
CHAPTER - I

INTRODUCTION

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1.1 GENERAL

Electrochromics are an important part of a larger category of switchable materials known as chromogenics [1]. The fundamental property of an electrochromic (EC) material is that it exhibits a large change in optical properties upon a change in either electric field. This optical change results in a transformation from a highly transmitting state to a partly reflecting or absorbing state, either totally or partly over the visible solar spectrum. The term electrochromism was first used in 1961 by Platt [2] when he discussed the shift of absorption and emission spectrum of certain pigments by several hundred angstroms when an electric field was applied.

The practical use of electrochromics has been known since about 1970. During the middle of the 1970's, many small digital information displays were developed, but the technology could not compete with the advance of liquid crystals for displays. Renewed interest in the area of electrochromics started again in the mid 1980's for large area applications such as for automotive mirror and windows for cars and buildings. This area of development has been growing ever since that time.

Electrochromic optical switching devices known as "smart windows" can be used for variety of applications. One of the most promising applications is for the regulation of incident solar energy and glare in buildings, vehicles, aircrafts, space crafts and ships. The world wide production of flat glass is about 1 billion m² per year. In USA alone glass production is about 470 million m² per year (1988), with about 25% for buildings and 11% for automobiles, so the potential for glass based glazing technology is very large. An example in how quickly new glazing products can penetrate the market, in just a few years, low emissivity or low coatings (some of these are transparent conductors) for windows have gained about 25% of the US residential glazing market. These coatings are used to reduce the radiative portion of heat transfer from glass surfaces. Electrochromic products already in the market place are automobile mirrors, which can automatically regulate glare according to light levels. Prototypes are being tested for automobile sun-roofs and visors. Future applications include automobile side and rear windows, architectural glazing and aircraft windows. Chromogenic devices can also be used for large-area information displays in applications where high switching speed is not required, such as for airport display boards. Also electrochromic eye glasses are being introduced as products by Nikon (Tokyo, Japan) in Japan and being developed by Eyeonics (Portland, OR) and PPG (Pittsburg, PA) companies.

The function of an electrochromic device, used in a glazing, is to control the flow of light or solar energy, according to solar energy management scheme or the desire of the user. This technology can regulate lighting and heating levels for energy load reduction [3,4]. Substantial savings in lighting and cooling energy consumption and installed equipment costs can be realized. From privacy point of view, this technology have a significant advantage over existing blinds and drapes. In last few years there has been significant growing interest in this technology and it is expected to be used in products in to the next century.

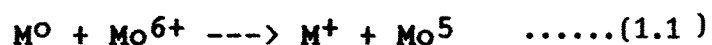
One of the most significant issues is the cost of these devices and the trades-offs between cost and benefit and cost and life time. The electrochromic window cost has been estimated to range from 100-1000 US\$/m². Some companies have set the goals of 100-250 US\$/m².

1.2 SURVEY OF LITERATURE ON MOLYBDENUM OXIDE

Molybdenum trioxide (MoO₃) has been investigated in the form of single crystal and thin films. Studies on electrochromism and photochromism in MoO₃ have been reported by several authors, some of which are cited below. A systematic study on optical and photoelectric properties of single crystals prepared by sublimation method and thin films of molybdenum trioxide were reported by S.K. Deb (1968)

[5] for the first time. The measurements were made on effect of UV irradiation on optical properties of MoO₃ thin films. A broad colour band was observed after UV irradiation. Optical absorption spectra, electrical conductivity and photoconductivity of MoO₃ single crystals and thin films have been reported.

Measurements of e.s.r. and optical spectra of the potassium and sodium molybdenum bronzes have been made in 1967 by P.G.Dickens and D.J.Neild (1968) [6]. In the formation of alkali metal molybdenum bronzes, and electron transfer process takes place as follows,



In 1963, a report on preparation and properties of sodium and potassium molybdenum bronze crystals was made by A Wold et al (1964) [7]. They studied pure MoO₂ crystals were grown by electrolytic reduction of MoO₃-Na₂MoO₄ mixture at 675°C. In addition both sodium molybdenum bronze and potassium molybdenum bronze crystals were grown from molybdenum (VI) oxide alkali molybdate metals under carefully controlled conditions.

Nadkarni and Simmons (1972) [8] investigated a technique, based on stimulated dielectric relaxation currents (DRC), has been used to analyse the defect properties of Al-MoO₃-Al system.

M.R. Tubbs (1974) [9] studied optical properties, colour centers and holographic recording of MoO₃ layers and reported some possible applications of MoO₃ layers in image recording and holography. He prepared the thin layers of MoO₃ by evaporation of B.D.H. "Vactron" material in vacuum at 10⁻⁵ Torr from electrically heated tantalum boats on to glass or silica substrates. He studied optical spectra and colour centers.

R.B. Dzhanelidze et al (1966) [10] studied optical and photoelectric properties of MoO₃ single crystals and thin films, while electron microscope observations of thin platelets of MoO₃ were reported by MoO₃ reported by L.A. Bursi (1969) [11].

Thomas C. Arnoldussen (1976) [12] reported the electrochromism and photochromism in MoO₃ films. He studied electrical properties of amorphous evaporated electrochromic MoO₃ in various ambients.

The MoO₂ and WO₂ were grown by vapour transport using appropriate ratio of metal powder and metal trioxide as starting material, I₂ as transporting agent and growth temperature of 850-925°C and have been examined as electrodes in H₂SO₄ solution, by Jean Horkans and M.W. Shafer (1977) [13].

Electrochemical properties and discharge kinetics

of thin layer hydrous molybdenum oxide were studied by David Elliott (1977) [14]. The layer hydrated molybdenum oxide (oxidation state IV and V) has been deposited electrochemically on a variety of substrates e.g. polycrystalline tin oxide coated glass.

High resolution transmission electron microscopy axial beam illumination was carried out on vacuum deposited WO_3 , TiO_2 and MoO_3 films by Makoto Shiojiri et al (1979) [15]. They showed that atomic structure of amorphous films gets changed to crystalline films by heat treatment Koichiro Hinokuma et al [16] prepared amorphous MoO_3 films by spin coating technique using a solution of peroxopolymolybdic acid. They reported electrochromism in these films and showed that colouration dynamics depends on formation temperature.

Krishnakumar et al have prepared the films by physical vapour deposition and their optical and electrical properties were reported. They found that films exhibit photochromism upon UV radiation.

Brian W. Faughnan (1977) [18] studied optical properties of mixed oxide of WO_3/MoO_3 electrochromic films. The mixed oxide films were made by co-evaporating WO_3 and MoO_3 from separate boats on to glass substrates coated with a conducting Sb-doped indium-oxide film. The electrochromic optical absorption occurs at higher energy than pure oxide.

Table 1.1 : Cathodically Colouring EC Materials

Material	Coloured state	Bleached state	Voltage step V	Colouring and bleaching	Electrolytes	Optical efficiency $\text{cm}^2/\text{Coul.}$	Remarks
WO_3	Blue (1.4 eV)	Trans- parent	0-1.5 to 2	100 ms	Aqueous non- aqueous solids. liquids. $\text{H}^+.\text{Li}^+$	115(633 nm) 75 (550 nm)	most viable
MoO_3	Purplish blue (1.56 eV)	Yellow	-	Bleaching slower than WO_3	Aqueous	Higher than WO_3	High solubil- ility in aqueous elect- rolytes longer open circuit memory than H_2WO_3
WO_3/MoO_3	Blue (2.1 eV)	Transparent	-	-	Aqueous	increase in opt.by 30 to 40 % in the visible region than for WO_3	system better suited to human eye (with peak response at 2.25 eV)
WO_2	Blue	Wine-red	-	Higher than WO_3	Aqueous	Higher than WO_3	stability not confirmed
V_2O_5	Evaporated films greenish blue yellow(low insertion) Blue or yellow black (High insertion) Sputtered purple films Grey		Higher energy required	Higher than WO_3	Li^+ in methanol	Very low as compared to WO_3 & MoO_3	Slower kinetics O.D. low
Nb_2O_5	Dark Blue (3.18 eV)	-	-	1 to 2 5	Aqueous Li^+ in	Low	Evolution of H_2 makes in nonsuitable for displays

...Contd

Material	Coloured state	Bleached state	Voltage step V	Colouring and bleaching	Electrolytes	Optical efficiency $\text{cm}^2/\text{Coul.}$	Remarks
TiO_2	Colourless (2.8-2.9eV)	Blue	0-1.15	-	Aqueous acidic	Low	H_2 evolution nonavailable
W_9NbO_2	-	-	-	More than WO_3 by an order	Aqueous acidic	-	Stability is better than WO_3
WO_3ReO_3	Blue	Colour less	-	Bleaching rate lower than WO_3	-	-	Inhibition to EC colouration
WO_3Au	Pinkred	Blue	-	-	Aqueous	-	Rate of dissolution same as WO_3

Table 1.2 Anodically colouring EC Materials

Material	Coloured state	Bleached state	Voltage step V	Colouring bleaching	Electrolyte	Optical Efficiency cm ² coul	Remarks
Tellurium oxide	Blue black	Metallic background	0.25 to 1.25 (RHE)	30 ms	0.5M H ₂ SO ₄ Li ⁺ , OH ⁻ F ⁻ , CN ⁻	30	-
Rhodium oxide	Dark green	Pale yellow	0.43 to -1.48 (RHE)*	t _{1/2} =20ms t _c =40ms	5 M KOH	20	Colouration peak at high anodic potential and partially evolution
Nickel oxide	Dark	Colourless			weak alkaline	20	
Cobalt oxide	Grey black	Red purple		1	weak alkaline	20	Limited open-circuit memory
Ni-Co (mixed)	Dark blue	Pale blue			weak alkaline		

* Reference hydrogen electrode.

The systematics of the energy shifts as a function of MoO_3 concentration and colouration density was determined.

EC was given wide spread attention through Debs [5] work on tungsten trioxide [19]. Electrochromism has been observed in oxides based on tungsten, molybdenum, nickel, cobalt, irridium, manganese, chromium, vanadium, titanium, niobium, tantalum, several mixed oxides and many organic materials [20]. It has been observed that some of the transition metal oxides exhibit cathodic EC while some exhibit anodic EC. Both anodic and cathodic electrochromic transition metal oxides have potential applications in the technology. Based on these oxides several EC devices have been fabricated. Some of these oxides with their properties and peculiarities are given in table 1.1. and 1.2 [21].

1.3 PURPOSE OF DISSERTATION

Layer systems with variable optical properties, especially with controllable light absorption, are of high interest for construction of displays and of transparent and reflecting optical instruments, and much effort is presently put into the development of systems which can overcome the deficiencies of the well-known liquid crystal devices.

Inorganic electrochromism is a very promising alternative since it offers various favourable properties e.g. sharp and nearly angle independent, high contrast,

continuously variable intensity of colouration, storage of information without energy supply, low driving voltage, sufficient colouration and bleaching rates, and a wide range of operating temperatures.

MoO₃ is a transparent, partially ionic 4d transition metal oxide material and survey of literature reveals that, it has a number of interesting optical and electrical properties, longer open circuit memory and high colouration optical efficiency than that of WO₃. which is widely used for EC device fabrication.

Various techniques such as vacuum evaporation [5,15] anodic oxidation [22], physical vapour deposition [17], spin coating [16] electrochemical deposition [14] and electrolytic reduction have been used to prepare these films. However, reports on preparation of MoO₃ films by spray pyrolysis technique (SPT) are not available, in the literature. It is observed that the physical properties of MoO₃ films are strongly dependent on the method of preparation. EC properties are also much dependent on the method of fabrication, as morphology, porosity, water content, crystallinity, optical and electrical properties of the films are critically sensitive to preparation conditions.

In the present work, it is planned to prepare MoO₃ films employing spray pyrolysis technique SPT is a

simple and inexpensive and hence requires less capital to deposit thin films over large areas than other conventional techniques and hence offers a possible solution for lowering the cost of these devices SPT also offers an advantage in controlling structure (amorphous/polycrystalline) of the film. It is an opportunity to control the crystal size and the microstructure and to reach a balance so that films with both good stability and fast kinetics can be made. The properties of films can be varied by changing the deposition parameters, which facilitates the preparation of films with desired properties.

The preparative parameters, like substrate temperature, spray rate, concentration of spraying solution etc. are optimised in order to obtain good quality films. These films have been characterised by means of structural, electrical and optical measurement techniques.

The electrochromic cell has been prepared for the study of the electrochromic characteristics. It consists of two F.T.O. coated glass plates, one plate has been deposited with MoO_3 film, which acts as a working electrode and other plate as a counter electrode. The cell was filled with H_2SO_4 solution.

Electrochromic properties of the cell are studied by using cyclic voltammetry, chronoamperometry, spectral transmittance, optical absorption, XRD etc techniques.

REFERENCES

- 1] C.M.Lampert, Solar Energy Mater. 11 (1984)
- 2] J.R.Platt, J.Chem.Phys. 34 (1961) 862
- 3] S.Selkowitz and C.M. Lampert, in : C.M. Lampert and C.G.Granqvist (Eds.), large area chromogenics : materials and devices for transmittance control (optical Engineering Press SPIE) Bellingham, WA 1990) p.504
- 4] S.Reilly, D.Arastch and S.Selkowitz, Thermal and optical analysis of switchable window glazings, solar Energy mater. 22 (1990) 1
- 5] S.K.Deb, Proc. Roy Soc. A 304, (1968) 211.
- 6] P.G.Dickens and D.J. Neild, Transactions of Faraday Society 65 (1968) 13
- 7] A. Wold, W.Kunnmann, R.J. Arnott and A.Ferretti Inorganic chemistry 3 (4) (1964) 545.
- 8] G.S.Nadkarni and J.g. Simmons, J.Appl.Phys. 43 (9) (1972) 3741
- 9] M.R.Tubbs, Phys. Stat. Sol. (a) 21, (1974) 253.
- 10] R.B.Dzhanelidze, I.M Purtse;adze. L.S Khitarishaili R.I. Chikovani and A.L. Shkolnik Soviet Phys.- Solid State 7, (1966) 2082
- 11] L.A.Bursill, Proc. Roy.Soc. A,311 (1969) 267.
- 12] Thomas C.Arnoldussen, J.Electrochem. Soc. 123(4) (1976) 527
- 13] Jean Horkans and M.W.Shafer, J.Electrochem. Soc. 124 (8) (1977) 1202.

- 14] David Elliott, J.Electrochem. Soc. 124,(8)(1977)1243
- 15] M. Shiojiri, T.Miyano and Chihiro kaito, Japanese Journal of Appl.Phys. 18 (10) (1979) 1937.
- 16] K.Hinokuma, A.Kishimoto and T.Kudo, J.electrochem. Soc. 141 (1994) 876.
- 17] S.Krishnakumar and C.S.Menon, Bull.Mater.Sci. 16 (3) (1993) 187.
- 18] B.W. Faughnan and R.S.Crandall, Appl.Phys. lett. 31 (12) (1977) 834.
- 19] S.K.Deb, Phil Mag. 27, (1973) 801.
- 20] C.G.Granqvist Physics of Thin Films Advances in Research and Development Mechanic and Dielectric Properties Vol.17 Edited by Maurice H. Francombe and John L Vossens Academic Press Inc. (1993) p.303
- 21] S.A. Agnihotri, K.K.Saini and S.Chandra Indian Journal of Pure and Applied Physics, 24(1986) 19.
- 22] M.R.Arora and r.Kelly J.Electrochem. Soc. 124(1977) 1493.