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David R. Rosseinsky, and Paul M.S. Monk

Electrochromic Materials and Devices

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

Electrochromic Materials and Devices

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Electrochromic Materials and Devices

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In memoriam

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We record with deep sadness the untimely death of our co-editor Roger J. Mortimer,
a fine academic colleague and friend, and initiator of this book.
We dedicate this book to his memory.

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Preface

Electrochromic materials have the property of a change, evocation or bleaching, of colour as effected either by an electron-transfer (redox) process or by a sufficient electrochemical potential. Although materials are usually said to be electrochromic when light is modulated by reflectance or absorbance in the visible region of the electromagnetic spectrum – colour changes perceptible to the human eye – interest in electrochromic devices (ECDs) for multispectral energy modulation, to include the infrared and microwave regions, has extended the working definition [1].

While the topic of electrochromism has a history dating back to the nineteenth century, only in the last quarter of the twentieth has its study gained a real impetus. So, applications have hitherto been limited, apart from the astonishing success of the 250 million Gentex anti-dazzle car mirrors that have been sold since 1987 and the adjustable-darkening windows of the Boeing Dreamliner aircraft. The ultimate goal of contemporary studies is the provision of large-scale electrochromic 'smart' windows/glazing for buildings at modest expenditure which, applied widely in the United States, 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 Gross Domestic Product (GDP) on air conditioning, a *sine qua non* for tolerable living conditions there. Importantly, note that only weak anti-thermal protection is provided by colour alone, the electrochrome itself getting heated. Hence, transparent metal oxides that can be electrochemically or otherwise reduced to form shiny metallic reflectors are of fundamental importance, though this process is widely under-emphasised. Numerous other applications have been contemplated, and for some, prototype devices have been developed. Applications include electrochromic strips as battery state-of-charge indicators, electrochromic sunglasses, reusable price labels, protective eyewear, controllable aircraft canopies, glare-reduction systems for offices, devices for frozen-food monitoring, camouflage materials, chameleonic fabrics, spacecraft thermal control, an optical iris for a camera lens and (non-emissive) controllable light-reflective or light-transmissive display devices for optical information and storage.

This edited book follows our earlier research monographs [2, 3] now with invited contributions from the main experts across the globe. Part One concerns electrochromic materials and processing and covers metal oxides, Prussian blue, viologens, conjugated conducting polymers, transition metal coordination complexes and polymers, organic near-infrared materials and metal hydrides. Part Two concerns nanostructured electrochromic materials and device fabrication and covers nanostructures in electrochromic materials, advances in polymer electrolytes for ECD applications, gyroid-structured electrodes for electrochromic (and supercapacitor) applications, layer-by-layer assembly of electrochromic materials and plasmonic electrochromism of metal oxide nanocrystals. Part Three describes the applications of electrochromic materials and covers solution-phase ECDs and systems, electrochromic smart windows and fabric electrochromic displays. Part Four covers device case studies, environmental impact issues and elaborations and includes a case study of an electrochromic foil, life cycle analysis (LCA) of electrochromic windows, a case study of the installation, operation, monitoring and user experience of electrochromic glazing in a UK office and photoelectrochromic devices. The book closes with an Appendix, where electrochromic materials and device performance parameters are defined, to include some cautions about their comparisons between different research laboratories.

References

1. Rauh, R.D. (1999) Electrochromic windows: an overview. *Electrochim. Acta*, **44**, 3165–3176.
2. Monk, P.M.S., Mortimer, R.J., and Rosseinsky, D.R. (1995) *Electrochromism – Fundamentals and Applications*, Wiley-VCH Verlag GmbH, Weinheim.
3. Monk, P.M.S., Mortimer, R.J., and Rosseinsky, D.R. (2007) *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge.

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