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Photoelectrochemistry and Spectroscopy of Conducting Polymer Electrodes

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ABSTRACT

Photoelectrochemistry and Spectroscopy of Conducting Polymer Electrodes

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The conductive properties of films of polyaniline, substituted polyanilines, polypyrrole and polythiophene formed on platinum electrodes have been studied using photoelectrochemical, spectroscopic and surface science techniques. Bands due to oxidised and reduced forms of the polymers were monitored using *in situ* Raman spectroscopy, with polyaniline giving separate bands and polypyrrole showing an apparent shift of the main ν_{CC} mode by $35 \text{ cm}^{-1} \text{ V}^{-1}$. X-ray photoelectron spectroscopy allowed the elements of the polymers to be quantified into their various oxidation states, particularly through a deconvolution of the N 1s peak. Microscopic mounds of polymer were seen under atomic force microscopy consistent with the extent of polymer growth.

The current response to a light flash perturbation on a milli-second time scale provided new information about the conducting polymers. For polyaniline in an insulating state, short-lived photocurrents were observed (less than 1.5 ms), while for polyaniline in a conductive state, longer-lasting photocurrents were observed (greater than 1.5 ms). Prolonged photocurrents indicative of high conductivity were observed up to a pH of 3.7, beyond which only shorter transients were obtained, consistent with previous polyaniline conductivity studies. The transition from conducting to insulating regions at more positive potentials was marked by the appearance of a short-lived cathodic photoresponse, which occurred at more positive potentials as the pH was lowered. Two models are proposed to account for the photocurrents. In the insulating state, the polyaniline film functions as a capacitance, with the fast transients being caused by discharge of surface states. In the conductive state, the prolonged anodic and cathodic photocurrents arise from redox processes with expulsion of solution species. Consistent with these models, polypyrrole showed only cathodic photocurrents (with anion release) and sulfonated polyaniline only anodic photocurrents (release of protons).

The stable yellow film of parathiocyanogen $(\text{SCN})_x$ formed by oxidation of SCN^- at a platinum electrode in warm methanolic solution was studied, and was shown to be insulating and electroinactive, with short-lived photocurrents unless exposed to potentials greater than 1 V. Oxidation of SeCN^- in aqueous solutions produced an analogous, though less stable, orange paraselenocyanogen film.

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Photoelectrochemistry and Spectroscopy of Conducting Polymer Electrodes

PAUL A. KILMARTIN

"Творческое долголетие - это прежде всего ученики ученого и ученики его учеников. Только при этих условиях возможна <<цепная реакция долголетия>> - одна из наисложнейших реакций в науке."

А.Н. Фрумкин (1895-1976)

"The long years of creativity - this is first of all about the pupils of the scientist and the pupils of his pupils. Only under these conditions is it possible for the 'chain reaction of long years' to proceed, one of the most complicated reactions in science."

A.N. Frumkin (1895-1976)

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LIST OF SYMBOLS AND ABBREVIATIONS

English Symbols

a	constant
A	ampere
A ⁻	anion
AC	alternating current
Ad	surface area difference (AFM)
ADC	analog-to-digital converter
AFM	atomic force microscopy
AR	analytical reagent
atm	atmospheres
ave.	average
B	benzenoid
B	bipolaron
C	coulomb
Calc.	calculated
C/N	carbon to nitrogen ratio
d	XRD spacings
DC	direct current
DMSO	dimethyl sulfoxide
e ⁻	electron
E	electrode potential
E	energy
<i>E</i>	electric field strength
EB	emeraldine base
E _{OXID}	oxidation potential
epr	electron proton resonance
Eqn.	equation
ES	emeraldine salt
ESR	electron paramagnetic resonance (spectroscopy)
E-step	potential step
Et	ethyl group

Expt.	experimental
eV	electron-volt
F	Faraday constant (96485 C mol ⁻¹)
FTIR	Fourier transform infra-red (spectroscopy)
FWHM	full-width at half maximum (XPS)
h	Planck constant
h ⁺	positive hole
Hz	hertz
I ₀	incident photon flux
IR	infra-red
ITO	indium/ tin oxide
j	current density
j _{photo}	photocurrent intensity
K	Kelvin
Kα	radiation (XPS)
L	length
L _x ,L _y	dimensions of surface (AFM)
LB	leucoemeraldine base
LS	leucoemeraldine salt
m	metre
M	mole per litre
M	molar mass
Me	methyl group
Milli-Q	water purified on the Milli-Q filter system
min	minute
N	newton
N	number of points
N ⁺	nitrogen radical cation
NMP	N-methylpyrrolidinone
NMR	nuclear magnetic resonance (spectroscopy)
P	polaron
PANI	polyaniline
PAR	Princeton Applied Research
PB	pernigraniline base
PDF	powder diffraction file
-Ph-	phenyl group -C ₆ H ₄ -
=Ph=	phenylene group =C ₆ H ₄ =

PP	polypyrrole unit
PPy	polypyrrole
prep.	preparative
p-TS	para-toluenesulphonic acid
PVC	polyvinylchloride
Q	quinonoid
R	gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
Ra	mean roughness (AFM)
rpm	revolutions per minute
Rq	standard deviation of height values (AFM)
s	second
s	strong
S	Siemens
SEM	scanning electron microscope
<i>she</i>	standard hydrogen electrode
SPAN	sulfonated polyaniline
SQ	semiquinone
std.dev.	standard deviation
STM	scanning tunneling microscope
t	time
T	temperature
UV	ultra-violet
V	volt
W	watt
W	width of space-charge layer
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
Z	height values (AFM)
Z_{ave}	average of height values
Z'	real component of impedance
Z''	imaginary component of impedance

Greek Symbols

α	absorption coefficient
α	polarizability tensor
δ	in plane deformation - bending mode
2θ	XRD spacings
μ	dipole moment
$h\nu$	photon
ν	wavenumber
ν_{CC}	carbon-carbon stretching mode
ρ	mass density
σ	charge density
Σ	summation sign
τ	time constant for exponential decay
Φ	work function (XPS)
Ω	ohm
ω	angular frequency
\boxplus	collective CC stretching mode (Raman)