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# ELECTROCHEMISTRY IN ELECTROCHROMISM-MANIFESTATION BY TRANSITION METAL OXIDES

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*The study of electrochromism of thin films of organic (conducting polymers such as pthalocyanine, polyaniline and polypyrrole) as well as inorganic materials such as $WO_3$, $NiO_x$, $IrO_2$ and transition metal cyanides such as prussian blue and its analogues, is gaining importance in recent years. A great deal of work is carried out to understand the mechanism of colour change, structure and composition of electrochromic films, physical and electrochemical stability, electrochromic reversibility and assembled cell durability. Among the choice of materials, transition metal oxides and mixed metal hexacyanoferrates of the prussian blue family offer themselves as good candidate materials because of their good stability and their ability to act as complementary system to each other. In this work, a state-of-the art report on the developments in the field of electrochromic systems on transition metal oxides is presented.*

*Keywords: Electrochromism, electrochemical stability.*

## INTRODUCTION

Electrochromics can be defined as a colour change induced in a material by an applied electric field or current. Some of the mechanisms which can produce colour change in solids or liquids in presence of an electric field include (a) formation of colour centres when electrons are injected in solids as a result of electron trapping (b) charge transfer from one type of impurity centre to another (c) electric field inducing a shift in absorption band (and hence colour) due to a tunnelling process (Franz-Keldysh effect), and (d) electrochemical redox reactions associated with colour changes [1].

### Electrochromic devices (ECDs)

The growing interest in electrochromic materials is mainly due to their possible commercial application in displays, sensors, cameras and windows. Electrochromic materials used in windows require an electrically conducting surface on the glass, such as indium-tin oxide (ITO), that is transparent to visible light. Electrochemical reactions occur on the conductive surface and produce a darkening of the glass, hence the amount of light that is transmitted into or out of an interior space can be easily regulated. This provides a user-controlled tinting of windows in automobiles, houses and other buildings that regulates glare; solar heating and privacy by a simple touch of a switch. The major problem preventing the large scale application of this technology is that long term stability has not been demonstrated for any electrochromic material. Many electrochromic substances can not survive the required long exposure to sunlight moisture or electrolyte solvents.

The Navy's interest in electrochromic materials is for missile applications in seepers that require automatic light intensity control. Mechanical devices are subjected to failures resulting from G-force stresses and the wear and corrosion of moving parts. Electrochromic systems have no moving parts and are limited by the stability of the materials and the reversibilities of the electrochemical reactions. Missile applications require a faster switching time (1 Hz) and a smaller size (5 $cm^2$) than required, for commercial applications such as windows. However, long-term stability (5 to 10 years) and good reversibility (100,000 cycles) are important requirements for missile applications. Another requirement is that

the light transmitted by this device should have good optical clarity.

### Device applications

The electrochromic phenomena in thin films of transition metal oxides have diverse applications from smart windows to neural networks. Some of the typical applications are:

i) electrically controllable window glass in architectural uses

ii) rear-view mirrors for automobiles

iii) truly absorptive displays

iv) high-resolution electrophotographic devices, using a combination of electrochromic and photoconductive layers

v) electron beam lithography, using differential etching of colored and uncoloured films

vi) photoelectrochemical energy conversion and storage; and

vii) solid state reprogrammable analog resistive devices for neural networks with full parallelism and self-learning capabilities.

### Electrochromic transition metal oxides - Tungsten oxide

Dark blue uniform thin films of $WO_3$ on ITO glass is prepared by potential cycling between -0.4 V and -0.7 V at 50 mV/s or by applying pulse voltage between -0.5 V and 0.25 V. Films are fragile and needed a heat treatment for at least one hour at $130^0$ before further use. Films are stable for ~ 3000 cycles in $LiClO_4$/PC between bleached (1.0 V) and coloured (-1.0 V) states vs Ag/AgCl.

### Cobalt oxide

Electrochromic films of cobalt oxide are also formed by electrodeposition from aqueous solution [2-4] using simple solutes such as $Co(NO_3)_2$ or $COCl_2$ in the initial deposition solution. A novel green product is reportedly attainable by this method - one of the few wholly inorganic systems to show such a colour and is formed using negative potentials [4]. The electrochromic transition is green to brown and is represented as follows:

$$\underset{\text{(Green)}}{3CoO} + 2OH^- \longrightarrow \underset{\text{(Brown)}}{Co_3O_4} + 2e^- + H_2O \qquad (1)$$

In a different electrodeposition procedure, cobalt is oxidatively dissolved in $H_2O_2$ [4]. The electrochromism of cobalt (III) oxyhydroxide CoO.OH has also been described [2].

Alternatively films of $LiCoO_2$ may be prepared by thermal evaporation, RF sputtering spray pyrolysis or sol-gel techniques [5]. The product of RF sputtering using powdered $LiCoO_2$ and slow deposition has the best optical properties [6]. Such films are polycrystalline [7,8], electron transfer to the $LiCoO_2$ electrochrome immersed in a $LiClO_4$-propylene carbonate solution results in electrochromic colour change from deep brown to transparent accompanied by removal of $Li^+$ [9].

### Indium tin oxide

ITO is a familiar, semiconducting thin film used as a conductive coating in the construction of optically transparent electrodes [10-13]. The intrinsic electrochromism of ITO is weak, the ITO film being colourless when oxidised and a very pale brown colour following reduction. Steele et al. [14-16] quote the contrast ratio of ITO as 7:1 with $Li^+$ as the inserted ion.

$$\underset{\text{Colourless}}{In_2O_3} + 2x\,(Li^+ + e) \longrightarrow \underset{\text{Pale brown}}{Li_{2x}\,In^{III}_{(1-x)}\,In^{I}_{2}O_3} \qquad (2)$$

Irreversible insertion can cause the failure of ITO based devices. The lack of reversibility may possibly be due to the formation of a thin surface layer of In as reduction product on the electrolyte facing side of the film [17].

ITO films can be prepared by electron beam sputtering [16] or RF sputtering [17,18]. ITO has been incorporated into ECDs as a counter electrode material [13,14,19,20] rather than as the primary electrochrome, because of its inherently weak electrochromism. Also, the movement of $Li^+$ species through the lattice is rather slow, diffusion coefficient = $6 \times 10^{-13}$ to $5 \times 10^{-14}$ $cm^2\ s^{-1}$ [13] or $1 \times 10^{-11}$ $cm^2\ s^{-1}$ [21]. Further operational problems also occur. Moisture levels must be minimised if ITO is to be used as a counter electrode since with $H_2O$ present, over-reduction occurs readily, forming elemental metal as the product. The use of anhydrous electrolyte

overcomes this problem. Secondly, low charge metal species within the reduced ITO are relatively soluble and leach into solution [22,23].

### Iridium oxide

The iridium oxide used in ECD devices is actually hydrated as iridium hydroxide $Ir(OH)_3$. The mechanism of colouration is still uncertain and two different reaction routes have been proposed. The first is based on cation loss [24,25].

$$Ir(OH)_3 \longrightarrow InO_2 + H_2O + H^+ + e^- \qquad (3)$$

(Colourless) (Blue/Grey)

while the second is based on anion insertion.

$$Ir(OH)_3 + OH^- \longrightarrow IrO_2.H_2O + H_2O + e \qquad (4)$$

Irrespective of whether the mechanism is hydroxyl insertion or proton extraction, $Ir(OH)_3$ is the bleached form of the oxide and the coloured form is $IrO_2$ [26-28].

There are two common methods of film preparation: electrochemical growth making anodic iridium oxide films (AIROF's) and sputtered iridium oxide films (SIROF's) are reported. Anodically grown films [24-27,29-33] are made by the potentiostatic cycling between -0.25 V and +1.25 V of an electrode in an iridium containing solution, commonly in an electrolyte of 0.5 M $H_2SO_4$ [24]. AIROF's have a contrast ratio as high as 70:1 and response times of 20-40 ms, which are faster than for tungsten or vanadium oxides in ECD's. They may be cycled for more than $10^6$ times. Solid state AIROF's have been made in which the electrolyte is polymeric, but these have slower response times [33].

Anodically grown films of iridium oxide [34] deposited by a periodic reversal of the electrolysis potential, with an aqueous iridium sulphate complex as precursor are pronounced [34] to be better than SIROFs. Blue SIROFs are reported to be very much similar to AIROFs in being totally decolourisable and in terms of write-erase response times and absorbance spectra, the similarity being confirmed by cyclic voltammetry [28].

### Molybdenum trioxide

Films of molybdenum trioxide can be formed by anodic oxidation of molybdenum metal in acetic acid [35] or by vacuum evaporation [36-38]. Films may also be deposited electrochemically from an aqueous solution prepared by dissolution of molybdenum metal in hydrogen peroxide [39]. Electroreduction of $MoO_3$ yields bronzes

$$MoO_3 + x\,(M^+ + e^-) \longrightarrow Mx\,MO^{VI}_{(1-x)}\,Mo^{V}_{x}\,O_3 \qquad (5)$$

(Colourless) (Blue)

with the distorted rhenium trioxide structure. Colour in the reduced state of $MoO_3$ is attributable to [37] an intervalence transition between $Mo^V$ and $MO^{VI}$ in the solid molybdenum bronze. Molybdenum bronzes show an improved open circuit memory (c.f. tungsten bronzes) with $H_xMoO_3$ films with similar values of x [40,41] leaving a colouration range of about 0.4 V before hydrogen gas evolves, the range for $WO_3$ is 0.5 V.

### Nickel oxide

Hydrated nickel oxide undergoes electrochromism involving a colourless reduced form and a dark brown oxidised form [40].

$$NiO_xH_y \longrightarrow [Ni^{II}_{(1-z)}\,Ni^{III}_{z}]\,O_x\,H_{(y-z)} + ZH^+ + 2e^- \qquad (6)$$

Nickel oxide films are typically amorphous, or microcrystalline to a slight extent; as determined by X-ray diffraction. Such films may be prepared by spraying aqueous nickel chloride [42] or nickel nitrate in aqueous butanol on to hot ITO [43]. A more common method of forming nickel oxide is RF sputtering [44-48] using an argon/oxygen gaseous mixture. Such films are deposited in their coloured state, but may be completely decolourised after only a few write-erase cycles [49] to become colourless or pale green. The colouration efficiency of RF sputtered nickel oxide is -36 $cm^2\ C^{-1}$. Films may also be prepared by DC sputtering [50,51], although the electrochromic properties of such films are easily harmed by warming [51]. Vacuum deposition of nickel oxide is difficult.

An alternative method of preparing $NiO_x$ films is electrodeposition, for example using an optically transparent electrode (OTE) immersed in (slightly alkaline) aqueous nickel nitrate [52-55] or using nickel sulphate solutions [56,57]. Films may be

grown by cathodising or cycling the potential [58] such films have colouration efficiencies as high as 50 $cm^2$ $C^{-1}$ [53] but a rather poor cycle life [59].

A study of the colouration process by Raman Spectroscopy [60] shows that formation of defective crystal structure appears to be a prerequisite for electrochromism. The reduced form of the oxide contains some $Ni^{3+}$ and water is trapped at the defects. In separate studies by Corrigan et al. [61] evidence from both electrochemistry and spectroscopy was found for the presence of quadrivalent nickel in the oxidised form of nickel oxide.

Most prototype electrochromic devices containing hydrated nickel oxide employ the film as the secondary electrode, for use in a complementary electrochromic sense, usually with tungsten trioxide [40] as the primary electrochromes. ECDs constructed with $Ni(OH)_2$ as the primary [40,53,56] have several advantages over conventional electrochromes like $WO_3$ in having excellent durability even in water, high contrast ratios of as much as 70:1 and most importantly is being inexpensive.

### Vanadium pentoxide

Vanadium pentoxide films may be prepared by evaporation in vacuo [37,62,63] or more commonly by reactive RF sputtering [64-68] using a high pressure of oxygen and a target of vanadium metal. Spin coating has also been used [69,70]. The electrochromic reaction is

$$\underset{\text{Pale blue}}{M_xV_2O_5} \longrightarrow \underset{\text{(Brown/yellow)}}{V_2O_5} + x\,(M^+ + e^-) \qquad (7)$$

where $M^+$ is usually $Li^+$. Thin film of $V_2O_5$ dissolves readily in dilute acid. Alternative electrolytes such as LiCl in anhydrous methanol [71] or $LiClO_4$ in propylene carbonate [64,65,67] are also used.

Cyclic voltammetry of sputtered $V_2O_5$ as a thin film supported on an OTE in a lithium-containing propylene carbonate electrolyte shows two well-defined quasireversible redox couples with anodic peaks at 3.26 and 3.45 V and cathodic peaks at 3.14 and 3.36 V relative to the $Li/Li^+$ couple in propylene carbonate [65]. These two pairs of peaks may correspond to the two phases of $Li_xV_2O_5$ identified by Dickens and Reynolds [72]. Since the electrochromic colours of $V_2O_5$ films are yellow and blue, the contrast ratio for such films is not great, hence the system is being investigated for possible use in ECDs as the secondary electrochromic layer counter electrode [62,64,65].

### Other oxide systems

There are several oxides which are electrochromic in nature, but are associated with inherent drawback which restrict their application for device fabrication. A summary on such oxide system is provided in what follows.

### Cerium oxide is electrochromic [73]

$$\underset{\text{Yellow}}{CeO_2} + x\,(M^+ + e^-) \longrightarrow \underset{\text{(very pale blue)}}{M_xCeO} \qquad (8)$$

Since the colour change is not intense and the movement of ionic charge through the oxide is slow this material is unlikely to have any electrochromic applications except as a secondary electrochrome.

Although films of iron oxide are electrochromic [74,75] the slight electrochemical irreversibility they evince will probably preclude their utilisation as viable electrochromes. For example, yellow/green films form on the surface of iron electrodes anodised while immersed in 0.1 *M* NaOH [75]. This coloured material is thought to be hydrated Fe(III)OOH. The film becomes transparent at cathodic potentials as hydrated $Fe(OH)_2$ is formed.

The electrochromic process in manganese oxide is complicated but appears to involve proton uptake:

$$\underset{\text{(Yellow)}}{MnO_2} + 2e^- + 2H^+ \longrightarrow \underset{\text{(Brown)}}{MnO_{(x-2)}\,OH_{(2)}} \qquad (9)$$

The coloured brown form of the oxide prevails at potentials more anodic than 0.8 V while the bleached yellow form occurs below 0.0 V. The electrochemistry of electrochromic $MnO_2$ films is complicated since deep cycles cause a loss of electrochromic activity. The intense electrochromic colour of the brown material is attributable to an optical transition between $Mn^{3+}/Mn^{4+}$ centres [76]. Raman Spectroscopic investigation of

electrodeposited $MnO_x$ films concluded that films were unsuitable for electrochromic applications owing to poor reversibility.

Among other oxides tried for ECD fabrication mention can be made of niobium pentoxide [77,78] palladium oxide [79], rhodium dioxide [80,81], ruthenium dioxide [82], titanium oxide [83]. These oxide films have low colouration efficiency and are not viable electrochromes for ECD inclusion. Niobium oxide shows promise as secondary electrochromes [77,78].

### Mixed metal oxides

Recently, many workers have prepared films of metal oxide containing other metal oxides. Such mixtures are often said to be 'doped'. The presence of even small amounts of a guest oxide within the electrochrome host can have profound effects on the spectroscopic characteristics of the material, its conductivity and the potential window available for electrochromic operation.

### Cobalt oxide mixtures

Cobalt oxides doped with Cu, Ni, Mo, W and Zn have been prepared by electrodeposition from an aqueous solution containing equimolar cobalt and dopant cation [4,84]. Incorporation of additional metal oxides greatly increases the colouration efficiency of the cobalt oxide and the product of reduction is more blue than for the pure CoO host. The films are also physically stronger. The diffusion coefficients D are generally much larger in mixed M/Co oxide films than in cobalt oxide alone. Notably, mixed metal oxide electrochromes containing cobalt colour cathodically while CoO itself colours anodically.

### Molybdenum trioxide mixtures

A film of the general formula $Mo_{(1-x)}W_xO_3$ is formed if molybdenum trioxide is co-evaporated in vacuo with tungsten trioxide. The wavelength maxima of mixed oxides following reduction are shifted relative to the pure oxides to higher energies [85,86]. For such mixed oxide films in the reduced state, the relationship between $\lambda_{max}$ and the quantity of charge injected appears complicated [49]. For a device prepared with the mixed film, the response time to produce a given contrast ratio will be correspondingly faster than for pure oxide films and the energy consumption of mixed oxide films will also be smaller. The observed decrease in electron mobility within mixed metal oxide films [86] is not thought to be deleterious to device performance.

### Nickel oxide mixtures

Corrigan et al. [3,87] have reported the preparation of nickel oxide films in which other transition metal cations are co- precipitated along with nickel during deposition, using an aqueous alkaline solution of $Ni(NO_3)_2$, together with the relevant metal in the ratio 10:1. Corrigan included the additional metal ions Ag, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Pb and Y [88]. Films containing tungsten can also be formed [84,90]. In all cases, the reduced films were essentially transparent, while the oxidised films exhibited intense, broad absorption bands throughout the visible region [3].

Such coprecipitation is stated to have a considerable effect on the switching speed of the electrochromic nickel couple [3]. Ce- Cr and La improving the colouration rate, while Ce-Cr and Pb cause slower bleaching [3]. Films containing yttrium have very slow colouration times (Ca. 10s) and films containing silver exhibited complicated behaviour [3]. Significantly for electrochromic display applications, coprecipitation of cerium or lanthanum ion appears to improve film durability [3].

### Tungsten trioxide mixtures

Electrochromic films of $WO_3$ have often been doped with metals such as platinum and gold [91]. $WO_3$ has also been doped with the oxides of barium [92] cobalt or nickel [89,90,93] molybdenum [94] tin [95] and titanium [96]. It has been shown that the oxide of Ag, Co, Cr, Cu, Fe, Mo, Ni, Ru or Zn can each be incorporated into a $WO_3$ matrix [90]. Film containing silver and copper are not very useful as they tend to form metallic products during reduction rather than yielding the desired doped oxide product. Films containing Co, Ni or Zn were the most promising in terms of contrast ratio and durability, and protonic diffusion through the oxide was also rapid.

$WO_3$–$TiO_2$ films have also been made either by sputtering [97] or using sol-gel intermediates [96,97].

Electrochromic $HNbWO_6$ in sulphuric acid has a similar transparent-to-blue electrochromic operation to $WO_3$ but with a superior stability to dissolution [98,99].

### Vanadium oxide mixtures

Vanadium pentoxide containing copper, silver or gold has been formed by laying down alternate layers of the constituents during vacuum evaporation of thin-film samples [100]. Films containing gold are superior to Ag-$V_2O_5$ or Cu-$V_2O_5$ films. Au-$V_2O_5$ is deposited as a green material, the colour becoming yellow after calcination at > 573 K. The electrochromism reported for Au-$V_2O_5$ has a possible colour change violet-to-green in the potential range -0.8 V to +1.2 V. A new red/violet colour was also observed at potentials below about -1.0 V.

Both Ag and Cu containing films were orange after calcination. On reduction Cu-$V_2O_5$ becoming dark brown, Ag- $V_2O_5$ turning blue/green. Cr-$V_2O_5$ and $NbV_2O_5$ have also received attention [101] as have $TiO_2$–$V_2O_5$ films made by a sol-gel process [102] or spin coating [103].

### Miscellaneous metal oxide mixtures

Electrochromic mixture of cerium oxide with either titanium dioxide or zirconium dioxide have been prepared via sol-gel intermediates [104]. Similarly $CeO_2$–$TiO_2$ films may be made by a dip coating procedure [105]. Iridium ruthenium coating electrodeposited on titanium is electrochromic [106].

Ternary oxides of the type $(Li_2B_4O_7)_{1-x}$ $(WO_3)_x$ [107] or sintered $(WO_3)_x$ $(Li_2O)_y$ $(Mo)_z$ (where M = Ce, Fe, Mn, Nb, Sb or V) [108], and oxides of the type Mx M'y $W_{(1-x-y)}$ $O_3$ (M,M' = Co, Cr, Mo, Ni, Zn) [108] have been reported. These systems show superior colouration efficiencies compared to any of the parent oxides alone.

A different class of mixture is seen when a metal oxide is dispersed in a conducting polymer. For example, tungsten trioxide with a polypyrrole [110,111] or polyaniline matrix has been reported to be electrochromic.

## CONCLUSION

The foregoing review presents a state-of-the-art report on electrochromic transition metal oxides and mixed metal oxides, with special reference to the methods of their preparation and their suitability for electrochromic device fabrication.

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