A new probe of superconductivity: quantitative measurements on defined electron transfer with solute at the interface between liquid electrolyte and oxocuprate electrode in the superconducting state

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The rate of electron transfer, between dissolved decamethylferrocene molecules and an oxocuprate high temperature superconductor [Tl 1223] electrode, represented in impedance spectroscopy by an electrical resistance term R_{CT}, is shown to be measurable (R_{CT} tending to dip around the superconducting transition temperature), so opening up the prospect of a new, controllably variable, probe of superconductivity.

There are now oxocuprate high-temperature superconductors (HTSCs) having superconducting transition temperatures T_c of 135 K.[1] Superconductivity at even higher temperatures would significantly enhance technological applicability. The resistanceless current in a superconductor is carried by paired charge carriers which form below T_c, usually together with an energy gap around the Fermi level in the density of states. Despite protracted efforts, the mechanism of oxocuprate HTSC superconductivity is not well understood.[2] Linking an understanding of the pairing mechanism to the oxocuprate structure clearly presents the most promising route to maximizing T_c by design; here we suggest a novel probe towards that goal, monitoring the rates of electron transfer directly to or from the HTSC at and about its T_c.

A liquid electrolyte (chloroethane with tetrahydrofuran and 2-methyltetrahydrofuran, plus a lithium salt electrolyte) is now available[3–6] in which the electron-transfer reactions of freely diffusing electroactive species, here ferrocene or decamethylferrocene, at macrosized Pt electrodes could be followed by cyclic voltammetry at temperatures as low as 99.5 K.[5] Next, at specially designed cryorobust HTSC electrodes[6] (including leads for the *in situ* determination, by a four-point resistivity measurement[6] on the electrode in use, of its superconducting transition temperature), charge transfer between freely diffusing ferrocene and a demonstrably superconducting HTSC microelectrode at 102 K could be clearly detected by cyclic voltammetry.[5] Now we have studied by impedance spectroscopy the temperature dependence of the charge-transfer rate (proportional to the charge-transfer conductance $R_{CT}{}^{-1}$), and report here our observations on electron transfer between decamethylferrocene and the HTSC Tl 1223 electrode comprising the recently synthesized[7] $(Tl_{0.5}Pb_{0.5})(Sr_{1.6}Ca_{0.4})Ca_2Cu_3O_9$.‡

The equipment has been described in detail.[6] The precise value of T_c for the Tl 1223 was determined by magnetic susceptibility (Fig. 1). The behaviour of an electrode/electrolyte interface can be represented§ by R_{CT} (inversely proportional to charge-transfer rate), and (in parallel) the parameter C_{eff} which approximates to the double layer capacitance; it can thus be examined by electrochemical impedance studies together with standard procedures§ for fitting the equivalent circuit elements. The variation of R_{CT} and C_{eff} with temperature, through T_c, is shown in Fig. 2 (together with a notional time-constant $R_{CT} \times C_{eff}$, and the parameter§ Φ) where increases or decreases from otherwise smooth curvature occur when the sample traverses T_c. Excursions from smooth curves in the temperature range about T_c have been repeatedly observed[8] for these parameters in solid-state electrochemical reductions of Ag^+ with an electrolyte of solid Rb_4AgI_5, and also for an oxocuprate electrode immersed in liquid electrolyte when the solvent itself has been reduced,[9] though a decrease rather than an increase in their capacitance parameters has been observed in these related systems. The limited amount of experimental data available has left interpretation of the HTSC transitions speculative apart from Kuznetzov's theory[2,10] and a recent primitive elaboration[11] of the Ginsburg–Landau SC model which effects a decrease in double-layer capacitance on temperature increase up to T_c. Gluzman and Kuznetzov[2] were able to account for the generally observed[8,9] 'hump' in the charge transfer rate around T_c without the participation of paired carriers (disfavoured by increased reorganisation energy of electrolyte[10]),¶ in contradiction of Lorenz *et al.*[8] who assign the increase in the Faradaic current around T_c to paired charge carriers. Lorenz *et al.*[8] do point out that the smaller electrolyte reorganisation energy in solids *cf.* liquids makes pair transfer more likely in their systems than in liquids, with the implication that no excursions from smooth curvature, or 'humps', should occur with liquid electrolytes. Without inflicting excessive violence on our results, excising extreme data points could just accommodate nil excursions from smooth curves (points × in Fig. 2), but such a conclusion can be settled only by further, improved, experiments. However, the major advance represented by our preliminary observations lies in demonstrating the accessibility of choice of

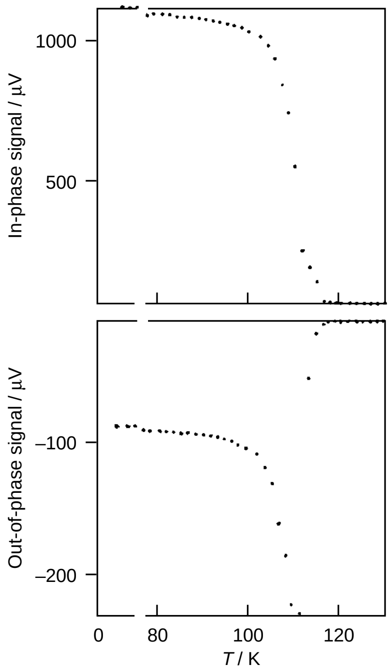

Fig. 1 Magnetic susceptibility measurements on Tl 1223 as in-phase and out-of-phase magnetometer signals showing T_c at 116 K

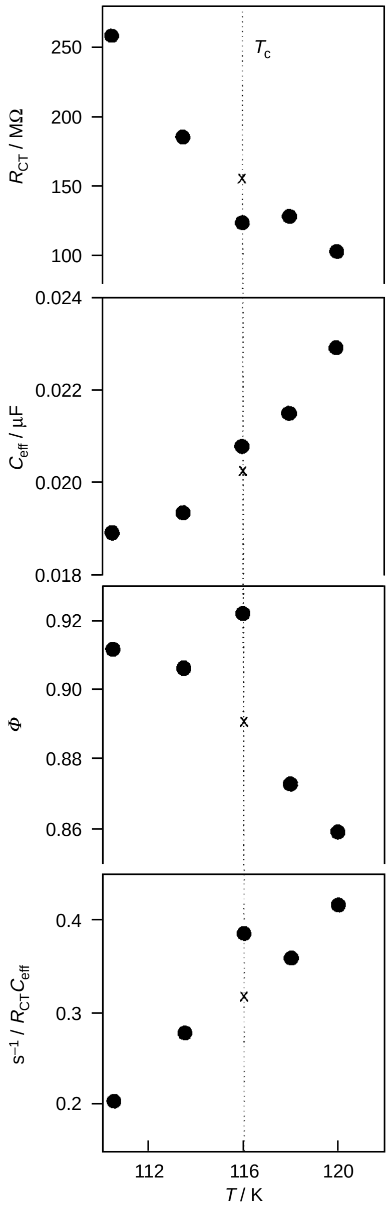

Fig. 2 Top to bottom: charge-transfer resistance R_{CT}, effective double-layer capacitance C_{eff}, phase parameter Φ and (inverse) effective time-constant $1/R_{CT}C_{eff}$ observed for DMFc/Tl 1223 at the electrolyte/electrode interface

solute electroactives, which here is a redox species rather than the electrolyte itself[8] or the actual solvent.[9] Neither of the previous studies[8,9] allows of control of the redox potential of the electroactive species, nor the use of electroactives with two linked redox sites¶ which offer the prospect of probing the transfer of paired charge carriers from within the superconductor. Such innovations should provide new insights into the superconductivity mechanism.[2] This creation of a new probe of superconductivity is clearly notable.

We thank the EPSRC for a grant.

Notes and References

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‡ The electroactive species was 5 mM decamethylferrocene (DMFc) with 0.2 M $LiBF_4$ in solvent comprising 16 : 7 : 1 by volume chloroethane–tetrahydrofuran–2-methyltetrahydrofuran. The apparatus[3–6] with the addition of a Solartron 1286 frequency response analyser monitored the electrode response over the frequency range 10–10^5 Hz to a perturbation of ±100 mV superimposed on the HTSC electrode, about the approximate electrode potential for DMFc–$DMFc^+$ of 0 V with respect to the commonly used Ag-wire quasi-reference electrode.

§ Solartron programmes ZPLOT and ZVIEW allow simulation of the observed electrochemical impedance *via* a model circuit consisting of resistance and capacitance-like ($\Phi \neq 1$) circuit elements. The phase-related quantity Φ, unity for a true capacitance, is often fitted as < 1 (*i.e.* $< 90°$ for the current : potential phase difference) for electrochemical processes.

¶ From electrostatic considerations Kuznetzov[10] predicts a disfavouring fourfold increase in the solvent reorganisation barrier for the transfer of paired charge carriers *cf.* transfer of single electrons, to a single acceptor site. However, for transfer to two separate acceptors, the reorganisation energy will increase only twofold, and the transfer should be best favoured if the spacial separation of the acceptors is commensurate with the coherence length of the superconductor. Such a condition will hold for an electroactive species with two appropriately spaced redox centres.

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Received in Cambridge, UK, 1st April 1998; 8/02475H