



UNIVERSITI PUTRA MALAYSIA

**ELECTROCHEMICAL STUDIES OF TETRATHIAFULVALENE, 7,7,8,8-
TETRACYANOQUINODIMETHANE AND THEIR MIXTURE**

NG GEOK KOON

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TETRACYANOQUINODIMETHANE AND THEIR MIXTURE**

By

NG GEOK KOON

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirement for the Degree of Master of Science**

April 2003



Dedicated to my parents, my brothers, my friends Lim, Ow Wee and Ng,
for their support, patience and friendship

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in the fulfilment of the requirement for the degree of Master of Science.

**ELECTROCHEMICAL STUDIES OF TETRATHIAFULVALENE,
7,7,8,8-TETRACYANOQUINODIMETHANE AND
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By

NG GEOK KOON

APRIL 2003

Chairman: Associate Professor Tan Wee Tee, Ph.D.

Faculty: Science and Environmental Studies

Cyclic voltammetry (CV) and Chronoamperometry (CA) were employed to study the electrochemical oxidation of microcrystalline tetrathiafulvalene (TTF) attached mechanically to the surface of a glassy carbon electrode and immersed in 1 M KBr solution. The effect of temperature, electrolyte concentration and scan rate were been examined. Multiple cycling (CV) was carried out to examine the reproducibility and stability of the redox materials generated at the electrode surface. Change in particle sizes of the oxidized TTF compound was examined by scanning electron microscopy (SEM).

Detection of non-monotonic rising current transient in Chronoamperometric data, a small maximum observed at cross-over of scan reversal into the anodic or cathodic wave and the presence of a large inert zone (hysteresis) even at low scan rate during

cyclic voltammetry as well as the electrode microscopy result are evidence of the nucleation and growth process occurring at the electrode-solid-electrolyte interfaces. Similar results and evidences obtained during electrochemical studies of TTF-TCNQ mixture compound.

Electrochemical behaviours of TTF and TCNQ in non-aqueous solution (0.1 M TBAPF₆/CH₃CN) have been studied. Highly reproducible and symmetrical anodic and cathodic peak observed indicating the occurrence of an electrochemically reversible reaction. The reaction is undergoing diffusion control process where the electrode surface concentration is directly proportional to the bulk concentration.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

**PENGAJIAN ELEKTROKIMIA BAGI TETRATHIAFULVALENE,
7,7,8,8-TETRACYANOQUINODIMETHANE DAN
CAMPURAN MEREKA**

Oleh

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Teknik siklik voltametri (CV) dan kronoamperometri telah digunakan untuk mengkaji pengoksidaan elektrokimia tetrathiafulvalen (TTF) bermikrohablur yang dilekatkan di permukaan elektrod karbon berkaca (3 mm diameter) secara mekanikal dan direndamkan di dalam larutan elektrolit KBr. Kesan-kesan suhu, kepekatan elektrolit dan parameter lain telah pun dikaji. Siklik voltametri berbilang telah dijalankan untuk mengkaji pengulangan and kestabilan bahan redoks yang dihasilkan pada permukaan elektrod. Morfologi sebatian TTF yang dioksidakan dikaji dengan mikroskopi elektron berimbas (SEM).

Pengesanan arus transien bukan monotonic dari data kronoamperometri serta maksimum kecil yang dikesan pada persilangan semasa imbasan pembalikan di gelombang anod dan katod, bersama dengan kehadiran zon lengai yang besar

(histerisis) walaupun pada kadar imbasan yang kecil dan keputusan dari SEM adalah bukti proses-proses penukleusan dan pertumbuhan berlakunya pada permukaan antara muka elektrod-pepejal-elektrolit. Keputusan yang setara juga diperhatikan semasa kajian elektrokimia untuk campuran TTF-TCNQ.

Tingkah-laku elektrokimia bagi TTF dan TCNQ dengan elektrolit bukan akues (0.1 M TBAPF₆/CH₃CN) telah dikaji. Puncak anod dan katod yang boleh berulang-balik dan simetri diperolehi menunjukkan kehadiran tindakbalas elektrokimia yang berulang-balas. Tindakbalas tersebut dikawal oleh resapan di mana kepekatan pada permukaan elektrod adalah berkadar terus dengan kepekatan larutan.

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I certify that an Examination Committee met on 24th April 2003 to conduct the final examination of Ng Geok Koon on his Master of Science thesis entitled "Electrochemical Studies of Tetrathiafulvalene, 7,7,8,8-Tetracyanoquinodimethane and their mixture" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Member of the Examination Committee are as follows:

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DECLARATION

I hereby declare that this thesis is based on my original work except for quotations and citations that have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



NG GEOK KOON

Date: 23rd July 2003

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LIST OF SYMBOLS AND ABBREVIATIONS

1. Symbol	Meaning
A	Electrode surface area (in cm^2)
C	Concentration of the analyte or reactant in the bulk solution (in mole/cm^3)
D	(a) Diffusion coefficient (in cm^2/s) (b) Diffusivity
D^0	Initial diffusivity of the material
e^-	Electron transferred or involved in a reaction
E_{pc1}	First reduction (cathodic) peak potential
E_{pc2}	Second reduction (cathodic) peak potential
E	(a) Potential of an electrode (in V or mV) (b) Peak potential (c) emf of a reaction
$E_{1/2}$	Measured half-wave potential in polarography or voltammetry
E_i	Initial potential
E_f	Final potential
$E^{o'}$	Peak potential formal reduction potential
E_p	Peak potential
$E_{p/2}$	Potential where $i = i_{p/2}$
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
E^0	(a) Standard potential for an electrode (b) Standard emf for a half- reaction
ΔE^0	$= E_1^0 - E_2^0$
ΔE^0	Difference in standard potentials for two couples
ΔE_p	Separation between the peak potential $ E_{pa} - E_{pc} $ in CV
F	Faraday constant, charge on one mole of electrons
I	Peak current
I_f	Forward current
I_p	Peak current (in A or mA)
I_{pa}	Anodic peak current
I_{pa}/I_{pc}	Anodic-to-cathodic peak current
I_{pc}	Cathodic peak current
K or k	(a) Constant (b) Equilibrium constant
n	(a) Number of electron transfer or equiv./mole (b) Number of electrons exchanged between one ion or molecule of a reactant and the electrode
Q	Charge (in Coulomb)
Q_{dl}	Capacitive charge (double layer), (in Coulomb)
R	(a) Gas constant (b) Resistance
t	(a) Electrolysis time (b) Time (in sec.)

T	Absolute temperature (in K)
ν	Scan rate (in mV/s)
τ	Forward step width (in second)
z	Charge on an ion in signed units of electronic charge
Γ	Surface excess of reactant (in mole/cm ²)
Γ_{O}	Surface excess of reactant during oxidation (in mole/cm ²)
Γ_{R}	Surface excess of reactant during reduction (in mole/cm ²)
σ	Conductivity
σ^0	Standard conductivity of the material

2. Abbreviation	Meaning
AbrSV (or ASV)	Abrasive stripping voltammetric technique, also known as Voltammetry of Microparticles (VMP)
Ag/Ag ⁺	Silver-silver ion reference electrode; Ag AgNO ₃ (0.001 M) (acetonitrile with 0.1 M TBAPF ₆)
Ag/AgCl	Silver-silver chloride reference electrode (3.0 M NaCl)
Au	Gold working electrode
CA	Chronoamperometry
CC	Chronocoulometry
CE	Counter electrode
CV	Cyclic voltammetry
EDX	Energy Dispersive X-Ray spectroscopy
GC	Glassy carbon working electrode
OSWV	Osteryoung square wave voltammetry
Pt	Platinum working electrode
RE	Reference electrode
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
WE	Working electrode
CH ₃ CN	Acetonitrile
DMA	Dimethylamine
KBr	Potassium bromide
TBAPF ₆	Tetrabutylammonium hexafluorophosphate
TCNQ	7,7,8,8-tetracyanoquinodimethane
TTF	Tetrathiafulvalene
“c ₀ ”	Label of small peak (shoulder) which appear in solid state cyclic voltammogram of TTF-TCNQ “reduction-shoulder”
“c ₁ ”	Label of cathodic peak which appear in solid state cyclic voltammogram of TTF-TCNQ “1 st couple”
“c ₂ ”	Label of cathodic peak which appear in solid state cyclic voltammogram of TTF-TCNQ “2 nd couple”
“a ₁ ”	Label of anodic peak which appear in solid state cyclic voltammogram of TTF-TCNQ “1 st couple”
“a ₂ ”	Label of anodic peak which appear in solid state cyclic voltammogram of TTF-TCNQ “2 nd couple”
1 st cycle	First cyclic sweep in cyclic voltammetric experiment

I-E or I(E) curve	Current-potential waveform in CV
I-t	Current-time transient in CA
Ox	Oxidation peak
Red	Reduction peak

CHAPTER 1

INTRODUCTION

1.1 Introduction

Voltammetry is a term used to designate a number of electrochemical techniques in which a faradaic current passing through the electrolyte solution is measured as an appropriate potential is applied to the polarizable or indicator electrode. Mass transport of the electroactive species occurs either by diffusion in an unstirred solution or by convection-diffusion in a stirred solution. The current produced was small and the electrolysis time is short, so that the concentration of the active species in solution is not sensibly changed during analysis since only a negligible portion of the electroactive substance is reduced or oxidized.

The study of the electrochemistry of solid compounds is a great importance both for the development of a fundamental understanding of interfacial reactions and for applied science. It was a great challenge to analyze solid sample directly by electrochemical methods. The problems involved were severe and success was seldom been achieved. In practice, someone might faces the problem as follow:



- (i) Solid compound with insufficient electrical conductivity cannot be used as electrode.
- (ii) Some solid compounds were rare (especially those synthetic compound such as TTF-TCNQ or fullerene) that the fabrication of electrodes could be difficult or even impossible.
- (iii) Electrochemical dissolution in an electrolyte solution, which leads to high current and large ohmic (IR) drop, and may thus, obscures the voltammograms, especially if several electrochemical signals occur at the same time.
- (iv) Some solid material from passivating films on the electrode surface, which would also obscure the measurements.
- (v) Voltammograms of solid compound were usually more complex than those dissolved species and thus more interference on voltammograms.

The simplicity and usefulness of the abrasion technique in solid state voltammetry have been recently described by Scholz and Lange (1992) and Bond et al. (1991, 1994, 1996). This method involved the preliminary mechanical attachment of microcrystalline solid particles onto the surface of a solid electrode. The electrode was then immersed in a solvent (electrolyte) in which the solid compound is insoluble. Its usefulness includes the qualitative and/or quantitative identification of the constituents of alloys, minerals, pigments, corrosion processes and non-conducting organic and inorganic

compounds. This technique is especially useful for the voltammetric studies of compounds that are insoluble in important solvent such as water.

Scholz and Lange (1992) attempted by using paraffin-impregnated graphite electrode (PIGE). Besides PIGE, glassy carbon electrode was commonly used.

Abrasive Stripping Voltammetry itself constitutes an interesting research area. For example, a complicated situation on the electrode surface can be elucidated by theoretical simulated the abrasive stripping voltammograms. Another intriguing aspect of abrasive stripping voltammetry is the possibility of obtaining new solid products resulting from the electrode reaction and of scaling up in larger electrolytic cells.

Organic conductor basically is the charge-transfer salts or often known as synthetic metals (synmetals). These materials exhibit the electrical properties of metals even though they most often contained no metal atoms in the electrically conducting framework. One of the reason many research activities on conducting material were based on organic materials was organic material were of lightweight (their density is about 1.5 to 2.0 g/cm³) compared to copper metal (where the density around 9 g/cm³). Due to their low density, these organic materials can be used as electronic components in automobile and space vehicle where weight is often kept to a minimum.