MOLECULAR CRYSTALS AND LIQUID CRYSTALS 79 (1-4), 5-23, 1982

CHEMISTRY AND ELECTROCRYSTALLIZATION OF ORGANIC METALS AND SUPERCONDUCTORS

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Considerable variation in the conditions of electrochemical crystal growth of $TMTSF_2X$ (i.e., constant current versus constant potential, ambient versus inert atmosphere, etc.) and in the purity of the constituents (donor, electrolyte, solvent) does *not* significantly affect the unusual low-temperature properties of this class of materials. Our results suggest that the electrocrystallization procedure may be self-purifying by selecting for conducting crystal phases with constituents having specific oxidation potentials and solubility properties. However, doping solutions with structurally and chemically similar constituents (i.e., TMTTF, and IO_4^- in ClO_4^-) leads to their incorporation in the crystal structure where they have a profound effect. Several mole percent of these dopants suppress superconductivity in the PF_6^- and ClO_4^- salts, and increase and broaden the metal-insulator phase transition.

Progress in the field of metal-like organic charge-transfer complexes has often been gated by fortuitous developments in the synthesis of new donor and acceptor molecules and, in particular, in the preparation of single crystals suitable for solid state measurements. The impressive progress over the last seven years for materials based on the π-donor tetrathiafulvalene (TTF) is, in no small way, the result of the synthetic flexibility of this material which has permitted a wide variety of systematic modifications to be prepared and converted into single crystal complexes. Bechgaard's recent discovery[1] that electrocrystallization can be applied to grow single crystals of tetramethyltetraselenafulvalene (TMTSF) with a variety of Lewis acid counter-ions that display new and unusual solid-state electronic properties has prompted considerable interest in the potential of this technique for new materials fabrication.

Previous studies have shown electrochemical techniques to be useful in preparing single crystals of charge transfer compounds involving polycyclic aromatics,[2,3] metal dithiolenes,[4] tetrathiafulvalene derivatives[1,5] and TCNQ.[5] Success in this area has been rather empirical, and little fundamental information is available concerning optimization of this technique to the fabrication of single crystals suitable for solid state characterization.

Briefly, the electrocrystallization method involves the application of a controlled oxidizing or reducing current which converts soluble donor or acceptor molecules to their less soluble oxidized or reduced complexes, respectively. This is schematically illustrated in Figure 1. In Bechgaard's initial work,[1] a constant current approach was employed in which an oxidizing current (usually several microamps) was applied such that diffusion-limited (and not active mass transport) processes controlled the production of TMTSF radical cations. Working and counter electrodes were separated using fine porous frittes to minimize side-reactions involving reduced species generated at the counter electrode. Care was taken to use highly purified materials (freshly distilled and dry reagent solvents, multiply recrystallized electrolyte and gradient sublimed donor).

In order to explore the sensitivity of the electrocrystallization conditions and initial chemical purity in affecting the interesting properties of $TMTSF_2X$ complexes, we have grown crystals under a wide variety of conditions, and examined their resulting solid state properties. We chose to also employ constant potential as well as constant current conditions since we were concerned about over-oxidation of TMTSF to its dication species (see Figure 1). The applied potential was controlled using a reference electrode (standard calomel), and set below the first oxidation peak potential for TMTSF of 0.40 volts, usually at 0.25 to 0.35 volts. Current levels were typically 2-8 microamps. Typical experimental conditions were: 0.05-0.10 molar electrolyte and 0.001 to 0.005 molar donor in methylene chloride solution. In some runs, acetonitrile was used as a solvent, but was found not to work as well as methylene chloride. Electrochemical runs were carried out on a vibration-free table and in the dark to avoid photochemical reactions that have been seen previously.[6] Runs were terminated usually in 4-6 days.

The overall conclusion of our studies is that within reasonable limits, the properties of $TMTSF_2X$ complexes are *not* a sensitive

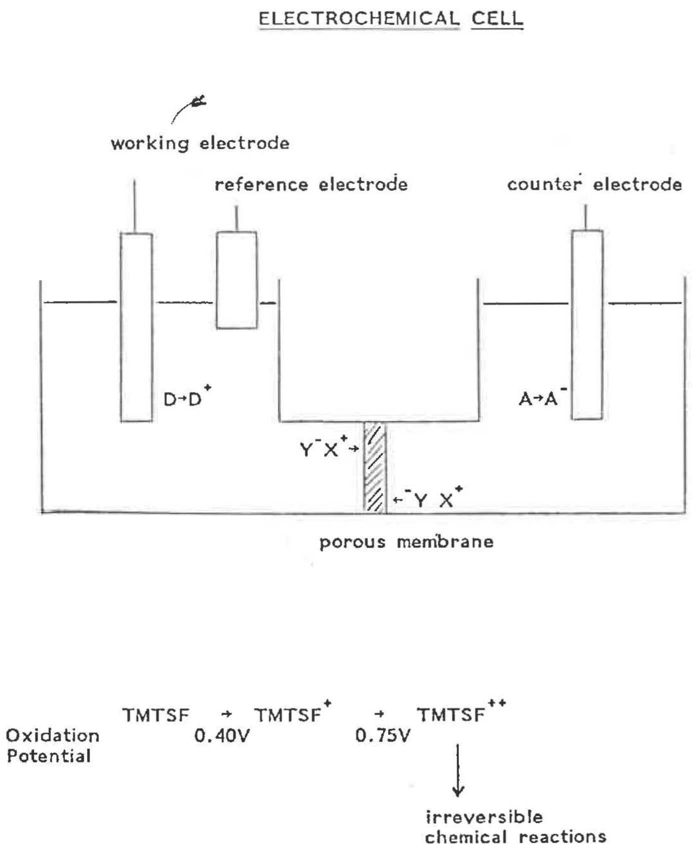

Figure 1. Schematic of Electrochemical Cell.

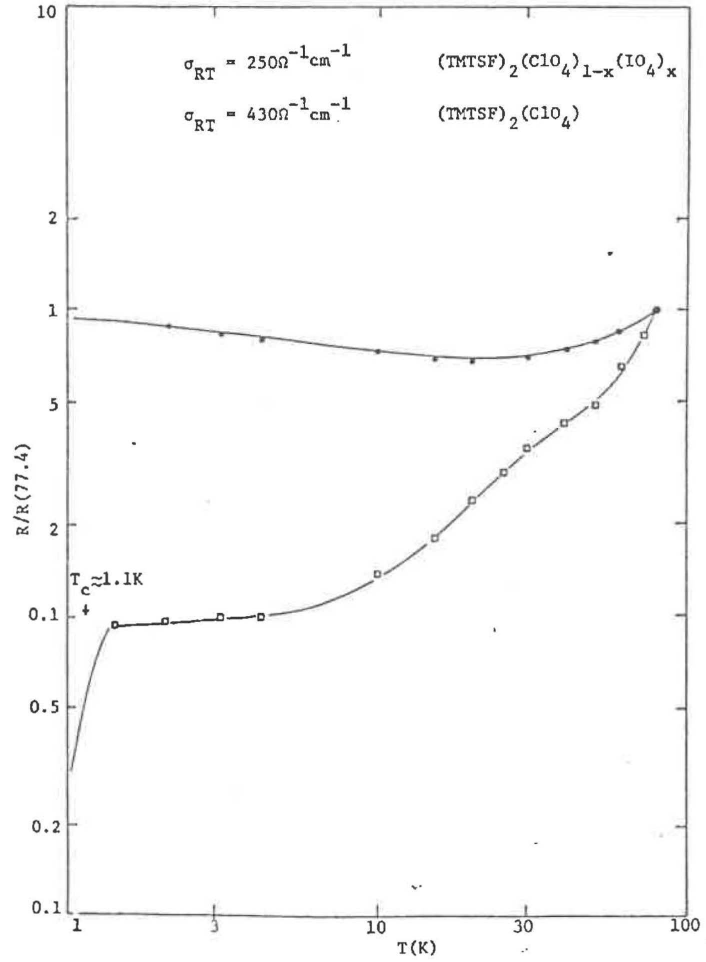

Figure 2. Conductivity vs. Temperature for $(TMTSF)_{1-x}$ $(TMTTF)_x$-PF_6 Alloys.

function of the conditions of electrochemical growth (i.e., constant current versus constant voltage, light versus dark room conditions, ambient air versus nitrogen, etc.) and of the purification procedures employed on chemical constituents. This latter conclusion was intially surprising, since one might have anticipated that the low-temperature properties of $TMTSF_2X$ complexes might be very sensitive to chemical impurities. However, the sharpness of the metal-insulator transition for $X=PF_6$, the observation of superconductivity in $X=PF_6$ under pressure and in $X=ClO_4$ at ambient pressure, and the nonlinear transport properties below $T_{M\text{-}I}$ remain essentially unchanged, even when commonly accepted precautions regarding purity and control of the crystal growing environment are neglected. Our results suggest that the electrocrystallization procedure may be *self-purifying* by selecting for conducting crystal phases with constituents having specific oxidation potentials and solubility properties. If, however, the crystal growing solution is "doped" with structurally and chemically similar constituents, they can be incorporated into the crystal structure where they have a profound effect on solid-state properties. For example, we have explored donor stack alloying in $TMTSF_2PF_6$ with the sulfur analog TMTTF[7] and counter-ion doping in $TMTSF_2ClO_4$ with IO_4. Small amounts of these dopants (several percent or less) destabilize the metal-insulator transition, inhibit superconductivity and suppress nonlinear effects.[7]

Figure 2 shows the effect of small amounts of TMTTF on the conductivity-temperature profile for $TMTSF_2PF_6$. Three percent TMTTF was found to significantly smear the metal-insulator transition and increase it from 11.5 to 17°K. The effect of counter-ion doping is illustrated in Figure 3 where a few percent incorporation of IO_4 in $TMTSF_2ClO_4$ ($x \approx 0.02\text{-}0.05$) completely suppresses the ambient pressure superconductivity.

We have found that there is an optimum "window" for the rate of electrochemical crystal growth. At current levels above about 10 microamps, crystal growth is very rapid and leads to extensive nucleation and produces microcrystals or powder. At low current levels (typically below 1 microamp), side reactions and diffusion from the electrode compete with nucleation at the electrode and lead to poor quality crystals and very low yields. Intuitively, one might expect very slow electrochemical growth to enhance the quality and size of crystal production. However, crystal growth apparently requires a sufficient rate of TMTSF cation production to cause precipitation of the complex in the vicinity of the electrode before it can diffuse away. It was not uncommon for us to obtain no crystals at all when current levels were much below 1 microamp. Our initial results with other donors suggest that the optimum current window probably varies somewhat from donor to donor, with the solubility of the resulting charge transfer salt playing an important role.

While constant current and constant voltage conditions gave identical results, we found that constant voltage conditions provide a more controlled end-point of a crystal run. As donor is consumed, the current will drop under constant voltage control, whereas constant current conditions will begin to further oxidize the $TMTSF_2X$ crystals (converting it to the dication species) in order to maintain the set current level.

We have explored a variety of cell designs and found no noticeable dependence on crystal quality; however, some designs are easier to use and adapt to various experimental conditions than others. When large numbers of cells are to be employed, we found cleaning of fritted glass cells a major problem in expenditure of time and in assuring freedom from contaminants. In this regard, the use of commercially available voltammetric cells that have been designed for cyclic voltammetry studies[8] seem ideally suited and flexible for general use. Figure 4 provides a schematic of this cell design with some comments on useful aspects of the cell in relation to electrocrystallization. In particular, the use of the disposable vycor frittes in heat-shrinkable teflon sleeves to connect working and counter electrode compartments provides great practical advantage. The twist-off bottom of the cell has been important in transferring those precious large (and fragile) crystals that one is, at times, fortunate to obtain.

The electrocrystallization technique appears to be quite general in its ability to provide single crystals of charge-transfer complexes. We have prepared a number of new materials based on tetraselenafulvalene derivatives; however, at this time, none of the donor modifications of TMTSF have been found to display its unique properties. For example, the dimethy analog of TMTSF with PF_6 gives a moderate conductor (σ_{RT}~30/ohm-cm) with a board maximum in conductivity around 200°K, while the parent donor, TSeF, gave single crystals with ClO_4 which were semiconducting ($\sigma_{RT} \approx 10^{-2}$/ohm-cm, $\Delta E \approx 0.15$ eV).

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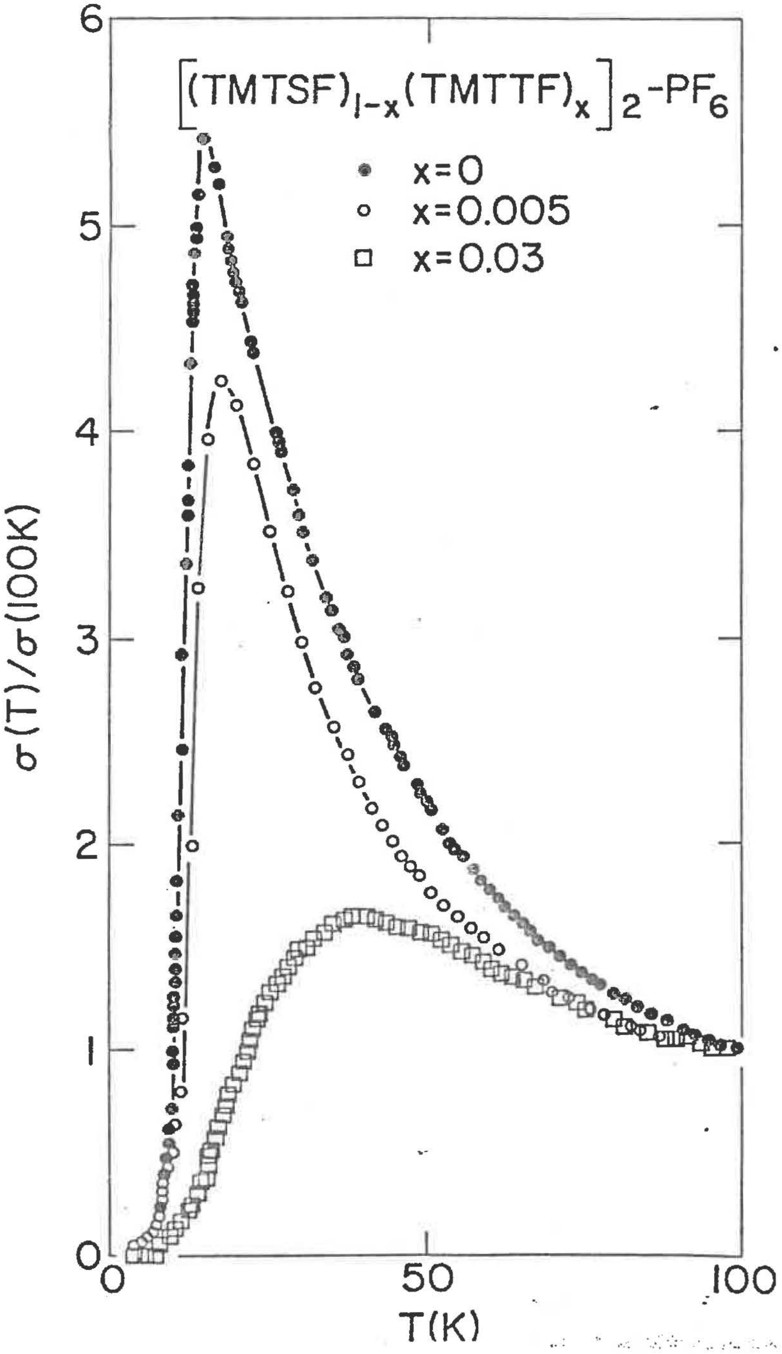
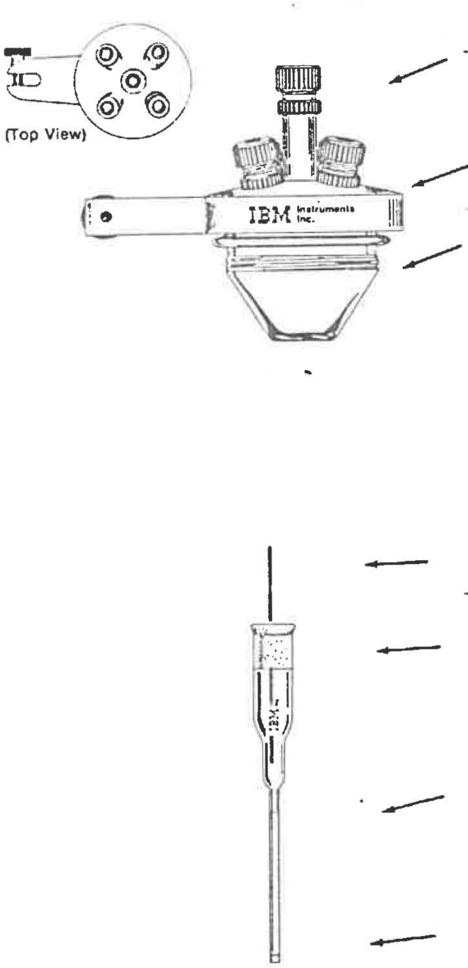


Figure 3. Resistivity vs. Temperature Date for $TMTSF_2ClO_4$ and Doped with IO_4.



Variable depth positiong of electrodes using O ring adapters

Screw-on teflon cap

Tapered working electrode compartment for 2-30 ml solutions

Pt electrode

Counter-electrode compartment

Teflon shunk tubing

Vycor porous fritte

Figure 4. Schematic of Commercial Voltammetric Cell (from IBM Instruments Inc.) Adapted for Electrocrystallization.