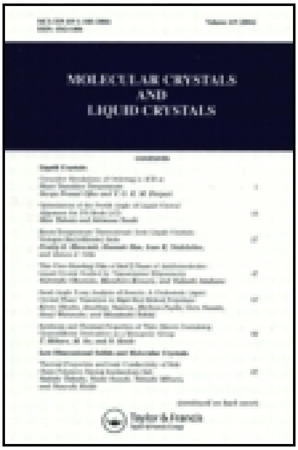

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ELECTROCRYSTALLISATION OF HIGHLY CONDUCTIVE THIA ADDUCTS*

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Conductive adducts such as $TTFX_n$ (X = halide) are more highly conductive when electrocrystallised galvano- rather than potentiostatically. With the latter method, current-time behaviour is diagnostic of crystal quality, five different classes of behaviour and product being discernible. Mixed-halide $TTF(I + Br)_n$ with n ∿ 0.7 as in the monohalides, can be electrocrystallised. Electrode and cell configuration and conditions also govern crystal properties and accessibility of products. Thus, conical electrodes of 4mm diameter and 9mm height with a vertical wire as counter -electrode give the largest $TTF(NO_3)_{0.55}$ crystals.
Higher temperature yields larger crystals.
Adduct compositions are sometimes governed by solvent.

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[†] Sir Arthur Reed Research Scholar, Exeter University, 1979 - 1980.

ADDUCTS AND CONDUCTIVITY

We have prepared a number of adducts[1-3] by potentiostatic and galvanostatic electrocrystallisation. We summarise many of our observations, on often new materials, as follows. Following the substance, the 296 K conductivity σ in Ω^{-1} cm^{-1} is given, together with the metal-insulator transition temperature and the conductivity there, if a metallic temperature coefficient of conductivity is observed. Thus, $\mathrm{TTF(NO_3)_{0.55}}$ (1200, 291 K, 1280)[4]; $\mathrm{TTF(HSO_4)_{1.17}}$ (29, 291 K, 35 to 64); $\mathrm{TTF(BF_4)_{0.6}}$ (19, 323 to 340 K, 52 - another, 156 at 296 K); $\mathrm{TTF(BF_4)_{1.15}}$ (0.02); $\mathrm{TTF(SCN)_{0.45}}$ (3790, probably metallic); $\mathrm{TTFI_{0.71}}$ (18, 317 to 332 K, 26.2); $\mathrm{TTF(Cl_{1.1}}$ (33, 265±10 K, 1460? - possible fracturing). Only 296 K studies follow, again with σ/Ω^{-1} cm^{-1} in parentheses. $\mathrm{TTFBr_x}$ ($x = 0.75$, 8; $x = 0.76$, 2800; $x = 0.77$, 04; $x = 0.78$, 21); $\mathrm{TTFI_x}$ ($x = 0.70$, 200; $x = 0.71$, 34; $x = 0.72$, 36.4; $x = 0.73$, 16.7); $\mathrm{TTFBr_{0.23}I_{0.46}}$ (1600); $\mathrm{TTFBr_{0.47}I_{0.24}}$ (43). $\mathrm{TTF\ F_{2.87}(H_2O)_{0.5}}$ (disc 0.00014); $\mathrm{TTF(ClO_4)_{0.71}}$ (disc, 9); $\mathrm{TTF(HCO_3)_{1.47}}$ (> 0.9); $\mathrm{TTFKC_2O_4(H_2O)_{1.5}}$ (> 0.005); $\mathrm{TTFSO_3C_6H_4CH_3}$ (disc, 2 x 10^{-6}); $\mathrm{TTF(B_4O_7)_{0.45}}$ (disc, 4); $\mathrm{TTF(N_3)_{0.19}}$ (>0.2); TTFTCNQ (430); $\mathrm{TTFSO_4CH_3}$(59); $\mathrm{TTF(OCN)_2}$ (disc, 1.1 x 10^{-6}); $\mathrm{TTF[(C_6H_5)B]_{0.86}}$ (disc, 9) $\mathrm{TTF[Fe(CN)_6]_{0.25}}$ (disc, 10.5); $\mathrm{TTF(AgNO_3)_{0.67}}$ (disc, 0.4) and also $\mathrm{TTTI_{0.72}}$ (>1100); $\mathrm{TTT(NO_3)_{0.74}}$ (>502). Of other groups of adducts we can cite an exceptionally conductive CuTCNQ galvanostatically produced in fragile, possibly single, crystals several cm long (780 Ω^{-1} cm^{-1}), and monoperylinium perchlorate (~0.8 Ω^{-1} cm^{-1}). In this paragraph > indicates 2-probe conductimetry on single crystals. These are underestimates, in contrast with the four-probe values otherwise cited; "disc" implies a compaction, necessarily used when the materials could only be obtained as powders or microcrystals.

We made 10 connexions to a TTF-TCNQ crystal, fig.1, to test various combinations of lead geometry

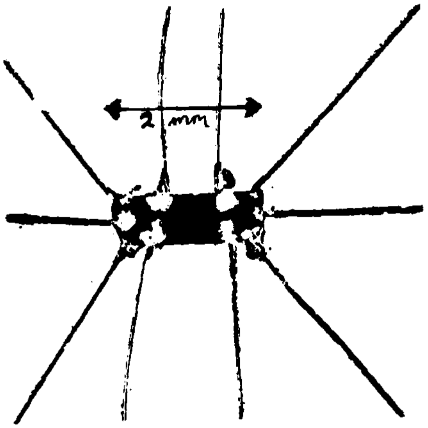


FIGURE 1. Ten Leads on TTFTCNQ single crystal.

Elaborations[5] of the Valdes[6] method, and the Montgomery method[7], give longitudinal conductivities of 406-431, and 427 Ω^{-1} cm^{-1} respectively (transverse, 3.3 Ω^{-1} cm^{-1}) at 293 K.

ELECTROCRYSTALLISATION

Both potentiostatic (constant potential) and galvanostatic (constant current) methods were used. The one or other black box employed to ensure the desired stasis are readily constructed by a skilled electronics technician, or are available commercially (PAR, Bruker, Tacussel etc.). To anticipate, we generally found that galvanostasis produced larger and better-conducting crystals, but we required preliminary potentiostatic studies to establish the best conditions and currents.

The Redox Reactions

$$TTF^{o} = TTF^{+} + e \quad \text{at anode}$$

$$(\text{or} \quad TTF^{o} = TTF^{2+} + 2e \quad " \quad " \quad)$$

$$\text{and} \quad 3Bu_4N^{+} + 3e = \tfrac{3}{2}Bu\text{-}Bu + 3Bu_3N \quad \text{at cathode}$$

$$TTF^{+} + nX^{-} = TTFX_n \ (\text{solid}).$$

These redox reactions represent overall stoichiometries, not mechanisms. The quaternary alkyl ammonium cation with anion X^- is used as inert medium electrolyte. Sometimes potentials yielding TTF^{2+} are used, presumably with the subsequent reaction

$$\tfrac{1}{2}TTF^{2+} + \tfrac{1}{2}TTF^{o} + mX^{-} = TTFX_m$$

or with further obvious possible elaborations.

Cells for Potentiostasis

The geometry is as in fig. 2.

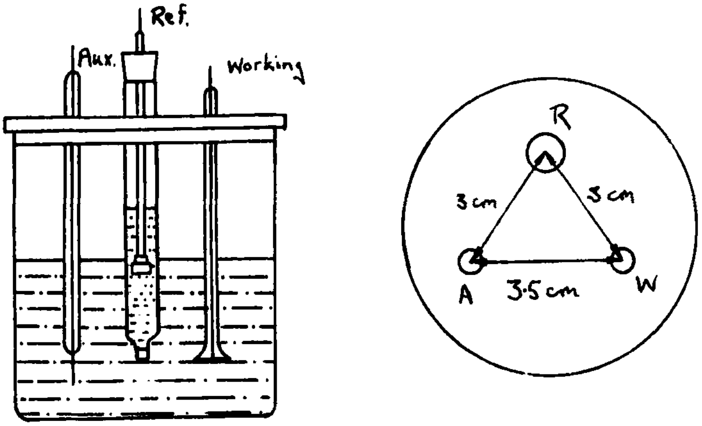


FIGURE 2. Cell geometry for potentiostatic experiments.

Other shapes for working electrodes are considered later; the horizontal disc with wire auxiliary is one of the best. The plane of the disc, of 1cm diameter, should bisect the 2cm long wire; these two electrodes should be separated by about 3.5cm, and the reference SCE should be equidistant, by 3cm, from both, in a triangular array. (Briefly, concentrations were $\sim$10mM in TTF and 10-100mM in say Bu_4NX; potentiostat potentials typically in CH_3CN were 0.5 to 0.76 V with respect to SCE, and in galvanostasis, currents were typically some few mA with electrode area $0.785cm^2$).

Current-time Behaviour in Potentiostasis on Platinum.

Textbooks[8] allude to expected current-time dependences arising from particular assumed mechanisms of electrocrystallisation, for the growth of elemental metals or inorganic salts. Thus, sharp or slow current rises, to maxima, are predicted [8] for rate-determining charge transfer with respectively "instantaneous" initial nucleation or slow "progressive" nucleation; sequential maxima occur with layerwise growth; plateaus occur with specifically conical crystal growth, but a maximum arises if the crystals are insulating. Diffusion control in two-dimensional growth gives a maximum if there is slow ("progressive") nucleation or simply an exponential-type drop if "instantaneous" initial nucleation. Similar ranges of behaviour, and a few more, are observed by us.

Before examining these, one experiment to establish a mechanistic detail merits note. It was assumed that conductive crystals grew at their protruding ends by virtue of their ability to conduct the redox electron to the metal electrode. However, with the working electrode face upwards and within 5mm of the solution surface, it was

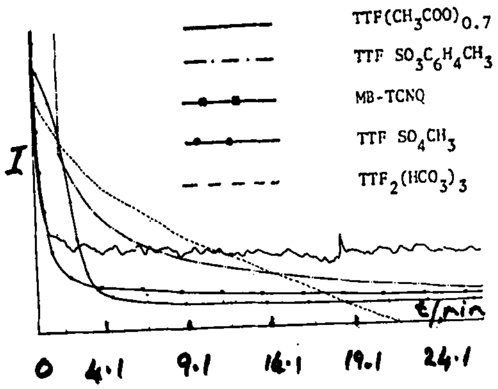


FIGURE 3 Current against time for Class A 1

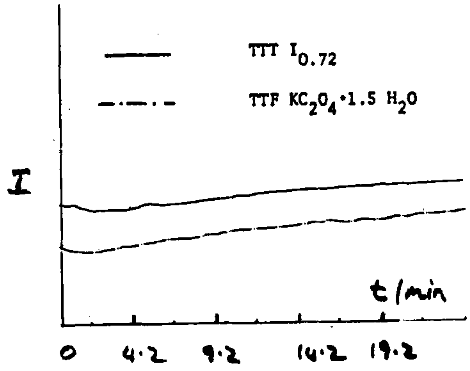


FIGURE 4 Current against time for Class A 2

FIGURE 5

Current against time for Class B 1.

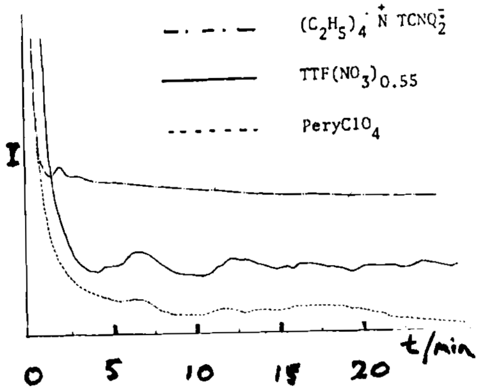


FIGURE 6

Current against time for Class B 2

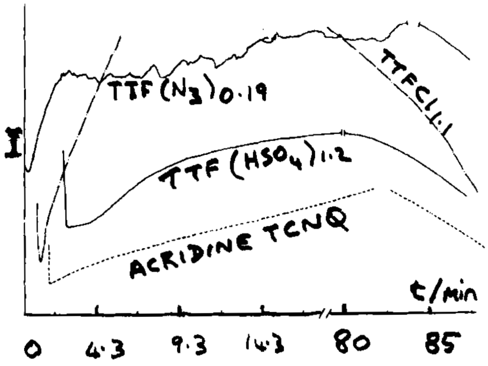
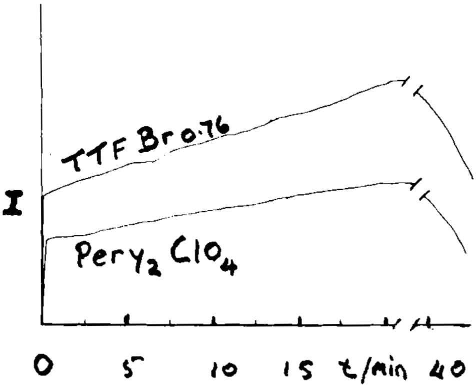


FIGURE 7

Current against time for Class B 3



observed that $TTFI_{0.71}$ crystals poked out through the liquid surface, establishing that for these at least the actual growth was occurring at the Pt surface, not the distant crystal end.

Current-time behaviour could be divided into 2 classes, figures 3 to 7, class A showing no maximum, class B exhibiting maxima or a maximum. Each has sub-groups, but generally class A gives powders with no or few crystals, class B gives good crops of crystals. In detail:

class A1 shows monotonously decreasing current I, for $TTFSO_3C_6H_4CH_3$, $TTF(CH_3COO)_{0.70}$, methylene-blue TCNQ(all partly adherent powders), $TTFSO_4$ and $TTF_2(HCO_3)_3$ (producing as well a few crystallites).

Class A2 shows a monotonously increasing I, and includes $TTFKC_2(H_2O)_{1.5}$ and $TTTI_{0.72}/PhNO_2$ which give powders and crystallites. (CH_3CN was the solvent throughout unless otherwise specified).

Class B1 shows an initial 2.5 minutes I drop, then several small maxima. Here $TTF(NO_3)_{0.55}$ and $PeryClO_4/PhNO_2$ show thickly adherent micro-crystals, with extensive batchwise crystal growth at edges. $(C_2H_5)_4N(TCNQ)_2/CH_2Cl_2$ grows uniform blocklets.

Class B shows an initial 1.5 minutes decrease then a rise to a maximum. $TTFCl_{1.1}$, $TTF(HSO_4)_{1.17}$, Acridine-TCNQ/CH_2Cl_2 form crystals, some falling, leaving a partly bare electrode; $TTF(N_3)_{0.19}$ forms microcrystals behaving similarly.

Class B3 shows a rapid rise of I sharply levelling off to a maximum; thus $TTFBr_{0.76}$, $TTFI_{0.71}$ (shown protuberant from solution) and $pery_2ClO_4/CH_2Cl_2$, which give adherent crystal growth from the electrode.

Mechanistic Speculation

Initially: an I decrease implies instant nucleation with diffusion control; an I increase progressive nucleation with diffusion controlled growth.

On-going: an I increase giving maximum/maxima indicates growth-rate control. Thus

A1: I decrease shows instant nucleation giving powder.

A2: instant (saturating) nucleation, followed by growth-control on saturated surface?

B1: instant surface nucleation giving way to edge crystallisation of successive crops.

B2: instant nucleation of non-adherent crystallites which saturate favourable attachment areas; growth on these areas. (Loss of surface nuclei restrains untrammeled growth).

B3: incremental nucleation with adherent crystal growth, probably on the Pt.

The main general conclusion to be drawn from this aspect of the study is that a potential should be chosen at which behaviour of type B is produced. No generalisation can be made as to the value of this potential, but frequently it corresponds to $E_p + 0.05V$ where E_p is the peak potential in a voltammogram run in the absence of the crystal-forming anion. A few trials will suffice to establish the appropriate setting.

Conditions for Galvanostatic Electrocrystallisation

The choice of current can be guided by potentiostat observations. If a potential is established giving good crystals, then a current set at somewhere between the early almost steady value and the maximum, as observed in potentiostat experiments, will in general produce even better crystals.

Specific experiments on $TTF(NO_3)_{0.55}$ in 1:10 donor: anion concentrations showed in support the following results

$i/\mu A\ cm^{-2}$	product
328-509	polycrystalline
509-636	single + polycrystalline
636-891 (maximum in potentiostasis)	single ∿5mm
> 1274	amorphous powder

These results were independent of choice between horizontal disc or conical working-electrode shapes.

Altering ratios of donor:anion and current densities can give rise to composition changes as in the TTF halide series in Table 1.

Perhaps the mixed halides are of particular interest; their monoclinic unit cells have been compared with those of the monohalide congeners.[3]

For $TTF(NO_3)_{0.55}$ a ratio of 10:1 in nitrate: TTF gives large (∿1cm) crystals, lower ratios giving smaller, <0.5 giving microcrystals.

A tentative conclusion may be reached, that the best and largest crystals are obtained when the rate of electron transfer to or from the electroactive species is made to match the natural rate of crystal growth of the prevailing adduct. It should be noted that the concentration of donor we employ (10 mM) exceeds that commonly employed by others (1 mM).

Table 1. Galvanostat Preparation of TTF Halides

Anion Source	Amount m mol	i/mA cm^{-2}	Product	σ/Ω^{-1} cm^{-1}
Me_4NBr	1	1.91	$TTFBr_{0.75}$	8
Et_4NBr	10	1.91	$TTFBr_{0.76}$	2800
"	10	3.44	$TTFBr_{0.77}$	104
Ph_4PBr	10	1.91	$TTFBr_{0.78}$	21
Me_4NI	1	1.91	$TTFI_{0.73}$	17
Bu_4NI	10	1.91	$TTFI_{0.72}$	36
LiI	10	6.74	$TTFI_{0.72}$	40
Bu_4NI	1[a]	4.59	$TTFI_{0.5}$ powder	$\sim 10^{-3}$
Et_4NBr + Bu_4NI	1 0.5	1.91	$TTFBr_{0.47}I_{0.24}$	43
Et_4NBr + Bu_4NI	0.5 1	1.91	$TTFBr_{0.23}I_{0.46}$	1600

[a] In THF; otherwise CH_3CN, 1 mmol TTF. (Four probe longitudinal conductivities quoted except $TTFI_{0.5}$). 100 ml solvent.

Solvent and Temperature

Besides the effect on composition of replacing CH_3CN by THF just noted, a further marked effect with perylene and perchlorate is established. With CH_2Cl_2 at 23°C and potentiostatting at 1.026 V (SCE), $pery_2ClO_4$ is formed as previously found.[9] When $PhNO_2$ at 23°C is used at 1.235 V (SCE), the mono-perylinium pery ClO_4 ensues; THF, $MeNO_2$, $PhCl_3$ + CH_2Cl_2 and CH_3CN all give no solid. Significantly, cooling to 10 or 0°C with $PhNO_2$ or CH_2Cl_2 yields powder rather than single crystals. $PeryClO_4$ notably exceeds $pery_2ClO_4$ in conductivity (0.8 cf. $\sim 10^{-7}$ Ω^{-1} cm^{-1}).

Regarding temperature, for $TTF(NO_3)_{0.55}/CH_3CN$ with 10:1 reactant ratio, it was found that from -40 to 0°C powder was formed, from 20 to 50°C, 2 - 10 mm single crystals ensued, while from 50 to 65°C, 10 mm single crystals were formed. This is thus a consistent trend, for substantially differing materials.

Platinum Pretreatment, Shape and Substitution.

Finally, we may note sundry tests of electrode pretreatment as a guide to size of product. (i) Immersion in aqua regia for 30 s (ii) anodising for 2 min at 17.5 mA cm^{-2} (iii) cathodising likewise (iv) heating and (v) stress by flexing, were tried in combination and (i) then (ii) then (v) were found to give the best ($\geqslant$5mm) crystals of $TTF(NO_3)_{0.55}$.

Regarding shape, 2 flag electrodes, 2 horizontal disc electrodes, and 2 conical electrodes (9 mm high, 4 mm diameter) were found unsatisfactory. A horizontal disc with wire auxiliary, or better still a cone with wire auxiliary, yielded large ($\geqslant$6mm) crystals. When the wire was enclosed by a frit even better crystals ensured, and this is undoubtedly good practice, to separate off the unwanted cathodic byproducts.

Tungsten gives micro-crystals of $TTF(OCN)_2$ while Pt yields no solid product. This is a wide area for investigation which we have only touched.

CONCLUSIONS

Whilst the observations reported are almost purely empirical, it is clear that rapid nucleation is to be avoided, and this factor alone may account for the observed effect of temperature: smaller nuclei are dissolved in warmer conditions, and their growth prevented, the fewer surviving nuclei providing larger crystals. Both conical and horizontal electrodes provide graded fields and so, probably, nuclei concentrations, also productive of better crystals. Clearly we need to study the initial microseconds of crystallisation more closely, to approach some quantitative formulation of the process.

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