Paul M. S. Monk, Roger J. Mortimer,
David R. Rosseinsky

Electrochromism:
Fundamentals and Applications

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Preface

The field of electrochromism has changed much since the idea of an electrochromic display was first suggested in 1969. The introduction of liquid-crystal displays has necessitated a sharp change of focus. The applications originally envisaged for electrochromic devices (ECDs) usually relied on a rapid response in for example high definition television or optical computers. Applications at present considered suitable for ECDs are large-area displays, such as notice boards for traffic or for transport termini, the electrochrome being utilised against a reflective background; other light modulators act in a transmissive sense and will comprise, for example, a thin electrochromic device covering one side of a whole window. This latter aim, the construction of the so-called 'smart window', is a major technological goal.

There have been many previous reviews of electrochromism. Such works either tackle the topic from a more-or-less applied angle, for example covering one type of application, or concentrating on a single electrochrome. There has not hitherto been a monograph dedicated solely to the whole subject of electrochromism. The present work, while not intended to include all citations – there are many thousand – is the first to give a complete overview of the whole subject. Because of the size of the literature, in compiling this monograph almost arbitrary selections were required, and a cut-off date of late summer 1994 became inevitable. In our view, any treatment of electrochromism must include the underlying science, some of which might, at first sight, be considered rather special: however, such basic treatments have generally proven invaluable in the understanding of electrochromic phenomena. We have also, where suitable, included 'hands on' detail not found elsewhere, which may be useful to those entering the field.

Most of the science underlying electrochromism here is presented from a chemical viewpoint since electrochromism is an electrochemically-induced colour change. We have, however, endeavoured to make the exposition accessible to physicists or materials scientists and engineers. Thus, most chapters contain a few references imparting general background information if needed, but we have nevertheless probably erred by assuming either too little or too much prior knowledge.

This work is divided into three sections. Part I provides a general background for readers perhaps unfamiliar with the field. We include elementary definitions such as that for colouration efficiency, which are well known to the electrochromism community but for which an actual definition is rather hard to come by. Some basic electrochemical theory is included also. Part I concludes with a section on the construction of ECDs.

Part II describes both inorganic and organic chemical systems being considered at present for use in electrochromic applications. Chemical systems are presented approximately alphabetically.

Part III presents recent elaborations of electrochromism in some present-day research. The elaborations comprise polyelectrochromism and photoelectrochromism (including a discussion of electrochromic printing).

The production of a work such as this relies on the help and goodwill of many, and we wish to acknowledge the help and support of the following. First, we thank Dr Ute Anton of VCH for her editorial expertise and advice. We thank Manju Merjara of the Chemistry Department, MMU, for typing some of the original manuscript.

Besides providing extensive computer know-how and type-setting expertise, Joe Russell of the MMU helped reproduce many of the figures.

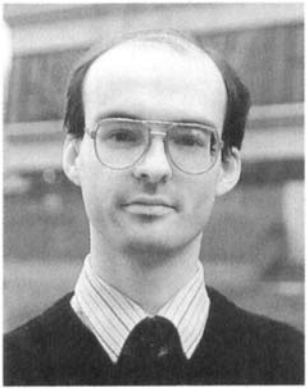
Figures have been reproduced by kind permission of the copyright holders, as follows: Butterworths (Fig. 4.4), Chapman and Hall (Fig. 12.1), The Electrochemical Society (Fig. 4.1), Dr E.R. Howells (Fig. 8.5), Elsevier (4.3 and 8.3), The Royal Society of Chemistry (Figs. 6.2, 8.2, 12.4 and 12.5) and the Society of Applied Spectroscopy (for Fig. 8.4).

We have had many helpful and stimulating discussions with other workers in the electrochromism community, in particular with Dr John Duffy, Dr Richard Hann, Professor Malcolm Ingram, the late Dr J. Brian Jackson, and Dr Robert Janes, Dr Poopathy Kathirgamanathan and Dr Andrew Soutar.

While the above have helped in producing this book, any errors remaining are ours.

P.M.S.M. R.J.M. D.R.R.
Manchester *Loughborough* *Exeter*

1995



Paul M. S. Monk is a lecturer in Physical Chemistry at the Manchester Metropolitan University. In 1990, he received his Ph.D. in chemistry from the University of Exeter having studied the electrochemistry of bipyridilium redox species. He then held a post-doctoral fellowship at the University of Aberdeen (1989–1991) performing research on rapid-response electrochromic devices based on tungsten-trioxide. His present research interests are mixed-metal oxide thin films for electrochromic purposes, novel (chiral) polyanilines and the effects of charge-transfer complexation on electron-transfer rates.

Roger J. Mortimer is a lecturer in Physical Chemistry at Loughborough University of Technology. In 1980, he received his Ph.D. from Imperial College having studied heterogeneous catalysis at the solid-liquid interface. He then held a post-doctoral fellowship at the California Institute of Technology performing research on polymer-modified electrodes. After a demonstratorship at the University of Exeter and lecturing positions in Cambridge and Sheffield, he took up his present post in 1989. His present research interests include electrochromism, electrochemical and optical sensors, and electrocatalysts for fuel cells.

David R. Rosseinsky has been reader in Physical Chemistry at the University of Exeter for as long as he can remember ('in the midst of life, we are in Exeter'). After M.Sc. research (Rhodes, South Africa) on electrolyte conductivities, a Ph.D. (Manchester) on aquo ion electron transfer, and a postdoctorate (University of Pennsylvania) effecting unintended siloxane-based explosions, two year's lecturing slog at the University of the Witwatersrand, South Africa, followed. Eyed up by Exeter during a further 3 year's postdoc (I.C.I. and Leverhulme), he was ultimately deemed fit for human consumption and appointed lecturer. He employs electrochemical probes in a wide variety of charge transfer processes: electron transfer rates in mixed valent solids, electrochemical photovoltaism, electrochromism, colloid electrodeposition, electropolymerisation, zinc-oxide electrophotography, composite electrostatic-charge acquisition, and high-temperature superconductors probed by liquid-phase electrochemistry around 100 K.

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Symbols and Abbreviations

Symbols

A	area of electrode
A	absorbance ('optical density')
A	ampere
C	Coulomb
c	concentration of dissolved species
CR	contrast ratio
D	diffusion coefficient; chemical diffusion coefficient
E	potential of electrode (either impressed potential or zero-current potential)
E^{o}	standard electrode potential
E_{OC}	open-circuit (zero current) potential
$E_{1/2}$	half-wave potential
$E_{pa(m)}$	potential of mth anodic peak in CV
$E_{pc(m)}$	potential of mth cathodic peak in CV
F	Faraday constant
h	Planck constant
i	current
I	intensity of transmitted light
j	flux
J	Joule
k	rate constant
k_B	Boltzmann constant
K	equilibrium constant
K_{sp}	solubility product
l	thickness
L	the Avogadro constant
n	number of electrons involved in electron-transfer reaction
n	as subscript – a number of groups or atoms in a formula
Q	charge per unit area
R	gas constant
s	second
T	thermodynamic temperature
T	transmittance
μ	ionic mobility

v	velocity of ion
V	volt
x	(as subscript) a number, often fractional, of atoms (ions) in a formula
x	(on par) a number, often fractional, of atoms (ions) in a reaction
x	insertion coefficient (consistent with the above)
y, z	(used as x, preceding)
z	charge number on ion
(M	abbreviation for the units mol dm^{-3})

α	electrochemical transfer coefficient (symmetry factor)
α	linear absorption coefficient (for optical absorption by solid species)
ε	extinction coefficient (molar absorptivity for species in solution)
ϕ	F/RT
η	colouration efficiency
η_o	overall colouration efficiency of electrochromic device
η_p	colouration efficiency of primary electrochrome
η_s	colouration efficiency of secondary electrochrome
ν	scan rate in cyclic voltammetry
ν	frequency of light
τ	response time; timescale
λ	wavelength
Ω	Ohm

Apparatus, Processes and Techniques

Abs	absorbance (optical density)
AC	alternating current
CE	counter electrode
CRT	cathode ray tube
CV	cyclic voltammogram
CVD	chemical vapour deposition
CT	charge transfer
DC	direct current
EBS	electron beam sputtering
EC	electrochromic
ECD	electrochromic device
EDAX	energy dispersive analysis of X-rays

ESR	electron-spin resonance
ET	electron transfer
FTIR	Fourier-transform infra red
IR	infra red
LCD	liquid-crystal display
LED	light-emitting diode
OTE	optically-transparent electrode
QCM	quartz-crystal microbalance
RE	reference electrode
RF	radio frequency
SCE	saturated calomel electrode
SEM	scanning electron microscope or micrograph
SHE	standard hydrogen electrode
SIMS	secondary-ion mass spectrometry
UV	ultra violet
WE	working electrode
XPS	X-ray photoelectron spectroscopy
XRD	x-ray diffraction

Materials

AIROF	anodically formed iridium oxide film
SIROF	sputtered iridium oxide film
AMPS	2-acrylamido-2-methylpropanesulphonic acid (polyAMPS is the derived polymer)
(aq)	aquo ion
bipm^{2+}	bipyridilium dication
bipm^{+}	bipyridilium radical cation
$\mathrm{bipm}^{\mathrm{o}}$	neutral bipyridilium-derived species
CPQ	cyanophenyl paraquat (1,1'-*bis*(*p*-cyanophenyl)-4,4'-bipyridilium)
DMF	dimethylformamide
e^{-}	electron
EtOH	ethanol
(g)	gaseous state [*cf.* (*l*) and (s)]
GC	glassy carbon
HCF	hexacyanoferrate

HV	heptyl viologen (1,1'-*n*-diheptyl-4,4'-bipyridilium)
MV	methyl viologen (1,1'-dimethyl-4,4'-bipyridilium)
ITO	indium tin oxide
(*l*)	liquid state [*cf.* (g) and (s)]
L	ligand
M	metal electrode; general metal or cation M^+ or M^{z+}
Me	methyl
MeCN	acetonitrile
MeOH	methanol
MV	methyl viologen (1,1'-dimethyl-4,4'-bipyridilium)
n	electron as negative charge carrier in solid
naph	naphthalocyanine
OP	osmium purple (iron(III) hexacyano-osmate(II))
p	positive hole as charge carrier through solid
PB	Prussian blue
s-PB	'soluble' Prussian blue
i-PB	'insoluble' Prussian blue
PG	Prussian green
PW	Prussian white
PX	Prussian brown (yellow in thin-film form)
pc	phthalocyanine
PC	propylene carbonate
PEO	poly(ethylene oxide)
Ph	phenyl
Pr	propyl
PVP	poly(vinyl pyrrolidone)
Q	quinone moiety
R	substituent
RP	ruthenium purple (iron(III) hexacyanoruthenate(II))
(s)	solid state [*cf.* (g) and (*l*)]
SIROF	sputtered iridium oxide film
TA	thiazine
TEAP	tetra-*n*-ethylammoniumperchlorate
TEAT	tetra-*n*-ethylammonium tetrafluoroborate
TPAP	tetra-*n*-butylammonium perchlorate

TBAT	tetra-*n*-butylammonium tetrafluoroborate
TCNQ	tetracyanoquinodimethane
TTF	tetrathiafulvalene
TSpc	tetrasulphonated phthalocyanine
X	general anion