ELECTROCHEMICAL STUDIES OF SOME ORGANIC CONDUCTING/ SUPERCONDUCTING MATERIALS (SYNMETALS)

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Introduction

The abrasive stripping voltammetry (AbrSV) or solid state voltammetry described recently by Scholtz and Lange (1992), Bond et al. (1994, 1997) was used to extract electrochemical properties of compounds such as some organometallic compounds in water which would otherwise prove impossible as these compounds are insoluble in water. In recent years, the discovery of a number of organic, charge transfer (CT) salts, known as synthetic metals (synmetals) including TCNQ-TTF (TCNQ = 7,7,8,8 tetracyano-pquinodimethane and TTF= Tetrathiafulvalene) and more recently the discovery of fullerenes (C_{60}) and its salt: fulleride (e.g. K₃C₆₀) have been found to exhibit superconducting properties (Williams et al. 1992). Some could exhibit this property even near ambient temperature and pressure. Although electrochemical information of these compounds have been determined however these information are mainly confine to solution(voltammetry) rather than solid state voltammetry.

Materials and Methods

Cyclic voltammetry (CV) and square wave voltammetry were employed to study the electrochemical oxidation/reduction of nanocrystals of TTF, TCNQ,C₆₀ and TTF-TCNQ synmetal attached mechanically at the surface of the glassy carbon electrode (3 mm diameter) and immersed in an aqueous electrolyte solution separately. Various parameters including pH, type of electrolyte and its concentration were varied to study the effect on the voltammogram. Redox (multiple) cycling (CV) was also carried out to examine the reproducibility and stability of the redox materials generated at the electrode surface. Effects of varying scan rate and scan reversal in cyclic voltammetry and the current time waveform behaviour in chronoamperometry were also assessed in order to determine the mechanism of the electrode reaction occurring at the electrode-solid-electrolyte interfaces. Morphological changes and insertion of ion(s) occurring at the electrode surfaces during cyclic voltammetry were examined by in-situ electrochemical optical microscopy, scanning electron microscopy and energy dispersive x-ray spectrommetry.

Results and Discussion

The overall electrochemical processes of TTF and TCNQ occurring at the electrode-solid-electrolyte interphases most likely follow the general equation:

xTTF + yZ X=Br,Cl, I, ClO ₄		$(TTF^+)_y(TTF)_{x-y}(X^-)_y +$	ye⁻
(solid)	(aq.)	(solid)	•
xTCNQ + ye M=K,Na,Li,NR4		\longrightarrow (M ⁺) _y (TCNQ) _y (TCN	Q) _{x-y}

(solid) (aq.) (solid)

 $x C_{60} + ye^{-} + y(nNBu_4^{+}) == (nNBu_4^{+})_y(C_{60}^{-})_y(C_{60}^{-})_{x,y}$ (solid) (nonaq.) (solid)

It was found that by a combination of the above mentioned voltammetric techniques that the overall process is under the rate control by nucleation and growth of the solid phases. In the redox cycling of nanocrystals of TTF. TCNO and Con unusual inert zone or hysteresis was observed between the oxidation and re-reduction peaks for TTF unlike those seen in the conventional redox cycling of solution species in nonaqueous electrolyte. The presence of hysteresis, the observation of maxima, a characteristic feature of cross over of scan reversal into the anodic and cathodic curves in cyclic voltammetry and the non-monotonic rising current transient observed during chronoamperometry, are evidences of nucleation and growth processes. TTF-TCNQ (1:1) synmetal was synthesised and characterised electrochemically. Differences between its solution voltammetry and solid state voltammetry using CV mode were observed and were similar to those of the starting materials.

Conclusions

The electrode reactions of TTF, TCNQ, TTF-TCNQ synmetal and C_{60} occurring at the electrode-solid-electrolyte interfaces can be characterised by the nucleation and growth processes.

References

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