

Electrochromic devices

C.G. Granqvist*

*Department of Engineering Sciences, The Ångström Laboratory, Uppsala University,
P.O. Box 534, SE-751 21 Uppsala, Sweden*

Available online 5 April 2005

Abstract

This paper reviews a number of recently discussed electrochromic devices, mainly for modulating optical transmittance. Data are given on all-solid-state and polymer-laminated constructions, with and without self-powering by integrated solar cells. Special attention is devoted to a novel flexible polyester-based device incorporating electrochromic tungsten oxide and nickel oxide. In particular the exposition covers some critical manufacturing aspects, including gas treatments for pre-charging of the individual electrochromic films in order to make them ready for facile device assembly as well as enhancements of the bleached-state transmittance through additions of wide band gap metal oxides to the nickel oxide.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Electrochromics; Films; Color; Optical properties

1. Introduction

Electrochromic materials can change their optical properties upon charge insertion/extraction. When thin films of such materials are integrated in devices, it becomes possible to modulate the transmittance T , reflectance R , absorptance A , and emittance E between widely separated extrema.^{1–3} A standard electrochromic design, such as the one in Fig. 1, has five superimposed layers on one substrate or positioned between two substrates in a laminate configuration. Normally the substrates are made of glass or flexible polyester foil. The central part of the five-layer construction is a pure ion conductor (electrolyte) that can be inorganic (often based on an oxide film) or organic (an adhesive polymer). The ions should be small in order to be mobile; protons (H^+) or lithium ions (Li^+) are preferred. This ion conductor bounds on an electrochromic film (tungsten oxide being a typical example) capable of conducting electrons as well as ions. On the other side of the ion conductor is a film serving as ion storage, ideally with electrochromic properties complementary to those of the first electrochromic film. This central three-layer structure is positioned between electrically conducting transparent films; the best material in terms of optical and electrical prop-

erties is $In_2O_3:Sn$ (known as ITO),⁴ while films of $SnO_2:F$ are less costly and readily available on large area glass substrates. When a voltage of the order of one volt is applied between the transparent electrical conductors, ions can be shuttled between the ion storage film and the electrochromic film. The electrons injected from the transparent conductors then alter the optical properties. A reversal of the voltage, or short-circuiting, brings back the original properties. The coloration can be stopped at any intermediate level, and the device exhibits open-circuit memory.

Electrochromism can lead to numerous applications, as illustrated in Fig. 2. A few of these—such as architectural “smart windows”, rear-view mirrors for cars, and some display devices—are presently (2004) available, at least to some extent. More products are likely to appear in the future, especially when practical manufacturing techniques and more durable products become better established. Among the many possibilities, one can mention variable-transmittance eyewear, variable-transmittance sunroofs for automobiles, and variable-emittance surfaces for temperature control of spacecraft.

2. Some recent electrochromic devices: a brief survey

Only a rough sketch of recent work on electrochromism is possible here, and the reader is referred elsewhere³ for

* Tel.: +46 18 471 3067; fax: +46 18 500 131.

E-mail address: claus-goran.granqvist@angstrom.uu.se.

ELECTROCHROMIC DEVICE

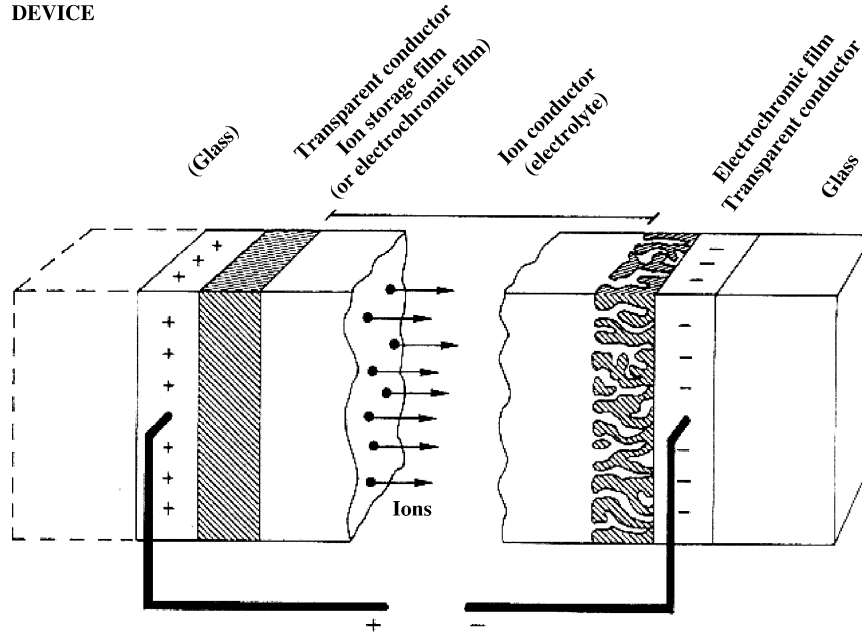


Fig. 1. Basic design of an electrochromic device, indicating transport of positive ion under the action of an electric field.

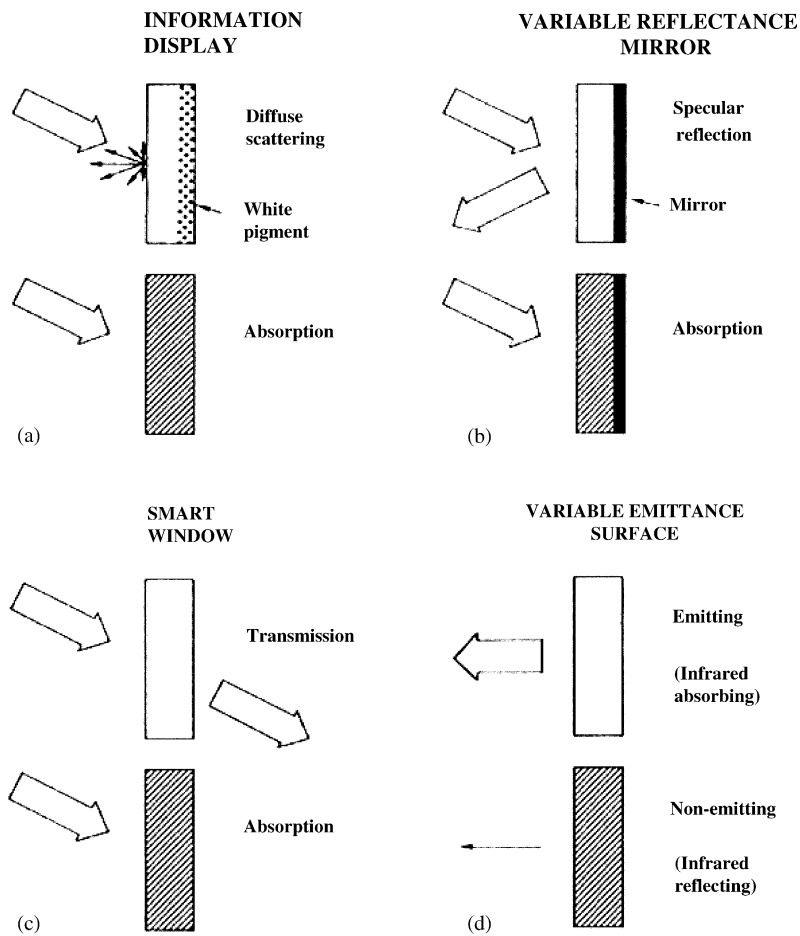


Fig. 2. Principles of four different applications of electrochromic devices. Arrows indicate incoming and outgoing electromagnetic radiation; the thickness of the arrows signifies radiation intensity.

detailed information. Several electrochromic devices backed by a single glass or polyester substrate have been studied by industries. Optical modulation has been effected by H^+ transport as well as Li^+ transport. High values of luminous and solar transmittance, and a large modulation range, are noteworthy for devices incorporating nickel oxide and iridium oxide; these materials exhibit anodic electrochromism (color under charge extraction) and are complementary to tungsten oxide which has cathodic electrochromism (colors under charge insertion).

Laminated devices represent another option. Among those operating with H^+ transport, the electrolytes have been based on polyethylene oxide (PEO), a copolymer of sodium vinylsulfonic acid and 1-vinyl-2-pyrrolidinone and poly-2-acrylamido-2-methyl-propane sulfonic acid. The counter electrodes were IrO_2 , $K_3Fe(CN)_6$ (known as “Prussian Blue”), polyaniline, or a mixture of the latter two. The modulation range for visible light can be large. Laminated devices with Li^+ transport and inorganic counter electrodes have been subject to many detailed investigations. The electrolytes were based on poly methyl methacrylate (PMMA) copolymerized with propylene carbonate or poly propylene glycol, polypyrrole, silane, glycidylxypropyl trimethoxysilane copolymerized with tetraethylene glycol, ormolyte (inorganic–organic hybrid electrolyte), poly ethylene glycol methacrylate copolymerized with PEO, or poly vinylidene fluoride; the polymers were made ion conducting by the addition of an appropriate Li salt. The counter electrodes employed either of V_2O_5 , TiO_2 with or without additions of ZrO_2 or CeO_2 , SnO_2 doped with Mo and Sb, CoO deposited with Li, and NiO deposited with or without Li. A large range of optical modulation, together with durability and reasonable color/bleach response times, were observed in several cases.

Modulation of the optical properties requires the application of a DC voltage of a magnitude that is conveniently obtained from solar cells. These cells can be external to the electrochromic device; alternatively, if semi-transparent cells are used, they can be integrated in a multilayer design comprising a superimposed solar cell and electrochromic tandem configuration. The solar cells investigated thus far have been of two types: dye sensitized nanocrystalline ones, and doped amorphous $SiC:H$. All of the solar-cell-powered tandem devices exhibit a small range of optical modulation, and most of them have a low transmittance in the bleached state, which gives a limitation for several uses.

Electrochromic devices for modulating the thermal emittance have been studied recently. Most of the devices exploit the fact that crystalline tungsten oxide is able to modify its infrared reflectance upon charge insertion/extraction. This surface must be exposed to the ambience either directly or via an infrared-transparent substrate such as CaF_2 , Si, or $ZnSe$. Charge is introduced via a grid electrode, normally of aluminum or gold, with a large open fraction. The counter electrode can be tungsten oxide, nickel oxide, or a polymer electrolyte.

3. An electrochromic foil: specific design features and properties

This section discusses in some detail the preparation of a flexible electrochromic foil. Particular attention is given to practical manufacturing technology and to optimization of the bleached-state transmittance. More details on this novel electrochromic device can be found elsewhere.^{3,5,6}

Electrochromic films based on WO_3 and NiO were made by DC magnetron sputtering onto 0.175-mm-thick polyester foil, pre-coated with an ITO layer having a resistance/square of $\sim 40 \Omega$. For research purposes, films were also prepared on glass plates with ITO layers having a resistance/square of 15Ω . Nickel oxide-based films containing Mg, Al, Si, V, Zr, Nb, Ag, or Ta were investigated with the objective of reducing the absorption in the visible range of the spectrum without compromising the electrochromic properties.^{7,8} Films of different compositions were produced by co-sputtering, and the sputtering power was varied until optimum electrochromic properties were found. The compositions of these films were determined by Rutherford Backscattering Spectrometry and can be represented by their atomic ratios between the additive and Ni according to $Mg/Ni = 0.80$ and $Al/Ni = 0.56–0.62$; the corresponding ratios of Si/Ni , Zr/Ni , Nb/Ni , Ag/Ni , and Ta/Ni have not yet been determined. The sputter targets of the optimized compositions were non-magnetic or weakly magnetic, i.e., they were suitable for large-scale, large-area deposition.

The study on the electrochemical and optical properties of the nickel oxide-based films used cyclic voltammetry in a KOH electrolyte. Specifically, normal T and near-normal R were measured by spectrophotometry, and spectral absorbance was evaluated from $A(\lambda) = 1 - T(\lambda) - R(\lambda)$, where λ denotes wavelength. Fig. 3 compares bleached-state data on $A(\lambda)$ for several different nickel oxide-based films. A significant decrease of $A(\lambda)$ was found at short wavelengths for additives being Mg, Al, Si, Zr, Nb, and Ta, whereas films containing vanadium or silver did not show any improvement in their optical properties compared to those of pure nickel oxide. One could note that metals known to form oxides with wide band gaps tend to yield low bleached-state absorbance. Similar beneficial effects were found for Mg addition to electrochromic iridium oxide.⁹

With regard to manufacturing, it is preferable to be able to deposit the films under conditions that make them ready for device lamination, or to have convenient processes for making the as-deposited films prepared for this. In the case of tungsten oxide, one can carry out the deposition in $Ar/O_2/H_2$ according to principles described in the literature.¹⁰ The hydrogen produces a blue color for the as-deposited films, and the key issue with regard to optimizing the gas mixture is to incorporate hydrogen into the film without creating oxygen deficiency. In practice, the optimization of the tungsten oxide films can be made by measuring their color in the as-deposited state.⁵ If these films are to operate in conjunction with nickel oxide-based films, the latter, ideally, should be

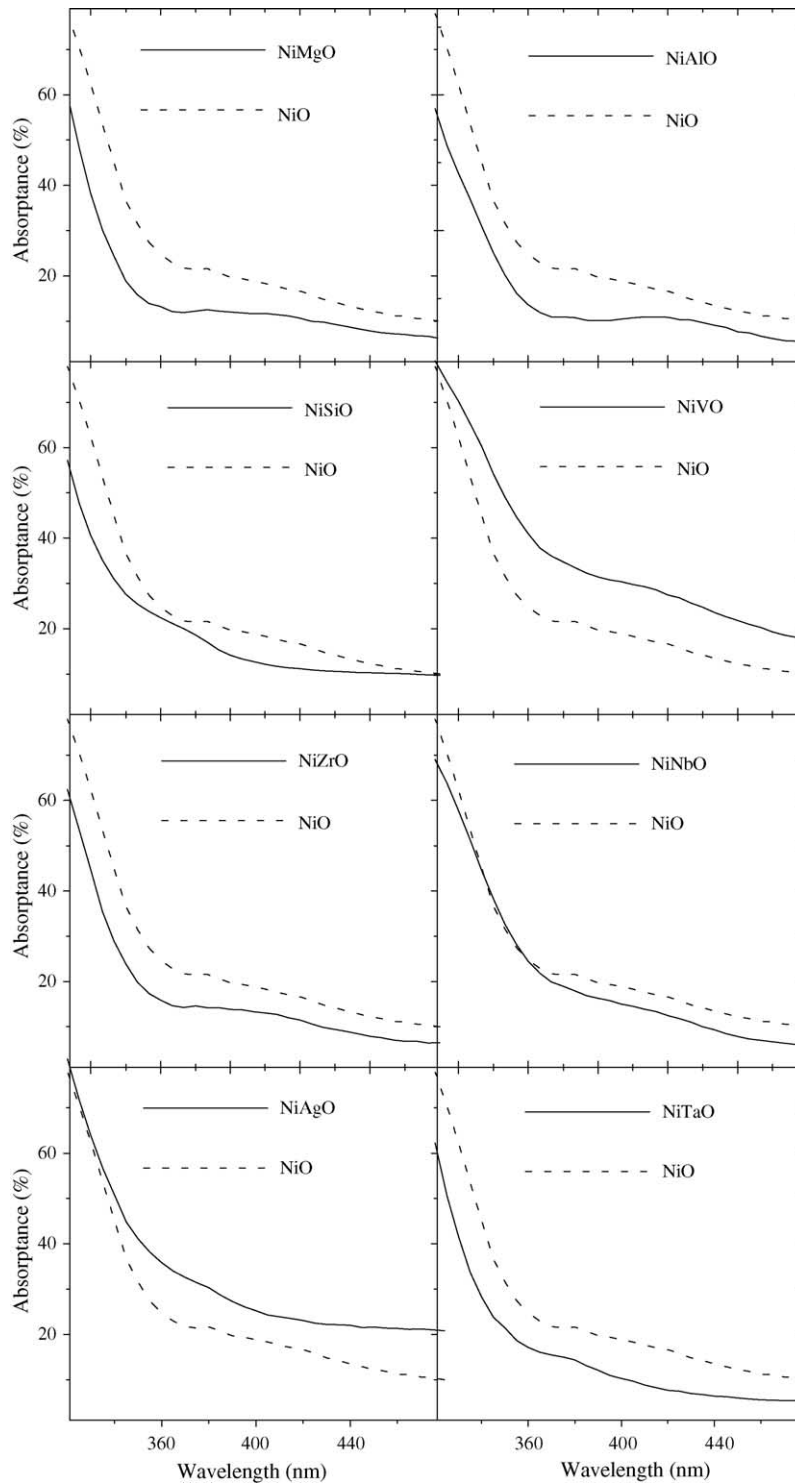


Fig. 3. Spectral absorbance of electrochromic nickel oxide-based films in their bleached state. The designation NiXO (with X being Mg, Al, Si, V, Zr, Nb, Ag, or Ta) indicates that X is present in the oxide but does not specify the amount.

made so that they are prepared for charge insertion prior to device assembly. Such discharged films are dark. However, the nickel oxide-based films normally are transparent in their as-deposited state and hence require pre-treatment before device lamination. Charge insertion via an electrochemical procedure is possible, in principle, but obviously unwieldy and

not suited for practical manufacturing. An alternative method for discharging, as discussed next, employs exposure to ozone obtained by ultraviolet irradiation of the film in the presence of oxygen.¹¹

Fig. 4 displays the decrease of the luminous transmittance, T_{lum} integrated over the eye's spectral sensitivity, as

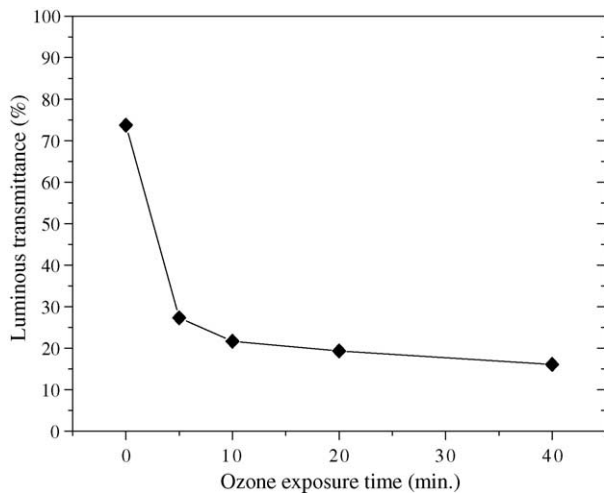


Fig. 4. Luminous transmittance vs. post-deposition ozone exposure time for a 220-nm-thick Ni–V oxide film produced by sputtering in Ar/O₂/H₂.

a function time when a conventional ozone photo-reactor was used to illuminate a 220-nm-thick NiV_{0.08} oxide film. The transmittance drops by some 50% during a few minutes, and a further decrease takes place for extended exposure times.

Polyester-based foils—one with a tungsten oxide film colored by sputtering in the presence of hydrogen and another with a nickel oxide film colored by post-deposition ozone exposure—were laminated together by a PMMA-based electrolyte using roll-pressing at a temperature of 80 °C.¹² The edges of the double foil were then sealed, electrical contacts were attached, and the electrochromic device was ready for testing and use.

Devices of the type described above were cycled between colored and bleached states using trapezoidal voltage pulses between -1.6 and $+1.5$ V, respectively. Fig. 5 shows transmittance at three different wavelengths for cycling with one full color-bleach cycle each 200 s. The optical modulation is

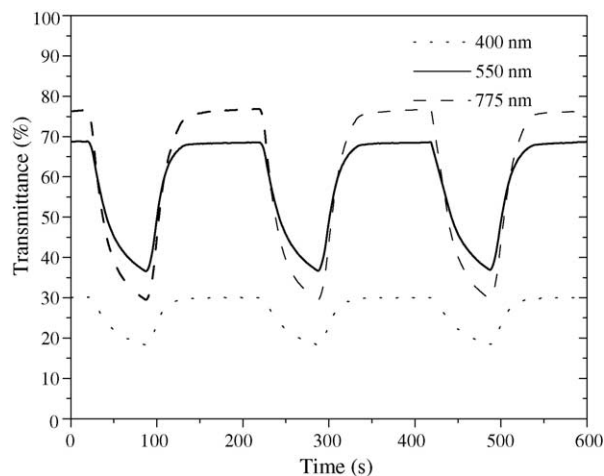


Fig. 5. Transmittance at three wavelengths vs. time for electrochromic switching of a laminated device described in the main text.

pronounced, especially for mid-luminous and red light. Most of the changes take place within a few tens of seconds after application of the pulse, but the coloration has not reached saturation even after several minutes. The foils are seen to change between a high level of about 70% and a low level of 35–40% at a wavelength of 550 nm. The span between the colored and bleached states has been shown to remain practically unaltered for at least 10,000 cycles in properly constructed devices. Lower transmittance levels, down to 25% or less in the colored state, could be reached for longer coloration times. It should be noted that the possibility of increasing T_{lum} by adding a wide band gap oxide to the Ni oxide has not yet been implemented for the investigations reported here. The devices have open circuit memory, which is an asset since electrical power must be drawn only to effect changes in the optical properties.

The work reported above has demonstrated techniques to produce flexible electrochromic foils with sufficient optical modulation range, dynamics, and durability for making them interesting for a range of applications, such as in smart windows with large energy efficiency (provided that their control strategy is adequate¹³). Other applications concern electrochromic foils in variable-transmittance eyewear, such as visors and goggles. Driving or riding safety, as well as comfort, require different transmittance levels for varying lighting conditions, and properties such as those illustrated above are excellent for these applications.

4. Conclusion

The first part of this paper briefly reviewed a large number of electrochromic devices for modulating optical properties. Some data were given on all-solid-state devices as well as on polymer-laminated devices, with and without self-powering by integrated solar cells. A number of designs were found capable of large optical modulation, as well as dynamics and durability sufficient for applications. A specific, flexible polyester-based device incorporating electrochromic tungsten oxide and nickel oxide was then discussed. The exposition covered, among other things, gas treatments for pre-charging of the individual electrochromic films in order to make them ready for facile device assembly, and enhancements of the bleached-state transmittance through additions of certain wide band gap oxides to nickel oxide.

References

- Granqvist, C. G., *Handbook of Inorganic Electrochromic Materials*. Amsterdam, Elsevier, 1995 (reprinted 2002).
- Granqvist, C. G., Electrochromic tungsten oxide films: review of progress 1993–1998. *Solar Energy Mater. Solar Cells*, 2001, **60**, 201–262.
- Granqvist, C. G., Avendaño, A. and Azens, A., Electrochromic coatings and devices: survey of some recent advances. *Thin Solid Films*, 2003, **442**, 201–211.

4. Granqvist, C. G. and Hultåker, A., Transparent and conducting ITO films: new developments and applications. *Thin Solid Films*, 2002, **411**, 1–5.
5. Azens, A., Gustavsson, G., Karmhag, R. and Granqvist, C. G., Electrochromic devices on polyester foil. *Solid State Ionics*, 2003, **165**, 1–5.
6. Azens, A., Avendaño, E., Backholm, J., Berggren, L., Gustavsson, G., Karmhag, *et al.*, Flexible foils with electrochromic coatings: Science, technology and applications, *Mater. Sci. Eng. B*, in preparation.
7. Avendaño, A., Azens, A., Niklasson, G. A. and Granqvist, C. G., Electrochromic nickel-oxide-based films with minimized bleached-state absorptance. In *Electrochromic Materials and Applications, Vol PV 2003-17*, ed. A. Rougier, D. Rauh and G. A. Nazri. The Electrochemical Society, Pennington, USA, 2003, pp. 80–90.
8. Avendaño, E., Azens, A., Niklasson, G. A. and Granqvist, C. G., Electrochromism of nickel oxide films containing Mg, Al, Si, V, Zr, Nb, Ag, or Ta. *Solar Energy Mater. Solar Cells*, 2004, **84**, 337–350.
9. Azens, A. and Granqvist, C. G., Electrochromism in Ir–Mg oxide films. *Appl. Phys. Lett.*, 2002, **81**, 928–929.
10. Giri, A. P. and Messier, R., Physical structure and the electrochromic effect in tungsten oxide films. *Mater. Res. Soc. Symp. Proc.*, 1984, **24**, 221–227.
11. Azens, A., Kullman, L. and Granqvist, C. G., Ozone coloration of Ni and Cr oxide films. *Solar Energy Mater. Solar Cells*, 2003, **76**, 147–153.
12. Wixwat, W., Stevens, J. R., Andersson, A. M. and Granqvist, C. G., An adhesive polymer electrolyte for electrochromic smart windows: optical and electrical properties of PMMA–PPG–LiClO₄. In *In Second International Symposium on Polymer Electrolytes*, ed. B. Scrosati. Elsevier Appl. Sci., London, 1990, pp. 461–465.
13. Azens, A. and Granqvist, C. G., Electrochromic smart windows: energy efficiency and device aspects. *J. Solid State Electrochem.*, 2003, **7**, 64–68.