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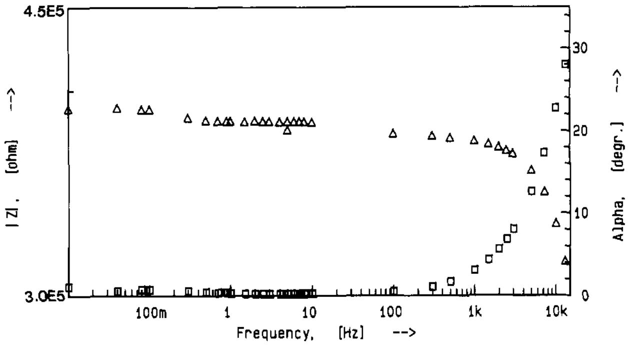

Figure 3. Bode plot of $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}(OC_2H_4SO_3Na)_{0.10}]_n$ at 25 °C: □, phase angle; △, impedance. Cell geometric factor: l/a = 0.113 cm^{-1}.

Hz to 5 MHz, using stainless steel electrodes, and some results are listed in Table I. A significant increase in ionic conductivity was observed when [2.2.2] cryptand was added into polymer 1. The conductivity increases as [2.2.2] cryptand is added and reaches the maximum when the molar ratio of sodium ion to [2.2.2] cryptand is 1:1. Addition of more [2.2.2] cryptand has negligible influence on conductivity. Arrhenius plots of the conductivities of the polyelectrolytes (Figure 1) show a gentle curvature, which is a typical behavior of ion transport in amorphous polymers.

A second set of ac impedance data was collected in the frequency range 10 mHz to 5 MHz,[10] using saturated sodium amalgam coated on copper plate as electrodes. The Na(Hg) electrodes are nonblocking with respect to the polyelectrolytes studied, $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}(OC_2H_4SO_3Na)_{0.10}([2.2.2]\mathrm{cryptand})_x]_n$, x = 0, 0.05, 0.10, and 0.20. In addition to the single arc obtained in the absence of cryptand, a smaller low-frequency arc is observed in the presence of cryptand. The Bode plot, Figure 2, of a cryptand-contained polyelectrolyte (x = 0.10) at 25 °C shows one minimum phase angle at which the impedance corresponds to the bulk resistance (R_b), around 0.5 kHz. A second minimum phase angle occurs around 60 mHz. By contrast, the Bode plot of the cryptand-free polyelectrolyte (Figure 3) does not have a second minimum phase angle down to 10 mHz. The resistance associated with this low-frequency feature is independent of potential (10, 20, and 30 mV were applied) and sample thickness. The latter observation strongly implicates an interfacial origin for the low-frequency arc. The Arrhenius plot of the low-frequency arc is linear over the temperature range studied (25–50 °C). We attribute the low-frequency arc to interfacial charge-transfer resistance primarily associated with the rate of sodium ion release from the [2.2.2] cryptand complex to the amalgam electrode. The activation energy (E_a) for this process is 17 kcal mol^{-1}. For comparison, the activation energy for the release of ($Na^+\subset 2.2.2$) in ethylenediamine solvent is 12.9 kcal mol^{-1}.[11]

When a [2.2.2] cryptand is added to a sodium phosphazene polyelectrolyte, a large increase in conductivity is obtained. Because the counterion is immobile, all of this conductivity increase can be attributed to the cation. Judging from T_g data, the presence of [2.2.2] cryptand does not alter the gross polymer dynamics, so the likely origins of increased conductivity are reduced cation–anion pairing and/or decreased interaction of the cation with the polymer-bound ether groups. Balanced against the greater effective mobility of the cation in the presence of [2.2.2] cryptand is a decreased efficiency of interfacial charge transport, apparently due to slow release of the sodium ion from the cryptand ligand. Even with this apparent charge-transfer resistance, the materials containing the [2.2.2] cryptand are significantly better electrolytes than the cryptand-free polyelectrolyte.

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Crystal Growth and Phase Selectivity of Organic Superconductors [β-$(ET)_2I_3$ (T_c = 1.5 K) and κ-$(ET)_2Cu(NCS)_2$ (T_c = 10.4 K)] on Graphite Electrodes

Hau H. Wang,* Lawrence K. Montgomery,
Chad A. Husting, Bradley A. Vogt,
Jack M. Williams,* Sandra M. Budz,
Michael J. Lowry, K. Douglas Carlson,
Wai-Kwong Kwok, and Vladimir Mikheyev

Chemistry and Materials Science Divisions
Argonne National Laboratory
Argonne, Illinois 60439

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In the relatively short period of time since superconductivity was first observed in organic salts in 1980 [bis(tetramethyltetraselenafulvalenium) hexafluorophosphate, T_c = 0.9 K/25 kbar],[1] almost three dozen organic superconductors have been reported,[2] and the maximum superconducting transition temperature (T_c) has risen by a factor of 10 [$(ET\text{-}d_8)_2Cu(NCS)_2$, T_c = 11.4 K/ambient pressure].[3] No experimental technique has played a more important role in the rapid development of this area than electrocrystallization. The preponderance of organic superconductors has been prepared by anodic oxidation of suitable organic substrates in the presence of supporting electrolytes that supply the desired counterions.[4] Although solvent, temperature, and current density are important experimental variables in electrocrystallization, the electrode material is the very heart of the oxidation reaction. To date, platinum has been the most commonly employed electrode material, and to prepare high-quality crystals, its treatment before electrocrystallization is critical.[5] It is surprising that the composition of the working electrode has received so little systematic attention, since it is one of the most obvious components to vary in seeking new conducting materials, and electrodes can be constructed from a variety of different substances (e.g.,

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Table I. Crystal Growth of $(ET)_2I_3$ by Electrocrystallization on Graphite Anodes[a]

anode treatment			
cleaned	polished	anal. method[b]	β phase, %
no	no	A	>95
no	yes	A	>95
yes	no	B	4
yes	yes	B	0

[a] All cells contained ~10 mg of ET and ~250 mg of NBu_4I_3 in 15 mL of purified THF (platinum cathode, anode current density of 0.8 μA/cm^2, 23 °C). The period of growth was from 4 to 7 days. [b] Method A: individual ESR crystal analysis. Method B: ESR line-shape analysis. See text.

Cu, Ag, Au, Ni, graphite). In this communication we describe the first[6] use of graphite electrodes for the preparation of two of the most extensively studied superconductors derived from bis(ethylenedithio)tetrathiafulvalene (commonly abbreviated BEDT-TTF or, simply, ET), β-$(ET)_2I_3$ and κ-$(ET)_2Cu(NCS)_2$. Graphite electrodes have been employed for high-temperature applications for many years due to their good thermal and electrical conductivity, mechanical strength, and stability toward most chemicals.[9] The use of graphite electrodes in solution is somewhat limited because graphite readily undergoes intercalation reactions under strongly oxidizing conditions.[10] A novel finding of the present study was that the two phases commonly encountered in electrochemical syntheses of $(ET)_2I_3$, the α and β forms, can be selectively prepared by using suitably fabricated and modified graphite electrodes. These results pave the way for the use of graphite as an inexpensive and versatile electrode material for the preparation of organic synthetic metals.

The electrocrystallizations were carried out following procedures described in the literature.[11] The conditions utilized for the electrocrystallization studies of $(ET)_2I_3$ are shown in Tables I and II. The graphite electrodes (3.1-mm o.d.) were spectroscopic grade (National Carbon Co.). The effect of polishing (000 emery polishing paper, Carborundum Co.) or "cleaning" in 1 M H_2SO_4 solution is noted in Table I. The cleaning procedure commonly used for platinum electrodes, which chemically modifies the graphite as discussed below, consisted of the following steps: (1) the working graphite electrode was connected to the negative post of a 3-V battery and an auxiliary platinum electrode to the positive post; (2) the electrical current was allowed to flow for 4 min, and the polarity was reversed for a second 4-min period; (3) finally, the original polarity was used for an additional 8 min. The electrodes were then rinsed briefly in water, soaked in distilled water and methanol for 10 min each, and dried with a heat gun (15 min). The same procedure was used for cleaning the platinum electrodes in Table II. The product morphology of each synthetic batch was analyzed by use of ESR spectroscopy. The ESR measurements were carried out at room temperature on an IBM ER-200 spectrometer equipped with a rectangular cavity operating in the TE_{102} mode. The α and β phases were identified by their room-temperature peak-to-peak line widths, which depend on orientation but fall into markedly different ranges.[12] The line widths of α-phase crystals vary from 70 to 120 G, while β-phase crystals are only 18.5–24 G. Depending on the size of the crystals, two different procedures were followed: procedure A, when large crystals were obtained in limited numbers, they were separated and characterized individually; procedure B, when microcrystalline powders were obtained, the ESR spectra were digitized (~300 points) on a Lundy 5688 graphics terminal with a bit pad and analyzed by a line-shape simulation program that fits first-derivative ESR spectra to a linear combination of Lorentzian derivatives.[13]

Table II. Crystal Growth of $(ET)_2I_3$ by Electrocrystallization on Platinum Anodes[a] and Chemical Oxidation[b]

special exptl conditions[c]	time required for nucleation	yield, %	anal. method[d]	β phase, %
	Electrocrystallization			
1.5 μA/cm^2	2–3 days	60–80	A	>95
4% H_2SO_4	1 day	70	A	75
4% H_2O	3 days	42	A	<9
8% H_2O, 2% H_2O_2	3 days	40	A	0
10 μA/cm^2	1 day	86	B	<4[e]
	Chemical Oxidation			
0.6 equiv of I_2	1 h	38	B	40
12 equiv of NBu_4I_3	1 h	60	B	1

[a] All cells contained ~10 mg of ET and ~200 mg of NBu_4I_3 in 15 mL of purified THF (platinum electrodes, anode current density of 0.8 μA/cm^2, 23 °C). Exceptions noted in table. The period of growth was approximately 12 days. [b] Carried out in boiling 1,1,2-trichoroethane. [c] Percentages refer to mole percent relative to ET. [d] Method A: individual ESR crystal analysis. Method B: ESR line-shape analysis. See text. [e] Less than 4% of an undentified phase with a line width of 33 G.

Table I summarizes the results of electrocrystallization experiments where $(ET)_2I_3$ crystals were grown under four different sets of experimental conditions. The results were duplicated in each case to ensure reproducibility. The most striking feature of the data in Table I is the change in crystal morphology upon cleaning the anode. Graphite electrodes that were not cleaned yielded the β phase predominately (>95%). Occasionally, one or two α crystals were noted. In contrast, the α phase was obtained in greater than 96% yield when the graphite electrodes were electrolyzed (cleaned) in dilute sulfuric acid. So far as we know, organic conductor morphology selection through electrode modification has not been reported previously. Cleaned platinum electrodes afford the β phase predominantly in carefully purified tetrahydrofuran[4] or chlorobenzene.[14] In the case of platinum electrodes, cleaning facilitates crystal growth and ensures reproducibility but does not dramatically switch the phase that is produced. Although the surfaces of the graphite electrodes were not visually altered by the cleaning procedure, the effect of polishing the electrodes was explored to determine if the

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change in morphology was related to surface smoothness. However, polishing had little or no effect on the morphological distribution of crystals from either the cleaned or uncleaned electrodes. One final point worth noting regarding the data in Table I is that all of the crystals grown on the graphite electrodes (α or β) took less time to start growing (overnight versus 2–3 days) and required lower current densities (0.8 μA/cm^2 versus 1.5 μA/cm^2) than is typical for platinum electrode syntheses.

The observed phase selectivity by use of treated and untreated graphite electrodes prompted us to perform several comparative electrochemical (platinum anodes) and chemical syntheses of $(ET)_2I_3$ (Table II). The selectivity is most likely associated with a chemical change in the graphite electrodes upon electrolysis. Anodic oxidation of graphite in sulfuric acid solution forms graphite–bisulfate, $C_{24n}{}^+HSO_4{}^-\cdot 2.5H_2SO_4$, where n is the stage number.[10] For n equal to 1 or 2, the materials are well characterized and correspond to sulfuric acid–bisulfate intercalation between every carbon layer or every two carbon layers, respectively. Under the "cleaning" conditions of the experiments in Table I, the graphite electrodes are incompletely oxidized, i.e., n equals a large number. Even so, the treated electrodes can easily take up a substantial amount of sulfuric acid. For example, with a low average state of oxidation, e.g., $n = 100$, a graphite electrode would contain 60 mol % of sulfuric acid relative to the organic heterocyclic component. The first entry in Table II provides typical experimental conditions and results for $(ET)_2I_3$ syntheses using platinum electrodes. The second shows the effect of adding a small amount of sulfuric acid. Crystal growth occurs at lower current densities, and less time is required for nucleation. The yield of $(ET)_2I_3$ is comparable to what is observed under the standard conditions, but now the α phase constitutes 25% of the products. Accordingly, sulfuric acid can significantly influence which morphology is produced. However, so can water. When 4 mol % of water is added, only 9% of the products is the β phase. This is an interesting observation, since water is usually rigorously excluded in $(ET)_2I_3$ preparations. Adding an alternative oxidant, such as aqueous hydrogen peroxide, gives crystals that are exclusively the α phase. Apparently, a variety of additives are capable of facilitating α-phase growth. The final electrocrystallization result in Table II illustrates what happens when the current density is increased substantially: the product is mainly the α phase and microcrystalline. It has been noted previously that rapid crystal growth at high current densities favors the formation of α-$(ET)_2I_3$.[15,16] Rapid crystal growth (1 h) is probably responsible for the formation of large amounts of α product in the chemical oxidations also. The room-temperature electrical conductivity of the α-phase crystals is greater than those of the β phase [$\sigma_{300}(\alpha \text{ phase}) = 60\text{–}250$ S/cm, $\sigma_{300}(\beta \text{ phase}) = 30$ S/cm].[15,16] It is conceivable that the higher conductivity of the α form plays a key role[17] in making α-$(ET)_2I_3$ the kinetically favored product under conditions of rapid crystal growth. It is noteworthy in this regard that α-$(ET)_2I_3$ is thermodynamically less stable than β-$(ET)_2I_3$.[18] Although the results in Table II do not provide an unambiguous picture of how the cleaned graphite electrodes produce the α form almost exclusively, they are highly compatible with the idea that intercalated sulfuric acid and/or associated water are responsible.

As a final test of our findings, crystals of the organic superconductor κ-$(ET)_2Cu(NCS)_2$ have also been prepared by use of graphite anodes. Although at least two other structural modifications of $(ET)_2Cu(NCS)_2$ are known,[19] only the κ phase has formed on either cleaned or uncleaned electrodes. Rf penetration depth measurements yielded $T_c = 10.2 \pm 0.1$ K for graphite-grown κ-$(ET)_2Cu(NCS)_2$.

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Formation of Boron Nitride Coatings on Metal Oxides

Robert T. Paine,* Chaitanya K. Narula,[†]
Riley Schaeffer, and Abhaya K. Datye*

Department of Chemistry
Department of Chemical Engineering, and
Center for Microengineered Ceramics
University of New Mexico
Albuquerque, New Mexico 87131

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In the past, thin films of ceramic materials including boron nitride have been prepared primarily by vapor deposition techniques.[1] These films are adequate for some applications; however, they vary a great deal in quality and purity.[2] To achieve several advanced materials goals that

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[†] Present address: Scientific Research Laboratories, Room E-3172, Ford Motor Co., Dearborn, MI 48121-2053.

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