A Study into the Use of Ion Beam Analysis for the Quantitative and Qualitative Analysis of Conducting Polymers

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A Study into the Use of Ion Beam Analysis for the Quantitative and Qualitative Analysis of Conducting Polymers

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Abstract

Since their discovery in the late 1970s conducting polymers have become increasingly used materials in many applications. They are utilised for their conductivity and/or their electroactive properties. These applications include sensor technologies, actuators, and battery materials.

The properties of conducting polymers rely on the extent of the reduction / oxidation or redox state, and hence the dopant levels, of the materials. The aim of this work was to investigate the use of the Ion Beam Analysis (IBA) techniques Rutherford Backscattering Spectroscopy (RBS), and Proton Induced X-ray Emission (PIXE) for the analysis of 'soft' organic materials, in particular, conducting polymers. These IBA techniques are not new, as they have been extensively used for the characterisation of many inorganic, 'hard', materials such as aluminium oxide and silicon oxynitride. While they have been used to alter the molecular structure, and hence the properties of conducting polymers in the past, little to no research has explored the use of ion beams as a tool for the characterisation of these materials.

Conducting polymers can either be prepared chemically or electrochemically. They are predominantly prepared in an oxidised state and this charge is balanced by negatively charged counter ions. In this work, the conducting polymers were formed electrochemically by deposition onto support materials at constant electrode potential. The number of counter ions required to balance the polymer chain depends on the type of conducting polymer formed and extent of oxidation. Issues such as the influence of the support material and extent of polymer oxidation on the extent of counter ions through the polymer films are of importance. Gaining knowledge of the dispersion of counter ions may provide new insights into the redox mechanisms for conductive polymers.

Complex bis terthiophene porphyrin conducting polymers were prepared and investigated for the uptake of zinc into the freebase porphyrin unit after polymerisation by acquiring elemental depth profiles using RBS analysis. Issues such as the influence of the support material and extent of polymer oxidation on the extent of counter ions through the polymer films were found to be of importance. Gaining knowledge of the

extent of counter ions provides new insights into the redox mechanisms for conductive polymers. The results were compared to those obtained for a sample where zinc was coordinated to the porphyrin prior to the polymerisation process. Unexpected high concentrations of both nitrogen and oxygen were found, which were interpreted to be due to entrapped cations originating from the electrolyte ($(Bu)_4N^+$), together with trapped water molecules, within the polymer films. The chlorine depth profiling assisted with understanding the extent of the perchlorate counter ion throughout the polymer films. The combination of both RBS and PIXE demonstrated that trace element impurities can be detected using ion beam analysis, which other analytical techniques are unable to do.

A series of polypyrrole films incorporating a range of counter ions were prepared as model compounds for study in the second section of this work. RBS and PIXE techniques were used to evaluate film homogeneity with respect to depth and to infer the counter ion / pyrrole unit ratio for each of the six PPy film formed.

RBS was also used to characterise a series of terthiophene-ferrocene based conducting co-polymers. The ratio of co-polymer monomer to terthiophene-ferrocene monomers and the dopant levels for the polymers were determined using a RBS deconvolution method developed in this study. This new method can be extended for characterization of a wide range of organic polymers.

The limitations of RBS for the analysis of these soft materials were identified. The advantage that RBS offers over other analytical techniques is that it provides a means for low atomic number element depth profiling in these materials.

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The only part of this thesis where I get to write whatever I want and I can't figure out where to start!

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List of symbols

Symbol	Description	Unit
c	calibration off set	keV
dQ	number of particles recorded by the detector	
$dQ/d\Omega)_i$	differential cross section	mb sr^{-1}
$d\sigma/d\Omega$	differential scattering cross section	
D	diffusion coefficient	$m^2 s^{-1}$
e	electron charge, charge on a proton	μC
E	potential (electrochemistry),	mV
	energy of incident ion (RBS)	MeV
E_0	initial potential (electrochemistry),	mV
	energy of incident particle (RBS)	MeV
E_1	upper potential limit (electrochemistry),	mV
	kinematic energy of incident particle (RBS)	MeV
E_2	finial potential	mV
E_K	kinetic energy of incident alpha particle	keV
f_r	roughness factor	at cm^{-2}
F	Faraday constant	C mol^{-1}
i	current density (electrochemistry)	mA cm^{-2}
	current density (IBA)	nA cm^{-2}
I	element	
j	flux	$m^{-2} s^{-1}$
k	Coulomb's constant,	N m^2 C^{-2}
	kinematic factor (RBS)	
K_α	X-ray produced from L-K shell	keV
K_β	X-ray produced from M-K shell	keV
l	depth	at cm^{-2}
L	thickness of target	cm
m	energy per channel	keV
M_0	mass of projectile ion	amu

M_1	mass of target atom	amu
n	linear response across all channels,	
	number of electrons transferred (Fick's Law),	
	number of atoms per unit volume in target (Scattering)	
N_i	number of incident alpha particles	counts
$(Nt)_i$	areal density	at cm^{-2}
$N(\theta)$	number of alpha particles scattered at angle θ	counts.msr
Q	total number of particles striking the target	
r	target to detector distance	cm
t	time	s
x	distance	m
Z	atomic number of target	
Z_1	atomic number of incident ion	
Z_2	atomic number of target atom	
$\delta c_{(x,\,t)} / \delta x$	concentration gradient	cm^{-4}
Δk	difference in k-factor	
ΔE_1	energy separation between particles scattered by two	
	different target elements	MeV
ΔM_1	mass difference	amu
$\Delta\Omega$	solid angle	sr
ε	stopping cross section factor	
$\varepsilon(E_{K,1})$, $\varepsilon(E_0)$	stopping cross section incident energies	keV / micron
θ	scattering angle	°
θ_{out}	angle detector is set at	°
γ	gamma	keV
%	percent	

List of abbreviations

amu	atomic mass units
Bridging TTh	Bridging terthiophene
Bu_4N^+	tetrabutylammonium ion
CA	chronoamperometry
ClO^-_4	perchlorate ion
CRI	Crown Research Institute
CV	Cyclic voltammetry
DBS	dodecylbenzenesulfonate
DCM	dichloromethane
DMSO	dimethyl sulfoxide
DSRI	Department of Scientific and Industrial Research
EDOT	3,4-Ethylenedioxythiophene
ERD	Elastic recoil detection
GC	Glassy carbon
GNS	Geological and Nuclear Sciences
HBS	4-hydroxybenzenesulfonate
IBA	Ion beam analysis
ICP	intrinsically conducting polymers
INS	Institute of Nuclear Sciences
ITO	Indium tin oxide
LOD	limit of detection
MS	methane sulfonate
NBS	3-nitrobenzenesulfonate
NMR	nuclear magnetic resonance
NRA	Nuclear reaction analysis
PIGE	Proton induced gamma-ray emission
PIXE	Proton induced X-ray emission
PTS	4-toluenesulfonate
Py	pyrrole
PPy	Polypyrrole

RBS	Rutherford backscattering spectrometry
RHS	right hand side
SB	4-sulfobenzoate
SEM	Scanning electron microscope
SHE	Standard hydrogen electrode
Si(Li)	Lithium drifted silicon
SIM	simulation mode
TaO	Tantalum oxide
TBAHFP	tetrabutylammonium hexafluoro-phosphate
TBAP	tetrabutylammonium perchlorate
TBATFB	tetrabutylammonium tetrafluoroborate
TTh-Fc	terthiophene-ferrocene
TTh-Por-TTh	bis terthiophene porphyrin
TTh-ZnPor-TTh	zinc coordinated bis terthiophene porphyrin