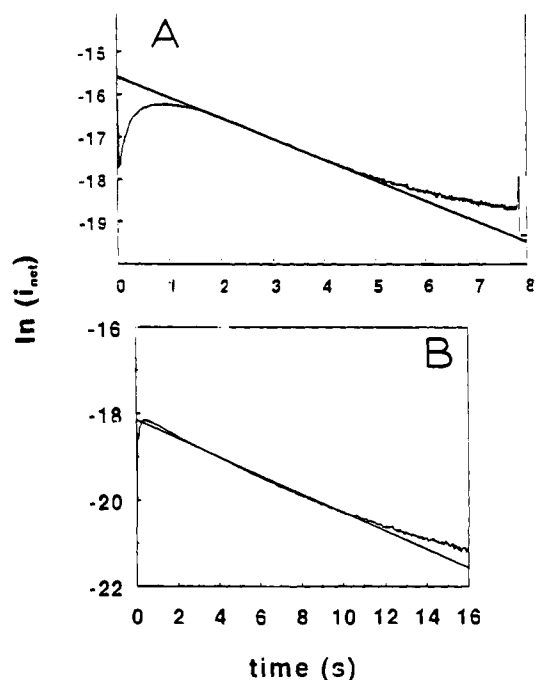
Figure 5. Curve A (124 K) and curve B (118 K): current—time response to potential step from $E°'$ (average of E_{peak} values) to n = −100 mV, for ferroceneoctanethiol monolayer chemisorbed as in Figure 4 onto the Ag film on a Tl$_{2212}$ HTSC electrode. In A, 190 nm Ag film was electrodeposited; in B 500 Å Ag film was evaporated. Currents, corrected for background, plotted as first-order decays give from the slopes $k_{app,-100}$ = 0.5 s^{-1} for A and 0.25 s^{-1} for B.

$\ln[i]$ *vs* time plots. We have carried out preliminary potential step experiments on Ag-coated Tl$_{2212}$ electrodes at temperatures above and below the 119 K HTSC T_c, as shown in Figure 5 for −100 mV reductive overpotential steps. The plots exhibit a mild curvature indicating that the reaction gradually slows as ferrocenium is reduced. The kinetic dispersion (nonuniformity) among the surface ferrocene population may reflect real differences in their reaction rate constants, as would arise through "defect sites",[10,11,15] or only apparent ones, as would arise from a distribution of ferrocene formal potentials.[29] Curved $\ln[i]$ *vs* time plots have been reported by Finklea et al.,[11] and are seen in our experiments on bulk metal electrodes[13] at low temperatures in the EtCl/PrCN solvent.

The charge passed during the roughly linear portions of the Figure 5 plots (see line) represents reduction of *ca.* 50% of the ferrocenium sites initially present at $E°'$, and the slope of the plot gives an average rate constant for this portion of the surface population. The rate constants k_{-100} obtained at 120 and 118 K are respectively 0.5 and 0.25 s^{-1}. Table 1 shows rate constants similarly obtained at other overpotentials at 118 K in the same experiment, which when plotted and extrapolated to zero overpotential give an estimate at the sub-T_c 118 K temperature of $k°$ = 0.05 s^{-1}. This rate constant is considerably larger than that obtained at 118 K and with incomplete resistance compensation on a HTSC/Au surface (0.0008 s^{-1}, *vide supra*),

(28) It would not be possible to observe the Figure 4 voltammetry at room temperature since the thermodynamic oxidation potentials for Ag metal and ferrocene are similar, obscuring voltammetry[13] at temperatures above 180 K. At the temperatures of Figure 4, however, the kinetics of Ag oxidation are more thermally quenched than are those of ferrocene oxidation. Nonetheless, we (conservatively) restrict the positive potential scan limit in voltammetric experiments, to avoid possible erosion of the Ag film with consequent damage to the monolayer. For the same reason, potential step experiments are conducted by stepping from $E°'$ only to more negative potentials.

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Table 1. Potential Step Rate Constants Obtained at 118 K (as in Figure 5B) for CpFeCp(CH₂)₈SH Chemisorbed on Evaporated Silver Coated Tl₂₂₁₂ (T_c = 119 K)

η (mV, vs $E^{\circ\prime}$)	k_{app} (s⁻¹)—	η (mV, vs $E^{\circ\prime}$)	k_{app} (s⁻¹)—
20	0.12	−100	0.29
−40	0.14	−125	0.41
−60	0.16	−150	0.46
−80	0.21		

but is in good agreement with results[13b] (0.07 s⁻¹ at 120 K) for octanethiol monolayers on bulk Au electrodes where proper positive feedback resistance compensation has been applied.

The Ag film in Figure 5B deposited on the Tl₂₂₁₂ HTSC was an evaporated film, while that in Figure 5A was electrochemically deposited by Ag⁺ reduction from anhydrous acetonitrile solution. Electrochemical deposition should allow growth of Ag films that both are very thin and have a high degree of crystallinity, properties which should be conducive to operation of a proximity effect at sub-T_c temperatures.

Conclusions

The above experiments demonstrate several aspects of Figure 1, scheme B. The results show that thin Au and Ag films deposited on Tl₂₂₁₂ HTSC, firstly, are stable and tolerant to exposure to a low-temperature organic electrolyte, secondly, they are stable to chemisorption and voltammetric redox-cycling of ferroceneoctanethiol monolayers, and thirdly, they retain a reasonably ohmic contact to the HTSC under these circumstances. The results also show, fourthly, that ferrocene can be stably attached to the HTSC/metal film interface with an alkane chain tunneling barrier. This is important in that manipulation of the alkane chain length makes it possible to retard the ferrocene electron transfer rates into ranges convenient for accurate measurements more devoid of uncompensated resistance effects than those above. It is also significant, as discussed above, that the electron transfer kinetics be slowed enough to allow measurements at overpotentials that equal the reorganizational barrier energy (λ) value for ferrocene electron transfers, as near-activationless reactions. On the basis of ongoing low-temperature experiments[13a,c] with other ferrocenealkanethiols, a chain length much longer than the present C-8, perhaps of order C-18 or longer, will be desirable for the above purpose. Finally, we have shown that well-defined voltammetry could be obtained down to at least 105 K, well below the superconducting transition temperature of the HTSC electrode underlying the thin metal film and attached molecular monolayer. The first (albeit approximate) measurement of monolayer electrode kinetics has been made using an electrode containing a HTSC component in a fluid electrolyte medium at sub-T_c temperatures.