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CHAPTER - II

**THEORETICAL BACKGROUND**

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## 2.1 THE BASIS TO ELECTROCHROMISM

Electrochromism (EC) is based on the formation of deep blue coloured bronzes from colourless oxides of polyvalent metals, as tungsten and molybdenum and relatively negative metals, an alkaline and alkali earths, or hydrogen, according to equation 2.1.



where  $0 \leq x \leq 1$

This reaction has been known for more than 160 years, was extensively investigated by Glemser in the forties [1,2] and first applied for optical purposes by Deb around 1970 [3]. More than 40 different bronzes have been synthesized [4]. Above equation is nonstoichiometric reaction i.e. X can be varied continuously from 0 to unity. Bronzes are thus partially reduced oxides of polyvalent metals which contain the cations of the reducing element and belong to the mixed valency compounds [5]. It is unique feature of some bronzes, e.g. lithium, sodium and hydrogen tungsten bronzes with small X, which is basically important for their application in all solid state electrochromic systems, that the cations are built into the oxide nearly without changing the volume of the solid phase [6]. In the case of alkali and hydrogen tungsten bronzes this is

achieved by a conversion of the distorted rhenium trioxide structure of tungsten trioxide into perovskite structure of the tungsten bronze, in which the alkali or hydrogen ion  $[M^+]$  are in the twelve fold coordination with oxides [7]. This, however, is a simplified picture, the actual structural changes are more complicated, particularly in the amorphous state of vapour deposited  $WO_3$  layers, which are applied in electrochromic devices, and with hydrogen as reducing element [8]. Detailed structural data, however, are lacking even for crystalline bronze [9,10].

The formation of alkali and hydrogen tungsten, as well as molybdenum bronzes is reversible.



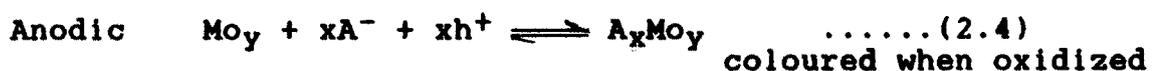
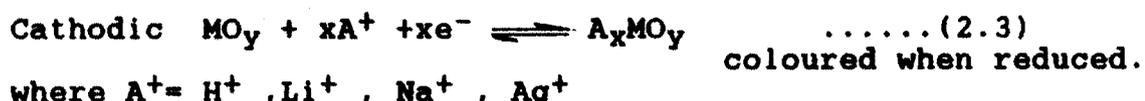
which is the prerequisite for their application in electrochromic devices. The position of the equilibrium (eq.2.2) is dependent on the standard free enthalpy of formation and on the relative concentrations, or mole fractions, of the components. The free enthalpies of formation of hydrogen (at  $X > 0.7$ ) and of lithium and sodium bronzes of tungsten and molybdenum are negative [11]; their magnitudes at a given  $X$  depends on the form in which the reducing elements are offered to the  $MoO_3$  i.e. whether the bronze is formed from the elements.  $M$ , its cation and an electron  $M^+ + e^-$  or its solvated cation and an electron,  $M^+ \cdot (solv) + e^-$ . This dependence is especially strong with hydrogen bronze because of the large standard enthalpies of

dissociation,  $1/2 \text{H}_2 \rightarrow \text{H}$  (+218 kJ/mole) [12], ionization,  $\text{H} \rightarrow \text{H}^+ + \text{e}^-$  (+ 1308 kJ/mole) [13], and hydration,  $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$  (-710 kJ/mole) [13] and  $\text{H}_3\text{O}^+ + n\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ (\text{hydr})$  (-401 kJ/mole) [13].

## 2.2 DEFINITION OF ELECTROCHROMISM :

Electrochromism and electrochemichromism are exhibited by a number of materials, both inorganic and organic liquids and solids. EC materials are able to change their optical properties in a reversible and persistent way under the action of a voltage pulse [14]. This change can be due to the formation of colour centres (or defect complexes) or to an electrochemical reaction that produces a coloured compound. Electrochromic colouration has been demonstrated in both anodic and cathodic devices. An electrochromic material must possess both ionic and electronic conduction. An electrochromic device can consist of many configurations depending on property requirements. The basic elements of an electrochromic device are two conductor layers to inject charge, an active electrochromic layer, an electrolyte or ion conductor (which may in some cases be an insulator) and an ion storage media which may be the (counter electrode) electrolyte, another electrochromic layer or may even be an integral part of the conductor layers. This sandwich configuration allows a reversible reaction to cycle between the electrochromic material and ion storage media, with

simultaneous injection\* of electrons or holes and protons or ions, depending on the material. An example of this process in  $\text{MoO}_3$  is shown in Fig. 2.1 and Fig.2.2 e.g. in an inorganic solids the ion-insertion reaction might be,



where  $\text{A}^- = \text{F}^-, \text{CN}^-, \text{OH}^-/\text{H}^+$   
and  $x$  is generally  $0 < x < 1$

### 2.3 MICROSTRUCTURAL ASPECT :

Some basic microstructural features are of decisive importance for electrochromism and leads to electronic band structure models capable of explaining, why certain materials become absorbing under ion insertion while others becomes transparent under ion insertion, i.e. why they can display cathodic and anodic electrochromism. Mo oxide crystals are built up from corner sharing  $\text{MoO}_6$  octahedra, as schematically illustrated in Fig.2.3 and 2.4. The oxide has a tendency to form sub-stoichiometric shear phases containing edge sharing octahedra. The crystal structures have been clearly displayed by high resolution electron microscopy. Open hexagonal phases are of particular relevance for electrochromism. The spaces between  $\text{MoO}_6$  octahedra are large enough to accommodate ions, i.e. the Mo oxide framework serves as an excellent intercalation/deintercalation host Fig.2.4 shows the positions for the intercalated ions

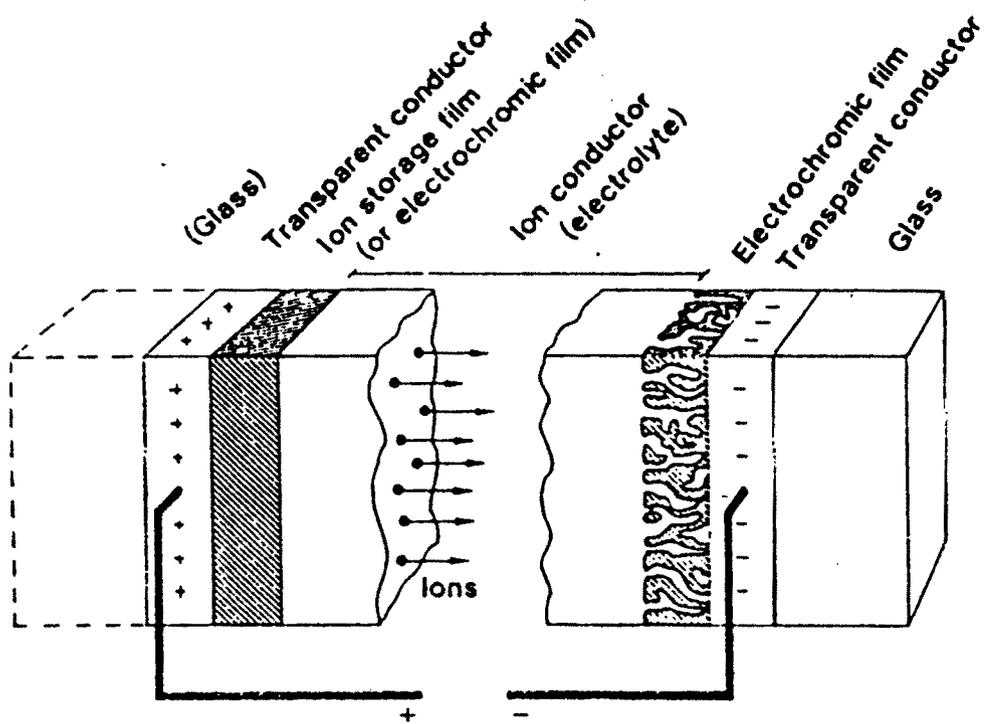


Fig.2.1 : Basic Design of An Electrochromic Device, Indicating Transport of Positive Ions Under Action of Electric Field.

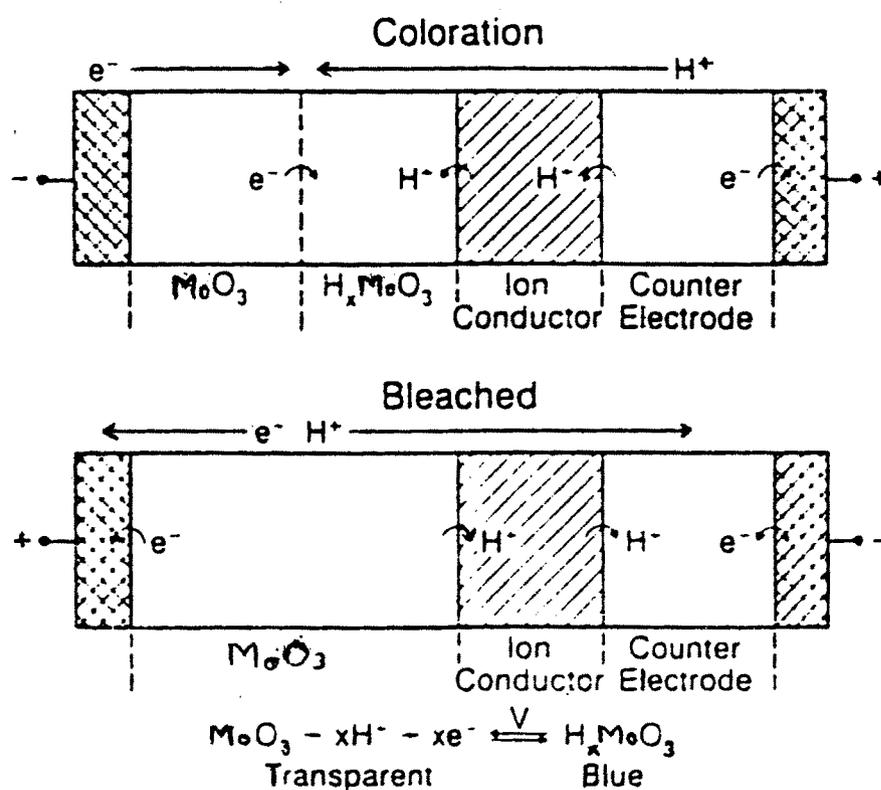


Fig.2.2 : Schematic of Colouration and Bleaching Reactions Within  $\text{MoO}_3$ . During Colouration the Reaction Proceeds with Injection of Protons and Electrons. During Bleaching Protons and Electrons are Depleted From the  $\text{H}_x\text{MoO}_3$  Layer.

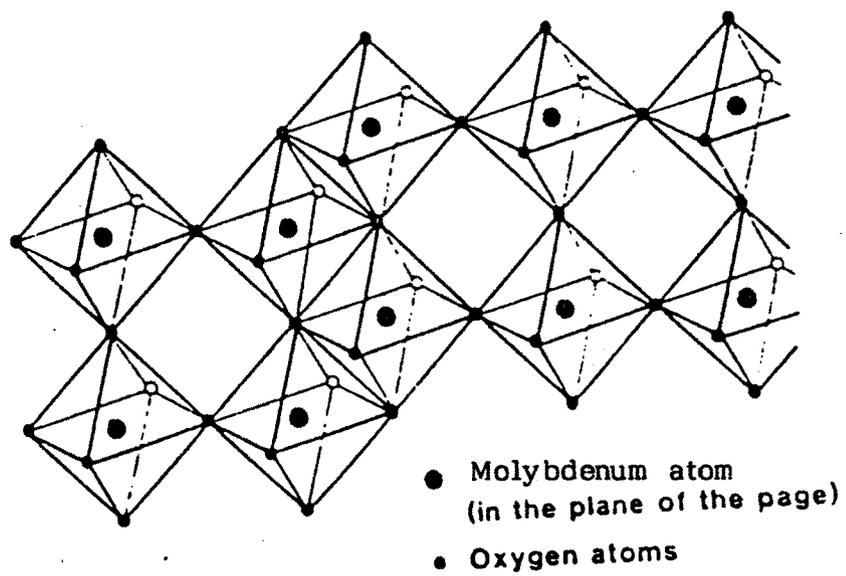


Fig.2.3 : Schematic Illustration of A Corner-sharing and Edge Sharing Arrangement of Octahedra in a Mo oxide Crystal.

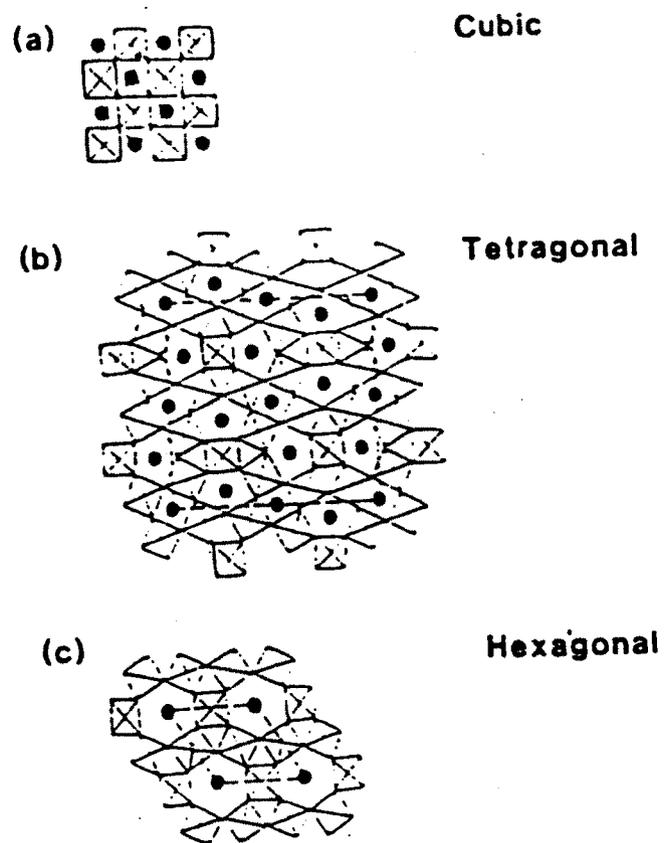


Fig.2.4 : Atomic Arrangements for Crystalline W oxide (a) Cubic (Perovskite), (b) Tetragonal, and (c) Hexagonal Structure Dots Indicate Sites Available for Ion Insertion. Dashed Lines Mark the Boundary of the Unit Cell.

in Mo oxide with three different crystal structures. Small ions ( $H^+$ ,  $Li^+$ ,  $Na^+$ ) can be accommodated in the cubic configuration, and ions upto the size of  $K^+$  can be incorporated in the tetragonal configuration while ions as large as  $Rb^+$ ,  $Cs^+$  and  $NH_4$  can be included in the hexagonal phase.

Electrochromism is associated with ion insertion/extraction processes that can be represented, by,



where Me - metal atom.

$I^+$  is a singly charged small ion such as

$H^+$  or  $Li^+$

$e^-$  is an electron

$n$  depends on the particular type of oxide e.g.  $n$  is 3 for defect perovskites, 2 for rutiles, 1.5 for carborundums, and 1 for rock-salts. Hence the electrochromic oxides can be divided into three main groups with regard to their bulk crystalline structures as Perovskite-like, rutile like and layer and block structures. They are discussed in this order below

#### The Perovskite Structure :

General composition  $CMeO_3$  is shown in Fig.2.5 . The Me ions occupy the corners of a primitive unit cell and O ions bisect the unit cell edges, C is the central atom. The corresponding defect perovskite  $MeO_3$  configuration is often referred to as rhenium oxide structure. It can

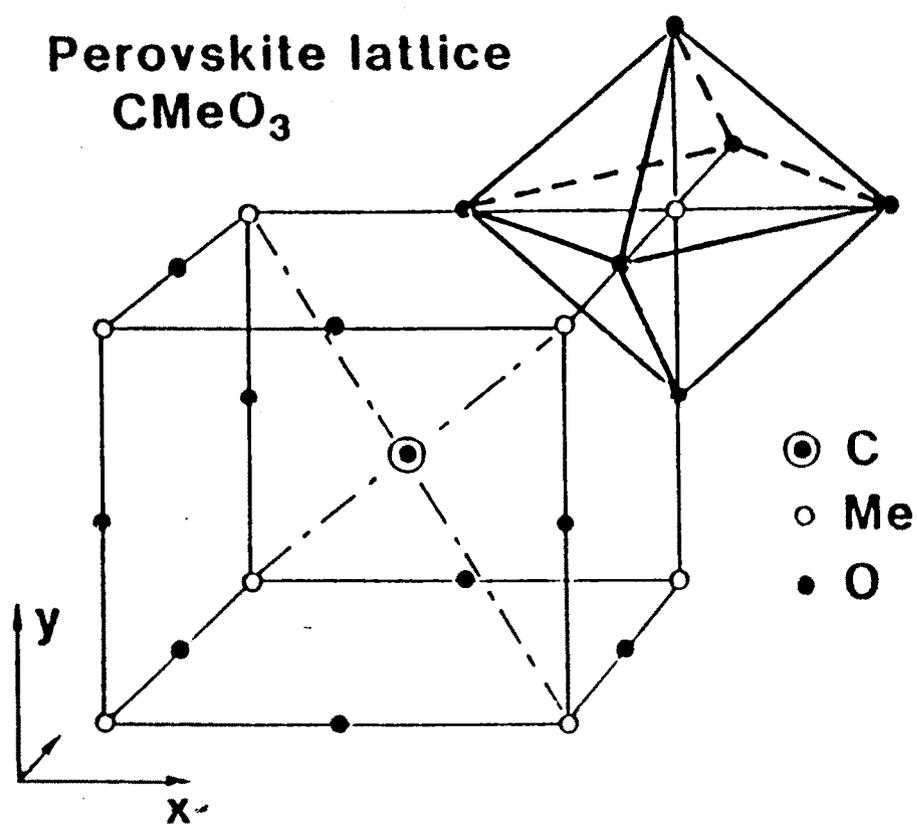


Fig. 2.5 Unit cell for the perovskite lattice.

visualise as an infinite frame-work of corner-sharing octahedra each with a metal ion surrounded by six equidistant oxygen ions. In between these octahedra there are extended tunnels that can serve as conduits and intercalation sites for small ions. Molybdenum oxide  $\text{MoO}_3$ , displays cathodic electrochromism [15]. Bulk crystals at room temperature have a structure consisting of corner-sharing chains of  $\text{MoO}_6$  octahedra that share edges with two similar chains; these layers are stacked in staggered arrangement and are held together by weak Vander Waal's forces. This unique structure is called the  $\alpha$ - phase. There is also a  $\beta$ -phase, that can be viewed as a metastable analogue of  $\text{WO}_3$ , which is of perovskite-type. Available data on thin films of Mo oxide strongly indicate that the structure is built from corner-sharing  $\text{MoO}_6$  octahedra in much the same way as for electrochromic tungsten oxide [16].

The rutile structure of at least a rutile like configuration, is present for a whole series of materials exhibiting cathodic or anodic electrochromism. The ideal structure can be thought of as built from almost octahedral  $\text{MeO}_6$  units forming a framework with infinite edge-shared chains. These chains are arranged so that they form an equal number of ideal vacant tunnels.

Titanium oxide  $\text{TiO}_2$ , can have different crystal structures. The anatase phase, which so far has attracted, most interest in connection with electrochromism, consists

of infinite planar double chains of  $\text{TiO}_6$  octahedra; these chains are connected by corner-sharing. Pronounced cathodic electrochromism has been observed [17].

Manganese oxide,  $\text{MnO}_2$ , has a crystal chemistry of great complexity. Most structures are built from edge shared  $\text{MnO}_6$  octahedra that share corners with other chains. The most common structures have tunnels with sizes (in units of  $\text{MnO}_6$  chains on each side) being 1 X 1 in  $\beta\text{-MnO}_2$  (rutile, or pyrolusite) 2 X 1 in ramsdellite, and 2 X 2 in  $\alpha\text{-MnO}_2$  (hollandite). An intergrowth phase between the pyrolusite and ramsdellite structures is known as  $\gamma\text{-MnO}_2$  (nsutite). Electrochromism was discovered recently, and ion insertion was found to lower the absorption [18].

Vanadium dioxide,  $\text{VO}_2$  is of rutile-type (tetragonal) above  $68^\circ\text{C}$  and is monoclinic below this temperature. Vanadium dioxide films are electrochromic and show a decrease of the absorptance under ion insertion irrespective of the temperature being below or above  $68^\circ\text{C}$  [19].

Ruthenium oxide,  $\text{RuO}_2$ , has rutile structure. Ions can be inserted and extracted, but the material remains absorbing no matter the ionic content [20].

Iridium oxide,  $\text{IrO}_2$ , is another rutile material. It is electrochromic and in contrast with the electrochromic

oxides discussed so far is clearly anodic and can go from an absorbing to a transparent state under insertion of one ion per formula unit [21]. Rubidium oxide,  $\text{RuO}_2$ , shows many similarities with Ir oxide, and ion insertion is able to lower the absorption significantly [22].

The layer and block structures form a somewhat undefined group of electrochromic materials, Niobium oxide,  $\text{Nb}_2\text{O}_5$ , has complex crystal chemistry. Various phases can be thought of as built from blocks (or columns) of  $\text{NbO}_6$  octahedra arranged in a  $\text{ReO}_3$  structure; structures conventionally denoted R- $\text{Nb}_2\text{O}_5$ , M- $\text{Nb}_2\text{O}_5$ , N- $\text{Nb}_2\text{O}_5$  and H- $\text{Nb}_2\text{O}_5$  are characterized by blocks of different sizes and interconnections. A structure derived from corner-sharing rutile blocks is designated B- $\text{Nb}_2\text{O}_5$ . Niobium oxide is electrochromic and goes from a transparent to an absorbing state upon ion insertion [23]. Tantalum oxide,  $\text{Ta}_2\text{O}_5$  has many properties in common with  $\text{Nb}_2\text{O}_5$ .

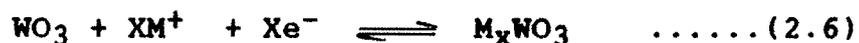
Among the cobalt-oxide related materials, both  $\text{HCoO}_2$  and  $\text{LiCoO}_2$  are of interest. The latter material can be represented as a layered rock-salt with alternate planes of Co and Li atoms. Both of these species are surrounded by six O in octahedral co-ordination; the  $\text{CoO}_6$  octahedra are compressed and the  $\text{LiO}_6$  octahedra are elongated.  $\text{HCoO}_2$  has a similar, though not identical, crystal structure. Absorption develops upon extraction of protons [24] or lithium ions [25].

Hydrous nickel oxide shows pronounced anodic electrochromism and goes from an absorbing to a transparent state under proton insertion [26]. The material is thought to contain layers of NiO<sub>6</sub> octahedra sharing edges, and the protonated transparent material is probably of brucite type, Ni(OH)<sub>2</sub>.

Vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>, can be described as consisting of distorted VO<sub>6</sub> octahedra or, alternatively and more properly, as consisting of square pyramidal VO<sub>5</sub> units. The latter representation highlights the layered structure. Vanadium pentoxide films are electrochromic and show a somewhat increasing overall absorption upon ion insertion [27]. They are capable of multi-colour electrochromism due to an apparent bandgap widening when ions are intercalated.

#### 2.4 SURVEY OF COLOURATION METHODS

Electrochromic colouration takes place upon ion intercalation and simultaneous electron injection, as in reaction



A similar colouration can be accomplished by several other means and it is suitable to look at these colouration schemes jointly. There are several reasons why this is convenient : one is that the underlying physics is similar so that a broad exposition of the colouring schemes for electrochromic films paves the way towards the

theoretical discussion that follows : another reason is that several colouration mechanisms can operate in parallel, which is of considerable relevance for some applications [28].

Fig.2.6(a,b,c,d,e,f,g,h) illustrates eight different ways to colour tungsten oxide, as well as examples of ensuing optical properties. It should be noted at the outset that all of these colouration schemes lead to broad and intense absorption bands peaked at an energy  $E_p$  between 1.5 and 0.9 eV.

Fig.2.6 shows the evolution of the spectral absorption coefficient when a charge density  $Q$  is inserted into a W oxide film from a  $H_2SO_4$  electrolyte [28]. An absorption band centered at nearly 1.3 eV increases monotonically upon increased  $Q$  and reaches a maximum absorption coefficient for intercalation of  $H^+$ ,  $Li^+$  and  $Na^+$  in many investigators.

Fig.2.6b shows "electrocolouration" which takes place when an electric field of  $\approx 10^4$  V/cm is applied along the film surface [3]. The colouration is associated with the permeation of ambient gas. UV colouration, illustrated in Fig.2.6c, is caused by irradiation with photon energies greater than  $E_g$ . Irradiation in air gives a rather weak absorption band [3] whereas a much stronger band can be accomplished by irradiation in an organic vapour [29].

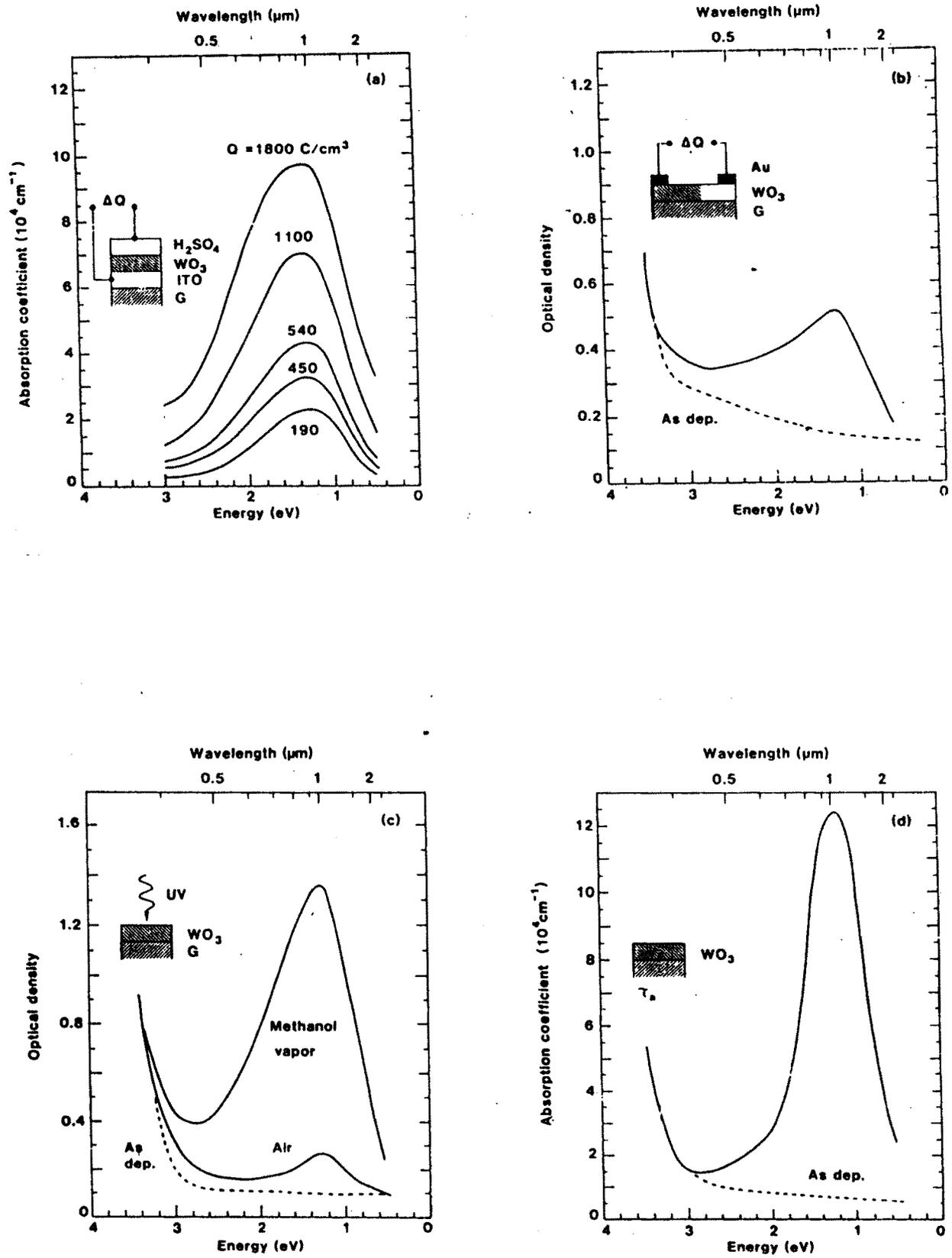


Fig.2.6 : (a,b,c and d)  
Survey of Colouration

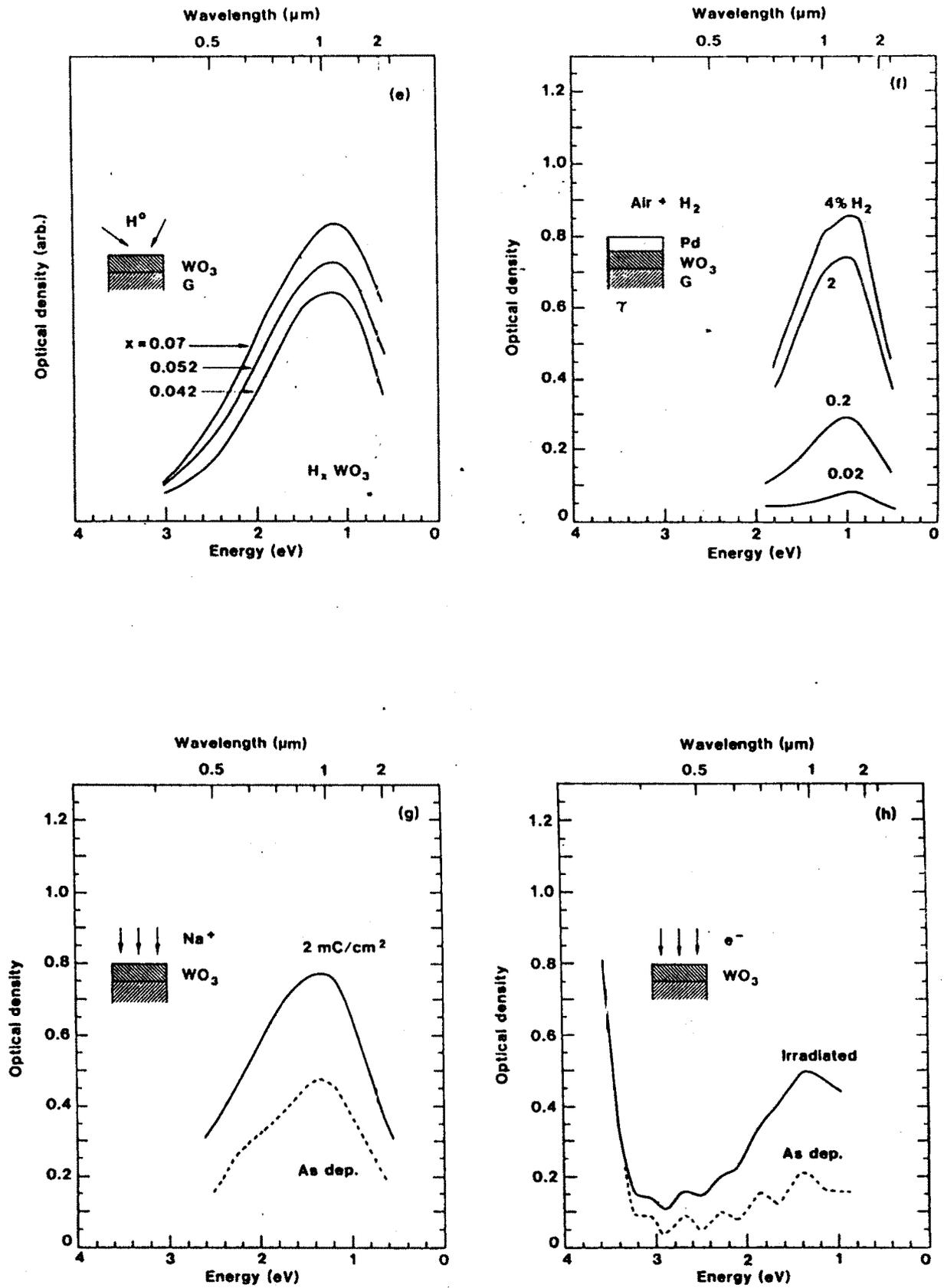


Fig.2.6 : (e,f,g and h)

*Handwritten note:* The effect of (e) ...

Survey of Colouration

Colouring upon vacuum annealing, shown in Fig.2.6d, may be termed "thermocolouration" [30]. Fig.2.6 e shows the colouration that occurs when a W oxide film is exposed to atomic hydrogen ( $H^{\circ}$ ) obtained, for example, from a mixture of HCl and Zn [31]. In a somewhat related technique, illustrated in Fig.2.6e shows the colouration occurs when a W oxide film is exposed to atomic hydrogen  $H^{\circ}$  obtained, e.g. from a mixture of HCl and Zn [31]. In a somewhat related technique, illustrated in Fig.2.6f,  $H_2$  gas is brought in contact with Pd layer on top of a W oxide film [32]. The Pd decomposes  $H_2$  catalytically, and  $H^{\circ}$  is ejected. The technique may be referred to as "Pd spillover" or "Hydrochromism". The film analyzed in Fig.2.6f had been deposited on to a hot substrate, which explains why  $E_p$  lies at  $\approx 0.95$  eV. Finally, W oxide films can be coloured by direct exposure to an ion beam [33] or an electron beam [34] as seen from Fig.2.6g and 2.6h.

## 2.5 CLASSES OF ELECTROCHROMIC MATERIALS

There are three general classes of electrochromic materials. (1) Transition metal oxides (primarily hydrous) (2) organic and (3) Intercalated materials. Within each class there are differences in morphology, liquid or solid phase, crystal structure, degree of order, and stoichiometry for each electrochromic material. There are also differences in device configuration and whether a solid or liquid ion conductor is used.

connected between 2 and 5 . With negative voltage on 2, colouration takes place and on reversing the polarity bleaching occurs.

Application of field during colouration brings about simultaneous injection of cations from the electrolyte and electrons from the transparent conducting coating. As a result of the electrochemical reaction (2.3) the film becomes blue.

The direction of reaction depending upon the sign of the applied voltage. The blue colour is associated with the formation of bronze. Despite different ways of preparation and difference in the metal ions injected into the particular EC films, all have essentially the same colour or optical absorption band. Thus, the nature of the injected ion does not appear to play an essential role in colouration; it enters the film only for charge compensation.  $\text{MoO}_3$  being an ion insertion material, with the insertion of cations, internal emf is developed, during colouration, the current flow is opposed by this internal emf. The current ceases when internal emf is equal to applied voltage. This sets up a limit for the minimum voltage to be applied. During bleaching, the developed internal emf is in the same direction as that of the applied voltage.

The colouration and bleaching phenomena are thus asymmetric. In colouration charges are injected while in

The bulk of the research published to date concerns transition metal oxides [35] within this large classification are some distinctions. The most popular system appears to contain the VI-B oxides. In this group are  $\text{WO}_3$  and  $\text{MoO}_3$ . Also, the group VIII oxides are within this category, where most of the parent metals belong to the platinum group (Pt, Ir, Os, Pd, Ru, Rh). Also, iron, cobalt and nickel are in the group VIII category. Currently, four of the group VIII oxide materials are known to exhibit electrochromism; electrochromism.  $\text{Ir}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{Rh}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{NiO} \cdot n\text{H}_2\text{O}$  and  $\text{Co}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . Unrelated oxides such as  $\text{V}_2\text{O}_5$  and doped  $\text{SrTiO}_3$  also show electrochromism. The remaining oxides may have electrochromism that is yet to be demonstrated. Candidates are  $\text{Pt}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{PtO}_2$ ,  $n\text{HV}_2\text{O}$ ,  $\text{PdO} \cdot n\text{H}_2\text{O}$  and possibly  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . Other important categories are organic compounds and intercalated materials. For the organic groups, the viologen, pyrazoline, lanthanide phthalocyanide, and anthraquinone groups and conductive organic polymers exhibit electrochromism.

## 2.6 CONFIGURATION OF ELECTROCHROMIC CELL

The sketch of a typical electrochromic (EC) cell with a liquid electrolyte is shown in Fig.(2.7). It is a sandwich structure in which 1 and 1' are glass plates, 2 is transparent conducting coating, 3 is the EC film, 4 the electrolyte and 5 the counter electrode. A battery is

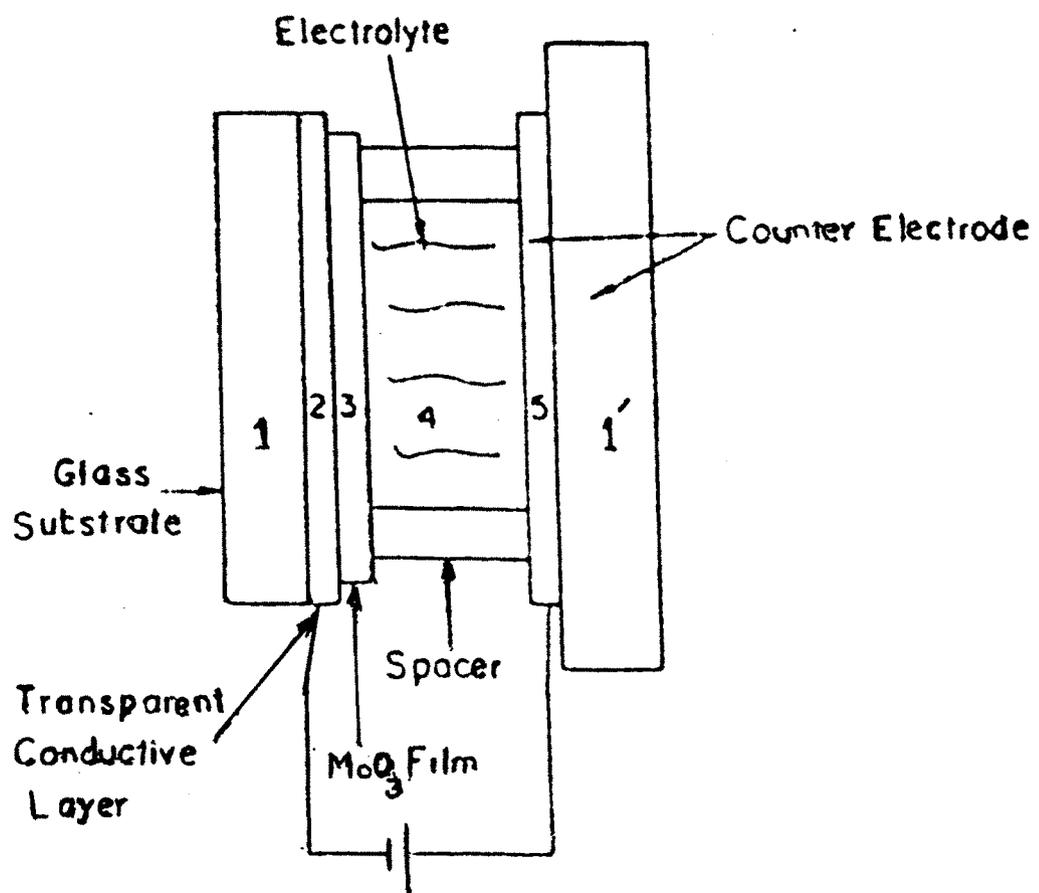


Fig.2.7 : Sketch of a Typical Electrochromic Cell with a Liquid Electrolyte

bleaching charges are extracted. The time required to colour or bleach a film is governed mainly by mobility of the injected ions at the film-electrolyte interface and in the film itself, as well as the internal emf due to ion insertion. Many factors such as nature of an electrolyte and counter electrode, morphology and water content of the electrochromic film etc. contribute to these parameters and their choice is very critical in an EC cell. The electrolyte can be solid or liquid and is usually of low pH, serving as a sink of the cations. The counter electrode can be metallic or coloured film itself. The properties of the electrolyte and the counter electrode, which control the speed, life and constant voltage operation of a typical EC cell, need vital consideration.

#### 2.6.1 ELECTROLYTES

Electrolyte is a large reservoir of cations which are needed for injection into electrochromic films for charge compensation during colouration. Proper choice of an electrolyte is very important for practical applications. The resulting EC cell should have fast response, reasonably long stability and reversibility. In view of this, the criteria for an electrolyte selection are :

- 1) high ionic conductivity and negligible electronic conductivity
- 2) wide temperature range for operation.

- 3) high electrochemical stability with respect to electrochromic films
- 4) high decomposition potential
- 5) high diffusion coefficient of cations in the electrolyte

Protons have highest mobility as compared to other cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ag}^+$  etc. and should lead to fastest EC cell. Protonic electrolytes have high conductivity also. Most of the work reported is on proton insertion from an acidic aqueous electrolyte. The electrolyte mixture had glycerol added to  $\text{H}_2\text{SO}_4$  in some cases to bring down the volatility and white pigment powders such as  $\text{TiO}_2$   $\text{VO}$   $\text{ZrO}_2$  were added to create a white diffuse background. Diffusion coefficient for protons was found to increase with degree of hydration of  $\text{WO}_3$  films while the long term chemical and electrochemical stability against dissolution was found to be adversely affected. Hydrated evaporated films immersed in an electrolyte of 10:1 glycerine :  $\text{H}_2\text{SO}_4$  in a sealed sample showed a dissolution rate of 25  $\text{A}^\circ\text{C}$  per day [36]. Further, colour-bleach cycling increased considerably the rate of dissolution. As a result, sulphuric acid based systems have short-cycle and short range lives. Commercially viable EC cells thus must have electrolytes free of sulphuric acid and preferably in a solid form. Most of the recent work reported is in this direction.

In such systems have hydrated dielectric films as electrolytes. In the fabrication process, layers of electrochromic material, the dielectric material and reflecting material (as a counter electrode) are coated by thermal evaporation successively using materials such as  $\text{Cr}_2\text{O}_3$  [37],  $\text{SiO}$  [38],  $\text{LiF}$  [39],  $\text{ZrO}_2$ ,  $\text{Ta}_2\text{O}_5$  [40], and  $\text{MgF}_2$  [41]. The response times of these EC cells were almost the same as that of EC cells with liquid electrolytes, which indicates the similarity in the mechanism. However, because of high electrical resistance at the solid electrode/electrolyte interface, strong fields were necessary. It is believed that water in the insulating layers is dissociated by the applied electric field, thereby providing the protons for coloration. This aspect shortened the life of the EC cells. Another unique problem with these EC cells was that of depositing a transparent conductor on to the EC film without altering the stoichiometry and hence the EC activity of the EC films.

EC cell with mixed oxides containing  $\text{Cr}_2\text{O}_3$  as electrolytes were investigated by Shizukuishi et al [42]. Long memory effect and low power dissipation were attained in EC cells with  $\text{Cr}_2\text{O}_3 : \text{V}_2\text{O}_5$  (50 wt %). This was attributed to stabilization of the coloured species in the electrolyte layer resulting from the changes in structure. The phenomenon of gradual reduction in contrast was observed under constant voltage operation, which was undesirable from

the practical point of view.

Hydrogen uranyl phosphate tetrahydrate  
( $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ) is solid proton conductor whose performance  
has been examined by Howe et al [43].

It was anticipated that the electrochemical stability of systems (EC cell) based on aprotic electrolytes would be improved to a large extent and work progressed to develop such systems. Since the colouration properties of EC material does not differ on insertion of  $\text{Na}^+$ ,  $\text{Li}^+$  or  $\text{Ag}^+$  instead of  $\text{H}^+$ . Various systems based on these ions have been investigated to a large extent. The electrochemical stability increases due to the use of these electrolytes. However, response time decreases because of low ionic conductivity and low diffusion rates of the ions. Lithium based system offer other advantages viz longer memory and resistance to oxidation compared to their proton counterparts. A higher voltage range can be used for  $\text{Li}^+$  based systems as compared to proton based systems. However, at high  $\text{Li}^+$  concentrations problems of  $\text{Li}^+$  metal precipitation may arise. The main drawback viz. the slow response, has been overcome by adoption of some of the newly developed techniques and hence  $\text{Li}^+$  based systems have shown promise for use in practical commercial devices.

Insertion of  $\text{Li}^+$  is reported to be useful with both liquid and solid electrolytes. Amongst liquid electro-

lytes, a typical combination is that of  $\text{LiClO}_4$  electrolyte propylene carbonate or dimethyl formamide. Care is to be taken to remove water from the non-aqueous solvents. Amongst all the systems, the combination of  $\text{LiClO}_4$  + propylene carbonate is most widely studied. Reversibility of the electrochromic process and enhancement of both colouring and bleaching kinetics were shown to be strongly dependent on water content in this electrolyte and in  $\text{LiClO}_4$  -dioxolene-water electrolyte [44].

#### 2.6.2 COUNTER ELECTRODE

The counter electrode is another part of an EC cell which is equally important as the electrolyte. The internal emf developed during colouration and bleaching depends on the nature of the counter electrode. The function of the counter electrode is to convert ionic conduction in the electrolyte to electronic conduction by electrochemical reaction and to store cations during the bleaching cycle. If the electrochemical reaction is not reversible, the response time and the life time of an EC cell deteriorate. Thus an ideal counter electrode should have the following properties

- 1) Non polarizing for ionic current flow
- 2) good conductivity for electrons
- 3) chemical stability with respect to the electrolyte
- 4) large capacity to store cations
- 5) reversible electrode reaction or small potential change

A counter electrode with such properties will have a long life and fast operation at a stable applied voltage. Most metal electrodes such as Pb, Pt, Ni, Ag, Au which are good conductors of electrons, are polarizing for ion-current flow. They show gradual decay in current because of depletion of cations in the electrolyte near the electrode. Current can be increased by applying higher voltages. Which might be accompanied by evolution of gases degrading the EC cell seriously.

Another commonly used [45] electrode is graphite painted on conductive substrates. Graphite because of its porous structure, provides a large surface area which is beneficial for colouration process. Complete polarizability is shown by fresh graphite electrodes in acidic electrolyte. Generally, with this electrode, relatively higher voltages are needed. The potential of a graphite counter electrode varies with long term operation and hence when subject to operation with a simple, constant drive voltage, non-uniform colouration between segments is observed. This demands setting up of a complicated drive.

The ideal non polarizable counter electrode is  $H_xWO_3$  for the proton based systems. While the alkali metal bronze is used for  $Li^+$  and  $Ni^+$  ion systems. It is found, that these counter electrodes gradually lose their colour leading to short life times for the device.

Recently EC cell with counter electrodes made up of iron-graphite mixture [46],  $\text{Fe}_2(\text{WO}_4)_3$  graphite mixture [47] or  $\text{FeK}_x\text{Fe}(\text{CN})_6$ -graphite mixture [47] (the latter two sintered on to NESA glass ) have been proposed. These are reported to be stable enough to drive at constant voltage. Reports are also available on the different counter electrode materials such as steel wire, Pt [50],  $\text{SnO}_2$  coated glass [51], ITO doped within or zinc oxide [52].

The cation storage capacity of the counter electrode has been increased by using high surface area carbon [48]. these electrodes can be easily fabricated in sheet form with standard paper making techniques and have the additional advantage of being reasonably good electron conductors. The low open-circuit voltage observed usually with this counter electrode was increased to a desired value by incorporating  $\text{MnO}_2$  in the electrode. Reasonably good shelf life and cycle life have been achieved.

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