ELECTROCHROMISM AND ELECTROCHROMIC DEVICES

Electrochromism has advanced greatly over the past decade with electrochromic substances – organic and/or inorganic materials and polymers – providing widespread applications in light-attenuation, displays and analysis.

Using reader-friendly electrochemistry, this book leads from electrochromic scope and history to new and searching presentations of optical quantification and theoretical mechanistic models. Non-electrode electrochromism and photo-electrochromism are summarised, with updated comprehensive reviews of electrochromic oxides (tungsten trioxide particularly), metal coordination complexes and metal cyanometallates, viologens and other organics; and more recent exotics such as fullerenes, hydrides and conjugated electroactive polymers are also covered. The book concludes by examining device construction and durability.

Examples of real-world applications are provided, including minimal-power electrochromic building fenestration, an eco-friendly application that could replace air conditioning; moderately sized electrochromic vehicle mirrors; large electrochromic windows for aircraft; and reflective displays such as quasi-electrochromic sensors for analysis, and electrochromic strips for monitoring of frozen-food refrigeration.

With an extensive bibliography, and step-by-step development from simple examples to sophisticated theories, this book is ideal for researchers in materials science, polymer science, electrical engineering, physics, chemistry, bioscience and (applied) optoelectronics.

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Contents

Preface

While the topic of electrochromism – the evocation or alteration of colour by passing a current or applying a potential – has a history dating back to the nineteenth century, only in the last quarter of the twentieth century has its study gained a real impetus. So, applications have hitherto been limited, apart from one astonishing success, that of the Gentex Corporation's self-darkening rear-view mirrors now operating on several million cars. Now they have achieved a telling next step, a contract with Boeing to supply adjustably darkening windows in a new passenger aircraft. The ultimate goal of contemporary studies is the provision of large-scale electrochromic windows for buildings at modest expenditure which, applied widely in the USA, would save billions of dollars in air-conditioning costs. In tropical and equatorial climes, savings would be proportionally greater: Singapore for example spends one quarter of its GDP (gross domestic product) on air conditioning, a *sine qua non* for tolerable living conditions there. Another application, to display systems, is a further goal, but universally used liquid crystal displays present formidable rivalry. However, large-scale screens do offer an attractive scope where liquid crystals might struggle, and electrochromics should almost certainly be much more economical than plasma screens. Numerous other applications have been contemplated. There is thus at present a huge flurry of activity to hit the jackpot, attested by the thousands of patents on likely winners. However, as a patent is *sui generis*, and we wish to present a scientific overview, we have not scanned in detail the patent record, which would have at least doubled the work without in our view commensurate advantages.

There are thousands of chemical systems that are intrinsically electrochromic, and while including explanatory examples, we incorporate here mostly those that have at least a promise of being useful. Our approach has been to concentrate on systems that colorise or change colour by electron transfer ('redox') processes, without totally neglecting other, electric-potential dependent, systems now particularly useful in applications to bioscience. The latter especially seem set to shine.

Several international gatherings have been convened to discuss electrochromism for devices. Probably the first was The Electrochemical Society meeting in 1989 (in Hollywood, Fl).[1] Soon afterwards was 'Fundamentals of Electrochromic Devices' organised by The American Institute of Chemical Engineers at their Annual Meeting in Chicago, 11–16 November 1990.[2] The following year, the authors of this present volume called a Solid-State Group (Royal Society of Chemisty) meeting in London. At the Electrochemical Society meeting in New Orleans (in 1994),[3] it was decided to host the first of the so-called International Meetings on Electrochromism, 'IME'. The first such meeting 'IME-1' met in Murano, Venice in 1994,[4] IME-2 in San Diego in 1996,[5] IME-3 was in London in 1998,[6] IME-4 in Uppsala in 2000,[7] IME-5 in Colorado in 2002 and IME-6 in Brno, Czech Republic in 2004.[8] Further electrochromics symposia occurred at Electrochemical Society meetings that took place at San Antonio, TX, in 1996[9] and Paris in 2003.[10]

The basis of the processes on which we concentrate is electrochemical, as is outlined in the first chapter. A historical outline is given in Chapter 2, and any reader not familiar with the electrochemistry presented here may find this explained sufficiently in Chapter 3. A fairly extensive presentation of twentieth-century electrochemistry in Chapter 3 seems necessary also to follow some later details of the exposition, and those familiar with this arcane science may choose to flip through a chapter largely comprising 'elderly electrochemistry', to quote from ref. 18 of Chapter 1.

Details of assessing coloration follow in Chapter 4, and in Chapter 5 attempts at theoretically modelling the electrochromic process in the most popular electrochromic material to date, tungsten trioxide, are outlined. In subsequent chapters, the work that has been conducted on a wide variety of materials follow, from metal oxides through complexed metals and metal-organic complexes to conjugated conductive polymers. Applications and tests finish the account. In order hopefully to make each chapter almost free-standing, we do quite frequently repeat the gist of some previous chapter(s).

A comment about the citations which end each chapter: early during our discussions of the book's contents, we decided to reproduce the full titles of each paper cited. Each title is cited as it appeared when first published. We have systematised capitalisation throughout (and corrected spelling errors in two papers).

In our account we have probably not succeeded in conveying all the aesthetic pleasure of studying aspects of colour and its creation, or the profound science-and-technology interest of understanding the reactions and of mastering the associated processes: this book does represent an attempt to spread these interests. However, further at stake is the prospect of controlling an important part of personal environments while economising on air-conditioning costs, thereby cutting down fuel consumption and lessening the human 'carbon footprint', to cite the mode words. There are the other perhaps lesser applications that are also promisingly useful. So, to a more controlled-colour future, read on.

DISCLAIMER: Superscripted reference citations in the text are, unusually, listed in full e.g. 1, 2, 3, 4 rather than the customary 1–4. The need arises from the parallel publication of this monograph as an e-book. In this version, 'each reference citation is hyper-linked to the reference itself, which requires that they be cited separately.'

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We owe much to our families, who have enabled us to undertake this project. We apologise if we have been preoccupied or merely absent when you needed us.

We also thank the numbers of kindly reviewers of our earlier book (and even the two who commented adversely) and much appreciate passing comment in a paper by Dr J. P. Collman and colleagues.

Though obvious new leaders exploring different avenues are currently emerging, if one individual is to be singled out in the general field, Claes-Goran Granqvist of the Ångstrom Laboratory, Uppsala, has to be acknowledged for the huge input into electrochromism that he has sustained over decades.

We alone are responsible for the contents of the book including the errors.

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Frontmatter
More information

Symbols and units

A	ampere, area
Abs	optical absorbance
$c(y,t)$	time-dependent concentration of charge at a distance of y into a solid thin film
c_{m}	maximum concentration of charge in a thin film
c_0	initial concentration of charge in a thin film
D	diffusion coefficient
$\overline{D}$	chemical diffusion coefficient
d	thickness of a thin film
e	charge on an electron
e^-	electron
$\mathcal{E}$	energy
E	potential
E_{a}	activation energy
$E_{\mathrm{(appl)}}$	applied potential
$E_{\mathrm{(eq)}}$	equilibrium potential
E_{pa}	potential of anodic peak
E_{pc}	potential of cathodic peak
$E^{\ominus}$	standard electrode potential
eV	electron volt
F	Faraday constant
Hz	hertz
i	current density
i	subscripted, represents component 1 or 2 . . .
i_{b}	bleaching current density
i_{c}	coloration current density
i_{o}	exchange current density
$\mathcal{J}$	imaginary part of impedance
J_{o}	charge flux (rate of passage of electrons or ionic species)
K	equilibrium constant
K_{a}	equilibrium constant of acid ionisation

K_{sp}	equilibrium constant of ionic solubility ('solubility product')
$l(t)$	time-dependent thickness of a narrow layer of the WO_3 film adjacent to the electrolyte (during electro-bleaching)
M	mol dm^{-3}
n	number in part of iterative calculation
n	number of electrons in a redox reaction
p	volume charge density of protons in the H_0WO_3
p	the operator $-\log_{10}$
Pa	pascal
q	charge per unit volume
Q	charge
R	gas constant
$\mathcal{R}$	real component of impedance
r	radius of sphere (e.g. of a solid, spherical grain)
S	Seebeck coefficient
s	second
T	thermodynamic temperature
t	time
v	scan rate
V	volt
V	volume
V_a	applied potential
W	Wagner enhancement factor ('thermodynamic enhancement factor')
x	insertion coefficient
$x_{(critical)}$	insertion coefficient at a percolation threshold
x_1	constant (of value ≈0.1)
x_o	proton density in a solid thin film
x, y, z, w or c	subscripted, non-integral composition indicators, in non-stoichiometric materials
Z	impedance
γ	gamma photon
ε	extinction coefficient ('molar absorptivity')
η	coloration efficiency
η_o	coloration efficiency of an electrochromic device
η_p	coloration efficiency of primary electrochrome
η_s	coloration efficiency of secondary electrochrome
η	overpotential

λ	wavelength
λ_{max}	wavelength maximum
Λ	ionic molar conductivity
μ	mobility, chemical potential
$\mu_{(ion)}$	mobility of ions
$\mu_{(electron)}$	mobility of electrons
ν	frequency of light
ρ	density of atoms in a thin film
ρ_0	constant equal to $(2\ e\ \rho\ d\ i_0)$
σ	electronic conductivity
τ_D	'characteristic time' for diffusion
φ_s	membrane surface potential
υ	kinematic viscosity
$\overline{\upsilon}$	velocity of solution flow
ω	frequency of ac signal

Abbreviations and acronyms

a	amorphous
ac	alternating current
AEIROF	anodically electrodeposited iridium oxide film
AES	atomic emission spectroscopy
AFM	atomic force microscopy
AIROF	anodically formed iridium oxide film
AMPS	2-acrylamido-2-methylpropanesulfonic acid
ANEPPS	3-{4-[2-(6-dibutylamino)-2-naphthyl]-*trans*-ethenyl pyridinium} propane sulfonate
aq	aqueous
AR	anti reflectance
ASSD	all-solid-state device
ATO	antimony–tin oxide
BEDOT	2,2′-bis(3,4-ethylenedioxythiophene)
BEDOT-*N*MeCz	3,6-bis[2-(3,4-ethylenedioxythiophene)]-*N*-alkylcarbazole
bipy	2,2′-bipyridine
bipm	4,4′-bipyridilium
c	crystalline
CAT	catecholate
CCE	composite coloration efficiency
CE	counter electrode
ChLCs	cholesteric liquid crystals
CIE	Commission Internationale de l'Eclairage
cmc	critical micelle concentration
CPQ	cyanophenyl paraquat [1,1′-bis(*p*-cyanophenyl)-4,4′-bipyridilium]
CRT	cathode-ray tube
CT	charge transfer

CTEM	conventional transmission electron microscopy
CuHCF	copper hexacyanoferrate
CVD	chemical vapour deposition
dc	direct current
DDTP	2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*] pyrazine
DEG	diethyleneglycol
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EC	electrochromic
EC	electrode reaction followed by a chemical reaction
ECB	electrochromic battery
ECD	electrochromic device
ECM	electrochromic material
ECW	electrochromic window
EDAX	energy dispersive analysis of X-rays
EDOT	3,4-(ethylenedioxy)thiophene
EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz-crystal microbalance
FPE	fluoresceinphosphatidyl-ethanolamine
FTIR	Fourier-transform infrared
FTO	fluorine[-doped] tin oxide
GC	glassy carbon
HCF	hexacyanoferrate
HOMO	highest occupied molecular orbital
HRTEM	high-resolution transmission electron microscopy
HTB	hexagonal tungsten bronze
HV	heptyl viologen (1,1′-di-*n*-heptyl-4,4′-bipyridilium)
IBM	Independent Business Machines
ICI	Imperial Chemical Industries
IR	infrared
ITO	indium–tin oxide
IUPAC	International Union of Pure and Applied Chemistry
IVCT	intervalence charge transfer
LB	Langmuir–Blodgett
LBL	layer-by-layer [deposition]
LCD	liquid crystal display
LED	light-emitting diode
LFER	linear free-energy relationships

LPCVD	liquid-phase chemical vapour deposition
LPEI	linear poly(ethylene imine)
LUMO	lowest unoccupied molecular orbital
MB	Methylene Blue
MLCT	metal-to-ligand charge transfer
MOCVD	metal-oxide chemical vapour deposition
MV	methyl viologen (1,1′-dimethyl-4,4′-bipyridilium)
nc	naphthalocyanine
NCD	nanochromic display
Ni HCF	nickel hexacyanoferrate
NMP	*N*-methylpyrrolidone
NRA	nuclear reaction analysis
NREL	National Renewable Energy Laboratory, USA
NVS©	Night Vision System©
OD	optical density
OEP	octaethyl porphyrin
OLED	organic light-emitting diode
OTE	optically transparent electrode
OTTLE	optically transparent thin-layer electrode
pa	peak anodic
PAA	poly(acrylic acid)
PAH	poly(allylamine hydrochloride)
PANI	poly(aniline)
PB	Prussian blue
PBEDOT-B(OC_{12})$_2$	poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-didodecyloxybenzene}
PBEDOT-*N*-MeCz	poly{3,6-bis[2-(3,4-ethylenedioxy)thienyl]-*N*-methylcarbazole}
PBEDOT-Pyr	poly{3,6-bis[2-(3,4-ethylenedioxy)thienyl] pyridine}
PBEDOT-PyrPyr(Ph)$_2$	poly{5,8-bis(3-dihydro-thieno[3,4-*b*]dioxin-5-yl)-2,3-diphenyl-pyrido[3,4-*b*]pyrazine}
PBuDOP	poly[3,4-(butylenes dioxy)pyrrole]
pc	peak cathodic
Pc	dianion of phthalocyanine
PC	propylene carbonate
PCNFBS	poly{cyclopenta[2,1-*b*;4,3-*b*′]dithiophen-4-(cyanononafluorobutylsulfonyl)methylidene}
PdHCF	palladium hexacyanoferrate

PDLC	phase-dispersed liquid crystals
PEDOP	poly[3,4-(ethylenedioxy)pyrrole]
PEDOT	poly[3,4-(ethylenedioxy)thiophene]
PEDOT-S	poly{4-(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-2-yl-methoxy}-1-butanesulfonic acid, sodium salt
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PG	Prussian green
PITT	potentiostatic intermittence titration technique
PMMA	poly(methyl methacrylate)
PMT	polaromicrotribometric
PP	plasma polymerised
PP	poly(1,3,5-phenylene)
PProDOP	poly[3,4-(propylenedioxy)pyrrole]
PProDOT	poly(3,4-propylenedioxythiophene)
PSS	poly(styrene sulfonate)
PTPA	poly(triphenylamine)
PVA	poly(vinyl acrylate)
PVC	poly(vinyl chloride)
PVD	physical vapour deposition
PW	Prussian white
PX	Prussian brown
Pyr	pyridine
Q	Quinone
RE	reference electrode
rf	radio frequency
RP	ruthenium purple: iron(III) hexacyanoruthenate(II)
RRDE	rotated ring-disc electrode
s	solid
s. soln	solid solution
SA	sacrificial anode
SCE	saturated calomel electrode
SQ	semi quinone
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SI	Système internationale
SIMS	secondary ion mass spectroscopy
SIROF	sputtered iridium oxide film
soln	solution

SPD	suspended particle device
SPM	solid paper matrix
STM	scanning tunnelling microscopy
TA	thiazine
TCNQ	tetracyanoquinodimethane
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMPD	tetramethylphenylenediamine
Tp*	hydrotris(3,5-dimethylpyrazolyl)borate
TTF	tetrathiafulvalene
UCPC	user-controllable photochromic [material]
UPS	ultraviolet photoelectron spectroscopy
VDU	visual display unit
VHCF	vanadium hexacyanoferrate
WE	working electrode
WPA	tungsten phosphoric acid
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRG	xerogel