A New Liquid Electrolyte allowing Sustained Macroelectrode Electrochemistry down to 99.5 K

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Solution-phase electrochemical experiments involving free-solute species (here ferrocene) on macro-sized electrodes have been achieved on Pt at temperatures down to 99.5 K by use of an EtCl–THF–2-MeTHF–LiBF$_4$ electrolyte.

Solution-phase electrochemistry of free-solute[1] species on superconducting electrodes at *ca.* 100 K, being a unique probe of the superconducting state,[2] has been limited[1] to brief (occasionally zero) experimental durations by the metastability towards solidification of the supercooled THF–EtCl–LiBF$_4$ electrolyte hitherto used.[1] In such experiments, accompanying high electrolyte resistances, R, associated with high viscosity, have necessitated the use of micro-electrodes, low currents i so avoiding high, obscuring, iR potentials. We now report stable fluid electrolytes useable down to 99.5 K, of hours-long permanence, which allow routine macro-electrode cryoelectrochemistry, demonstrated here by ferrocene/ferrocenium (Fc/Fc$^+$) cyclic voltammetry on Pt: micro-electrodes often involve difficult fabrication, characterisation and interpretation.

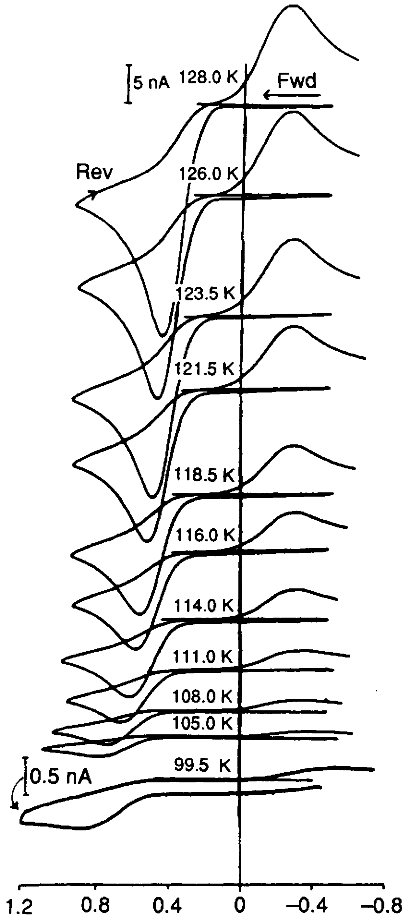

Fig. 1 Variable-temperature cyclic voltammograms (at potential scan rate 25 mV s^{-1}) of 5 mmol dm^{-3} ferrocene on a 0.3 mm Pt disc in 0.6 mol dm^{-3} LiBF$_4$/16 : 7 : 1 EtCl-THF-2-MeTHF. Fwd indicates the forward process $Fc \rightarrow Fc^+ + e_{Pt}$. Rev indicates the reverse process $Fc^+ + e_{Pt} \rightarrow Fc$.

Low-temperature voltammetry of ferrocene in this work was followed on a 0.3 mm diameter Pt disk electrode in the cryoelectrochemistry cell described previously,[1] within a nitrogen-cooled cryostat (±0.1 K). The mixed solvent composition, expressed as a volume ratio at *ca.* 273 K, was originally 2 : 1 chloroethane–tetrahydrofuran, this plus 0.6 mol dm^{-3} LiBF$_4$ allowing a maximum of *ca.* 10 min experimentation after syringe injection of the total electrolyte solution into the cell pre-cooled to *ca.* 100 K. Solidification of the supercooled electrolyte threatened to occur from <110 K as indicated by light-scattering nucleation points observed through the windows of the cryostat jacket. Addition of *ca.* 4% 2-methyltetrahydrofuran (replacing an equal volume of THF) substantially increased both the lifetime and the fluidity of the supercooled state, the resultant lowering of electrolyte resistance permitting the use of macro-electrodes. Cyclic voltammetry between 128 and 99.5 K (Fig. 1) established the reliability obtained, reproducibility at fixed temperatures after both 10 and 20 min measurement intervals being excellent. Incipient slow nucleation of solid at cell walls, evident below *ca.* 108 K, did not interfere, being remote from the electrodes. Signal persistence for >1 h at *ca.* 100 K is routinely achieved, with pre-cooling of the cell to the target temperature.

While possibly distorting solution-resistance effects are currently being examined by impedance measurements, the form of the voltammograms accords with simulations[3] of CVs for quasi-reversible electron transfer at low temperature. Study of such electrochemical phenomena is now clearly accessible, as is the application of these cryoelectrochemical advances to the study of superconducting electrodes.

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