A Liquid-electrolyte Voltammetric Probe of Superconducting Oxocuprates through the Transition Temperature T_c

Stephen J. Green,[a] David R. Rosseinsky[a] and Derek C. Sinclair[b]

[a] *Department of Chemistry, The University, Exeter, UK EX4 4QD*
[b] *School of Materials, Houldsworth Building, The University, Leeds, UK LS2 9JT*

New free-solute ferrocene/ferricinium electrochemistry, in liquid electrolyte on Tl-containing oxocuprate superconducting electrodes studied at several temperatures above and below T_c shows no discontinuities or abnormalities at the transition, in contrast with solid-electrolyte behaviour but possibly in accord with theoretical predictions regarding vibronic interactions or reorganisation barriers.

Apart from a preliminary study by us,[1] electrochemistry on HTSC (high-temperature superconductor) oxocuprate electrodes through T_c as a probe of the superconducting state, has hitherto been restricted to HTSC/(solid electrolyte) interfaces,[2,3] which show a 'hump' in the faradaic current over the approximate range $T_c \pm 6$ K, and to nonfaradaic processes at an HTSC/(liquid electrolyte) interface.[4] Because of the metastability of the original liquid electrolyte we employed, our experiments on oxocuprates, necessarily as microelectrodes, were of brief duration.[1] Later, with an improved liquid,[5] we were able to study liquid-electrolyte faradaic electrochemistry on macro Pt electrodes down to 99.5 K ($<T_c$ of several oxocuprates.) Here the oxidation response of ferrocene (Fc), $\mathrm{Fc} \rightarrow \mathrm{Fc}^+ + e_{\mathrm{Pt}}$, appears quasi-reversible, *i.e.* the current is partly limited by the charge transfer (CT) rate at the electrode. Comparable experiments now on oxocuprates, again employing liquid electrolyte, hence allow comparisons with the solid-state studies, and with aspects of theoretical treatments.

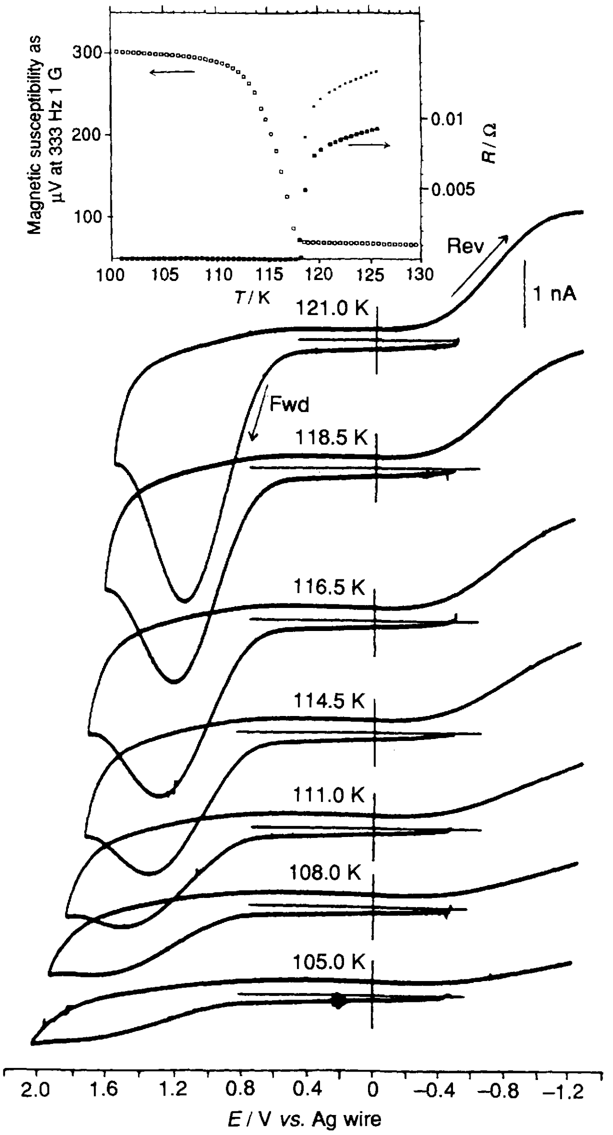

Fig. 1 CVs with temperature of $\mathrm{Fe} \rightarrow \mathrm{Fe}^+ + e_{\mathrm{HTSC}}$ on Tl 1223 with insets of conductimetry and magnetometry showing transition at $T_c \cong 118$ K; 25 mV s^{-1}

Electrodes comprised segments of compacted discs of the oxocuprates, Tl 1223 $\{(\mathrm{Tl}_{\frac{1}{2}}\mathrm{Pb}_{\frac{1}{2}})\mathrm{Sr_2Ca_2Cu_3O_\delta}\}$ (sintered after compaction), and Tl 2223 $\{\mathrm{Tl_{1.7}Ba_2Ca_2Cu_3O_\delta})$ (sintered, crushed then compacted), encapsulated in Stycast resin as previously outlined,[1] but with larger exposed area (diameters *ca.* 0.1 mm). Four-point leads were attached[1] to the inner, buried, end of the oxocuprate fragment, for *in situ* conductimetric monitoring of the superconducting transition. Ferrocene (10^{-3} mol dm^{-3}), in the 16:7:1 EtCl–THF–2-MeTHF/LiBF$_4$ (0.6 mol dm^{-3}) electrolyte, was introduced into the cell pre-cryostatted down to *ca.* 130 K. While the Tl 2223 sample, having appreciable grain-boundary resistance, allowed the expected resistance drop at *ca.* T_c to be observed, such changes in the more highly conductive Tl 1223 segments were masked by the unavoidable lead resistances in the miniaturised electrode assembly,[1] and T_c here was established by conductimetry and magnetometry on separate sections of the same sample. The CVs (Fig. 1) on Tl 1223, for $\mathrm{Fc} \rightarrow \mathrm{Fc}^+ + e_{\mathrm{HTSC}}$ and its reverse, yielded peak anodic currents i_p (related to the zero current base for electrolyte alone) plotted *vs.* T in Fig. 2. The electrode of Tl 2223, <0.1 mm in diameter, from CVs (Fig. 3) of more microelectrode-like response, gave the i_P (here plateau) values also presented in Fig. 2 (together with i_P

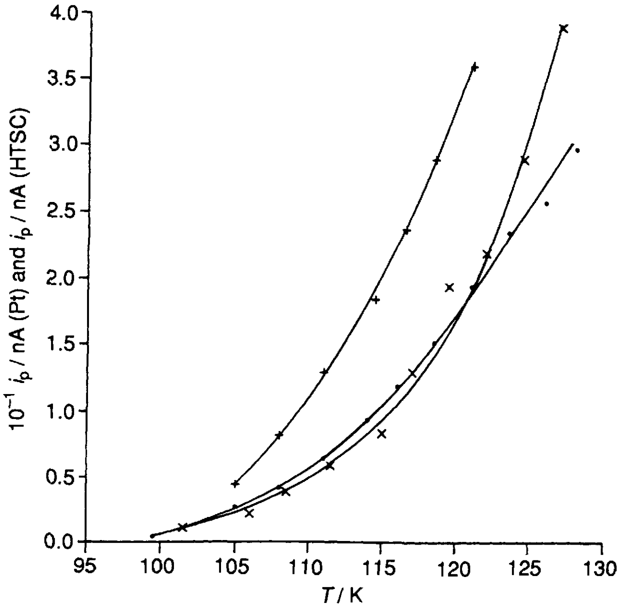

Fig. 2 i_P *vs.* temperature for Tl 2223 (×), Tl 1223 (+), Pt (●)

for the Pt electrode[5]). In general the HTSC CVs are more 'smeared out' than those obtained previously[5] on Pt, an effect which has been attributed to surface roughness[6] which also accounts for the capacitative hysteresis-like looping of Fig. 3. Both HTSC plots of i_P *vs.* T (Fig. 2) over the transition range show small excursions from smooth curvature, in either direction, which however resemble those on Pt; thus no clearcut discontinuities or abnormalities about T_c are evident. The absence of the current hump observed with solid electrolytes,[3,7–14] which from theory[15] ensues for the transfer of single (non-superconducting) electrons with weak electron/solvent-mode coupling, could thus imply stronger coupling in the liquid-electrolyte case. If, alternatively, the hump is[14] directly a consequence of Cooper-pair transfer,[15] its suppression for liquid systems is then ascribable to the larger liquid-electrolyte reorganisation energy[16] associated with $\varepsilon_\infty^{-1} - \varepsilon_0^{-1}$ (the inverse high- and low-frequency permittivities respectively), arising from the higher ε_0 of polar liquids. As the gross current in our experiment is governed by[17] diffusive, CT-rate, solution-resistance and double-layer effects, combination(s) may mask a more subtle T_c-related response, which would require resolution from these factors.

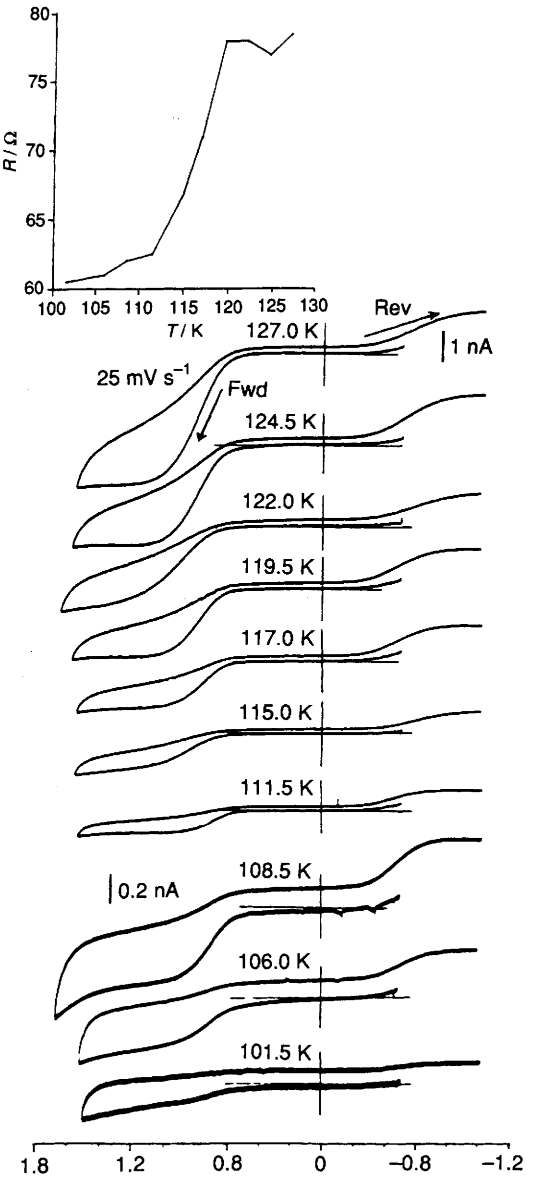

Fig. 3 As Fig. 1 but on Tl 2223; inset shows *in situ* resistance monitoring of $T_c \cong 112$ K (onset 119 K)

The achievements reported here of observing macro-scale faradaic current at an HTSC/(liquid electrolyte) interface through the superconducting transition provide the opportunity of distinguishing between the possible origins of T_c-induced effects, outlined above, on one- and two-electron (Cooper pair) CT currents, by impedance-spectroscopy resolution of the gross current. Since Cooper pairs can undergo transfer to two electroactive sites, the paired-electron current is[16] governed by the separation of the electroactive sites as set by concentration squared[16] for single-electron electroactives, or the separation within dual-site electroactives like biferrocenes, both simply varied in liquid electrolytes.

We thank Merck Ltd. and the SERC for funding.

Received, 29th March 1994; Com. 4/01882F

References

1 S. J. Green, D. R. Rosseinsky and M. J. Toohey, *J. Am. Chem. Soc.*, 1992, **114**, 9702.

2 A. Pinkowski, J. Doneit, K. Juttner, W. J. Lorenz, G. Saemann-Ischenko, T. Zetterer and M. Breiter, *Electrochim. Acta*, 1989, **34**, 1113.

3 J. O'M. Bockris and J. Wass, *J. Electroanal. Chem.*, 1989, **267**, 329.

4 S. R. Peck, L. S. Curtin, J. T. McDevitt, R. W. Murray, J. P. Collman, W. A. Little, T. Zetterer, H. M. Duan, C. Dong and A. M. Hermann, *J. Am. Chem. Soc.*, 1992, **114**, 6771.

5 S. J. Green, D. R. Rosseinsky and M. J. Toohey, *J. Chem. Soc., Chem. Commun.*, 1994, 325.

6 J. T. McDevitt, M. Longmire, R. Gollmar, J. C. Jernigan, E. F. Dalton, R. McCarley, R. W. Murray, W. A. Little, G. T. Yee, M. J. Holcomb, J. E. Hutchinson and J. P. Collman, *J. Electroanal. Chem.*, 1988, **243**, 65.

7 A. Pinkowski, J. Doneit, K. Juttner, W. J. Lorenz, G. Saemann-Ischenko, T. Zetterer and M. Breiter, *Physica C*, 1989, **162–164**, 1039.

8 A. Pinkowski, J. Doneit, K. Juttner, W. J. Lorenz, G. Saemann-Ischenko and M. Breiter, *Europhys. Lett.*, 1989, **9**, 269.

9 A. Pinkowski, W. J. Lorenz, G. Saemann-Ischenko and M. W. Breiter, *Solid State Ionics*, 1990, **40/41**, 822.

10 A. Pinkowski, K. Juttner, W. J. Lorenz, G. Saemann-Ischenko and M. W. Breiter, *J. Electroanal. Chem.*, 1990, **286**, 253.

11 M. W. Breiter, W. J. Lorenz and G. Saemann-Ischenko, *Surf. Sci.*, 1990, **230**, 213.

12 A. Pinkowski, K. Juttner and W. J. Lorenz, *J. Electroanal. Chem.*, 1990, **287**, 203.

13 W. J. Lorenz, G. Saemann-Ischenko and M. W. Breiter, *Ber. Bunsenges. Phys. Chem.*, 1991, **95**, 1055.

14 I. Engelhardt, R. Speck, J. Inche, H. S. Khalil, M. Ebert, W. J. Lorenz, G. Saemann-Ischenko and M. W. Breiter, *Electrochim. Acta*, 1992, **37**, 2129.

15 A. M. Kuznetsov, *Electrochim. Acta*, 1992, **37**, 2123.

16 A. M. Kuznetsov, *J. Electroanal. Chem.*, 1990, **278**, 1.

17 L. K. Safford and M. J. Weaver, *J. Electroanal. Chem.*, 1992, **331**, 857.