CHAPTER- II

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2.1 History of Electrochromism

Optical effects of various kinds have been studied for centuries in transition metal compounds. One example is prussian blue, a hexacyanoferrate that was discovered by Diesbach in 1704 in Berlin [1]. This material is an excellent dye having electrochromic properties. It can be changed reversibly between deep blue and transparent states by ion intercalation / deintercalation process.

Tungsten trioxide plays a special role in electrochromism. The stoichiometric material is yellowish to greenish in bulk form. It can be chemically reduced to produce a blue compound, Berzelius [2] reported as early as in 1815 that the colour change took place when hydrogen was passed over gently warmed tungsten trioxide. Colour changes obtained by reacting tungsten oxide with sodium were reported in 1924 by Wohler [3].

Electrochemical, rather than purely chemical reduction of tungsten oxide has also been studied extensively for many years. In particular, the work done by Kobosew and Nekrassow in 1930 [4], who found that tungsten oxide powders could coloured blue by electrochemical reduction in acidic solution. A reversible colour changes during electrochemical treatment of sodium tungsten bronzes, were mentioned in 1951 by Brimm et al. [5].

A first step towards an electrochromic device was taken in studies on the colouration associated with electrolytic reduction of artificially produced particulate molybdenum and tungsten oxide layers. Such layers were proposed in 1942 for applications to 'electrolytic recording paper' by Talmey [6].

The work cited thus far, did not lead to wide spread interest in electrochromism. In 1969, however, the situation was changed by Deb's publication of a widely known and cited paper [7]. It was subsequently followed by a more detailed account of electrochromism in W oxide films [8]. Those two papers mark the beginning of the scientific and technical enquiry into electrochromism. The term 'electrochromism' was introduced by Platt [9] to represent electric-field dependent changes in optical absorption spectra of organic dye molecules dissolved in organic solvents.

Electrochromism in niobium oxide was reported by Palmik et al. in 1974 [10]. Palmik's paper quotes patent specifications and 'USSR Author's certificates' dating back to 1963, which makes it likely that an electrochromic effect had been documented in Nb oxide well before the widely known work by Deb. Electrochromism in Nb was mentioned in 1977 by Witzke and Deb [11].
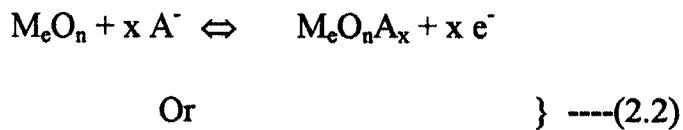
2.2 The basis of Electrochromism

Electrochromism is based on the formation of coloured compound from oxides of polyvalent metal upon insertion or extraction of small ion like H^+ or OH^-, Li^+, F^- etc., according to the following equation

For cathodically material:

$$M_eO_n + x A^+ + x e^- \Leftrightarrow A_xM_eO_n \qquad (2.1)$$

For anodically colouring material:

$$M_eO_n + x\,A^- \Leftrightarrow M_eO_nA_x + x\,e^-$$

Or } ----(2.2)

$$M_eO_n + xA^- + xh^+ \Leftrightarrow A_xM_eO_n$$

Where, M_e is metal atom; A^+ is a singly charged small ion like H^+ or Li^+; A^- is a singly charged small ion like OH^- or F^-; e is an electron; n depends on the particular type of oxide; x is generally $0 < x < 1$.

In cathodically colouring EC material, the colouration takes place upon intercalation (insertion) of H^+ or Li^+ ions and bleaching takes place upon deintercalation (extraction) of H^+ or Li^+ ions. Coloured compounds (bronzes) are partially reduced oxides of polyvalent metal, which contain the cation of the reducing element (H^+ or Li^+) [12].

In anodically colouring EC material, the colouration takes place upon intercalation of OH^- ions and bleaching takes place upon deintercalation of OH^- ions. For anodic colouring EC materials, reaction can be written in terms of both OH^- and H^+ ions, which usually require hydrated form of oxides [13].

The position of equilibrium (equation 2.1 and 2.2) is dependent on the standard free enthalpy of formation and on the relative concentration or mole fraction of the component [14].

An EC device consists of many configurations depending on property requirement. The basic elements of an EC device are; 1) two conductor layers to conduct charge 2) an active electrochromic layer 3) an electrolyte or ion conductor (which may in some cases be an insulator) and 4) an ion storage media which may

be the electrolyte, another electrochromic layer or may be an integral part of the conductor layer. This sandwich configuration (Figure 2.1) allows a reversible reaction to cycle between the EC 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 for cathodic colouration in Nb_2O_5 is shown in figure 2.2

When a voltage is applied between the transparent electrical conductors, as indicated in figure 2.1, a disturbed electric field is set up and ions are moved uniformly into and out of the electrochromic film. The charge balancing counter-flow of electrons through the external circuit then leads to a variation of the electron density in the electrochromic material and thereby a modulation of their optical properties.

The ionic and electronic conductivities must be sufficient for electrochromic film and ion storage film. The transparent electrical conductor must have low resistivity. The ion conductor should have sufficient ion conductivity and low enough electron conductivity.
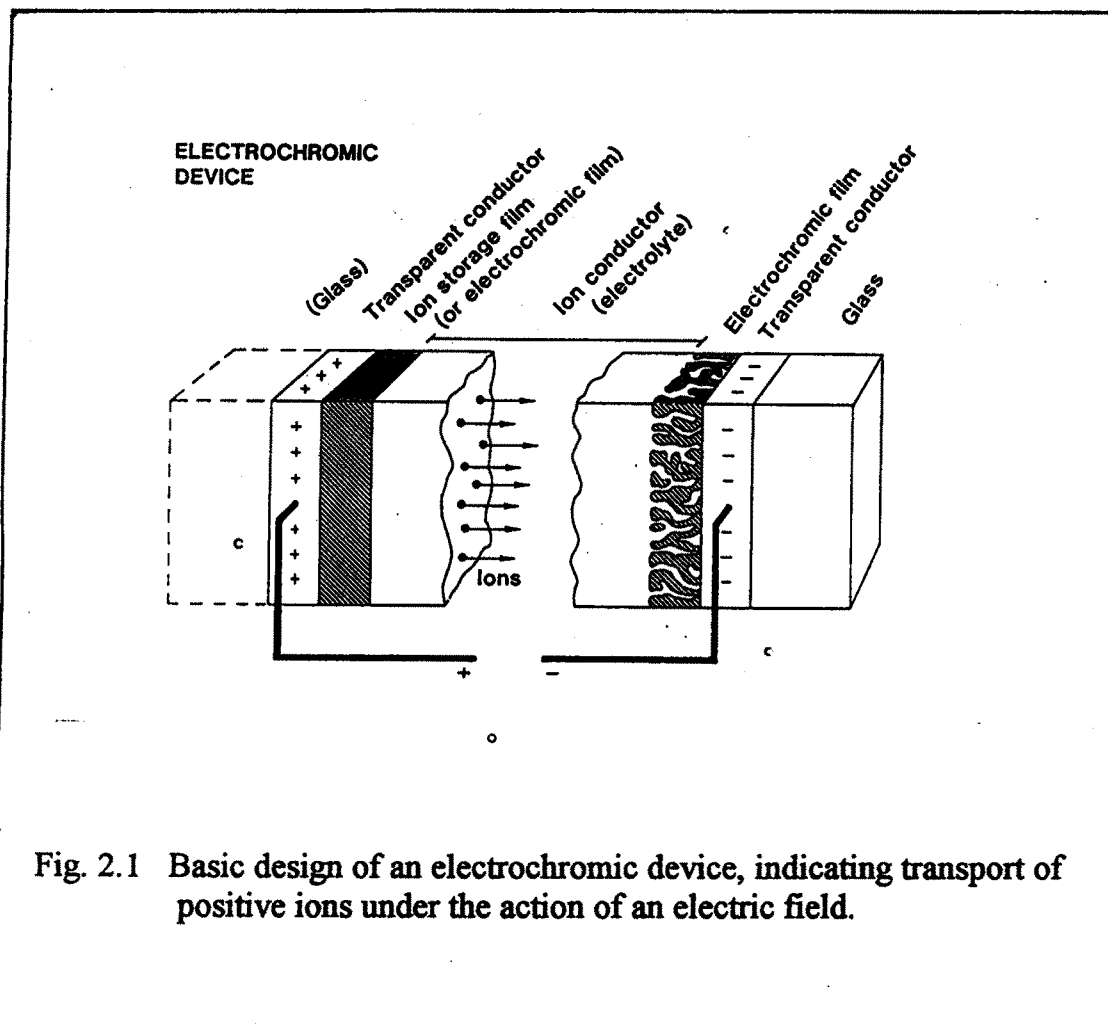
ELECTROCHROMIC DEVICE

(Glass)

Transparent conductor

Ion storage film (or electrochromic film)

Ion conductor (electrolyte)

Electrochromic film

Transparent conductor

Glass

Ions

Fig. 2.1 Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field.

Cathodic Colouration

Anodic Bleaching

$$Nb_2O_5 + xH^+ + xe^- \Leftrightarrow H_xNb_2O_5$$
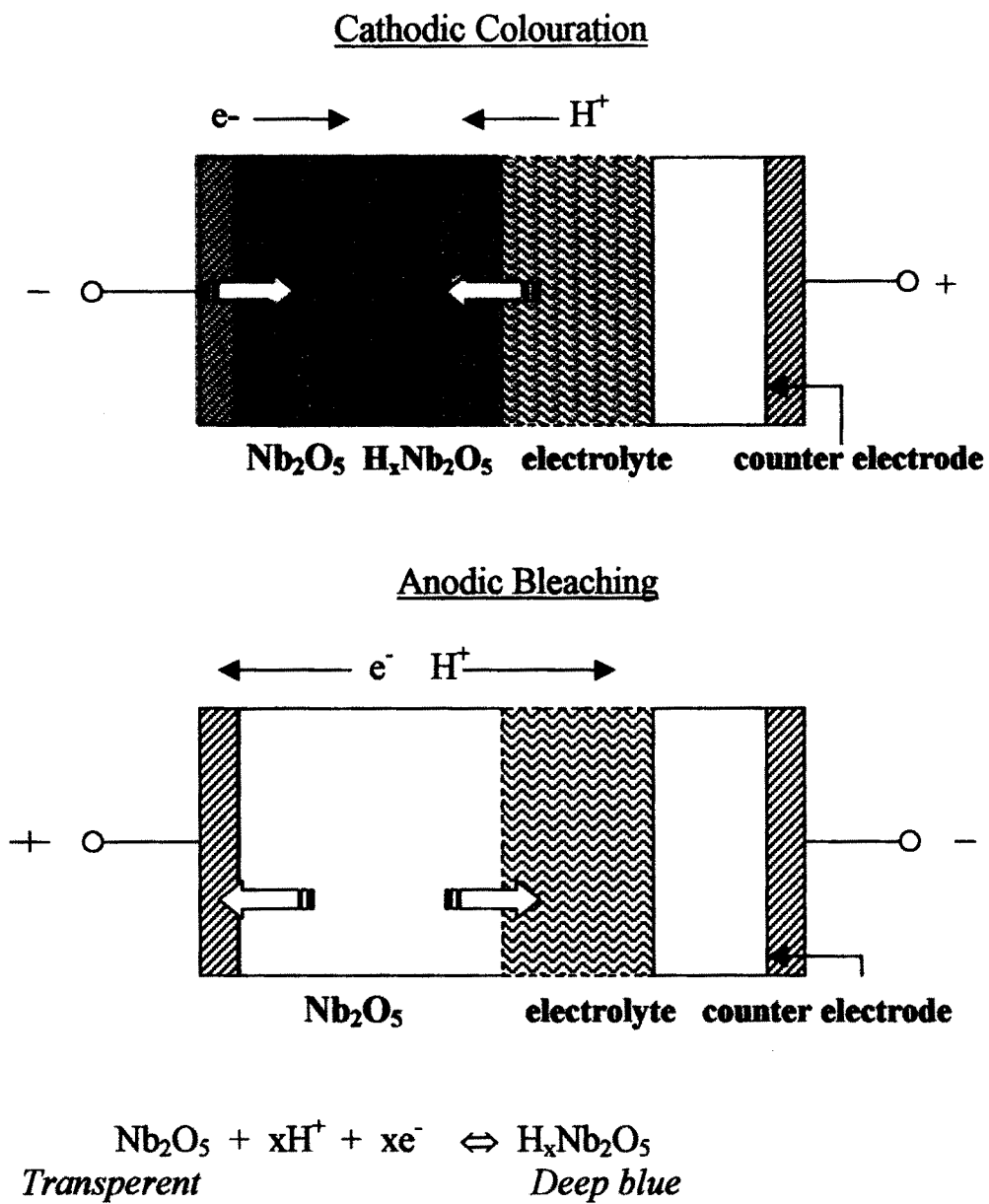
Transperent   *Deep blue*

Figure 2.2 Schematic of colouration and bleaching processes within Nb_2O_5

2.3 Areas of application of electrochromic devices

There are many uses of electrochromic (EC) materials whose optical properties can be varied reversibly and persistently by a low voltage signal. There are four main application devices, illustrated in figure 2.3.

Figure 2.3(a) refers to electrochromic information display. The device embodies (include) an electrochromic film in front of a diffusely scattering pigmented surface. The electrochromic film can be patterened or be a part of seven-segment numeric display unit. It is possible to achieve excellent viewing properties with better contrast particularly at off-normal angles than in the conventional liquid crystal based displays (LCD). Although an electrochromic system display needs to compete with both CRT and LCD display for commercial viability, they possess many advantages over both. EC device consume little power in producing image, they have open circuit memory and high contrast and there is no limit in principle, to the size an ECD can take. EC devices can be used for large information display applications where high switching speed is not required such as aircraft display boards. The ECD can be poly electrochromic if the active component responds to different potential with variety of colours [15].

The second figure 2.3 (b) refers to mirror with variable specular reflectance. This application seems to be a most mature one and anti-dazzling rear view mirrors built on EC oxide films are currently available for cars and trucks. At night, the light of following vehicles cause a dazzle on reflection from the driver's
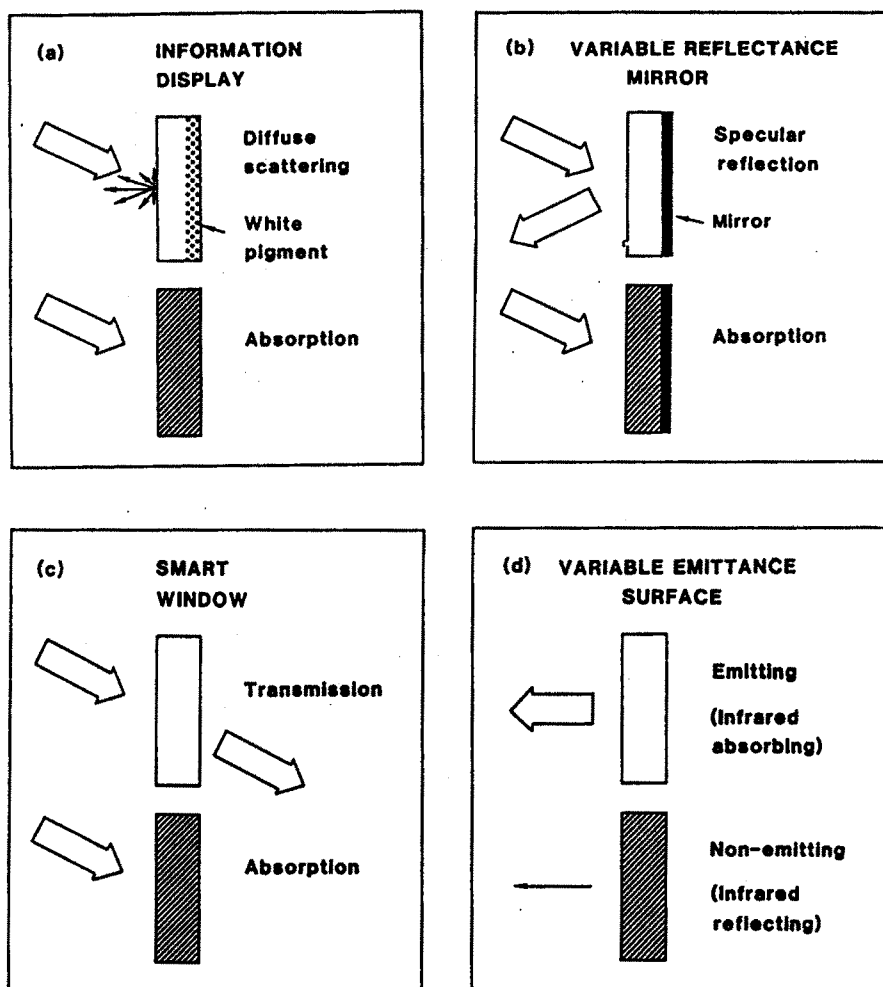
Fig. 2.3 The principles of four different applications of electrochromic devices.
Arrows indicate incoming and outgoing electromagnetic radiation;
the thickness of the arrow signifies radiation intensity.

or the door mirror; this can be prevented by formation of an optically absorbing electrochrom over the reflecting surface [16].

Electrochromic 'smart window' application is sketched in figure 2.3(c). The basic idea is to make architectural or automotive window with variable transmittance so that a desired amount of visible light and / or solar energy is introduced. Such a window can lead to energy efficiency as well as comfortable indoor climate. The term 'smart window' was coined in 1984 by Sevensson and Granqvist [17]. 'Smart window' can be used for the regulation of incident solar energy and glare in vehicles, aircrafts, spacecrafts and ships. Whole windows in a room, office or through a car windscreen, may be refereed to as light shutters. From privacy point of view, this technology has a significant advantage over existing blinds and drapes. Also, electrochromic eyeglasses are being introduced as products by Nikon (Japan) and being developed by Eyeonics (Portland OR) and PPG (Pittsburg PA) companies.

Variable emittance surfaces outlined in figure 2.3 (d) are based on a special device design with a crystalline electrochromic film at the exposed surface of an EC device. Intercalation / deintercalation of ions makes this surface infrared reflecting / absorbing i.e., the thermal emittance is low / high. The emitted radiative power is proportional to the emittance. Variable emittance surfaces can be employed for temperature control under conditions when radiative exchange dominates over conduction and convection, such as for space vehicles.

2.4 Configuration of Electrochromic cell

The sketch of a typical electrochromic (EC) cell with liquid electrolytes is shown in figure 2.4.

It is a sandwich structure in which 1 and 1 are glass plates, 2 is a transparent conducting coating, 3 is the EC film, 4 is the electrolyte and 5 is the counter electrode. A battery is 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 (2.1) the film becomes coloured. The direction of reaction depends upon the sign of the applied voltage. Despite different ways of preparation and differences in metal ions injected (or ejected) into (out of) the particular EC film, all have essentially the same colour or optical absorption band. Thus the nature of the injected ions does not appear to play an essential role in colouration, it enters the film only for charge compensation. Nb_2O_5 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 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 EC 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.

2.4.1 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 electrolyte selection are:

1) High ionic conductivity and negligible electronic conductivity.

2) Wide temperature range for operations.

3) High electrochemical stability with respect to electrochromic films.

4) High decomposition potential.

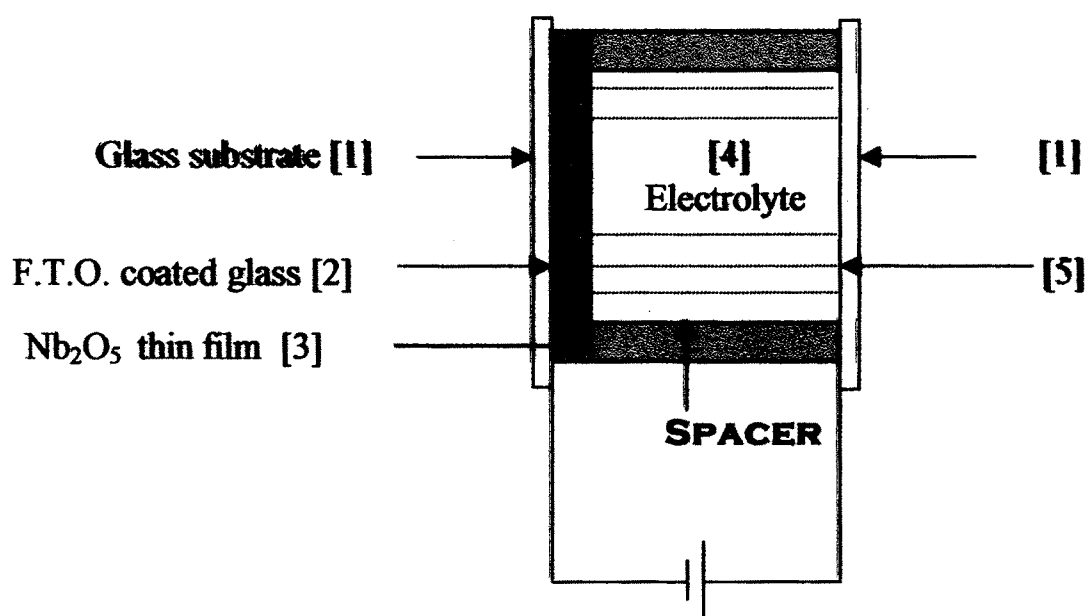5) High diffusion coefficient of cations in the electrolyte.

Glass substrate [1] → [4] Electrolyte ← [1]

F.T.O. coated glass [2] → ← [5]

Nb_2O_5 thin film [3] →

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Figure 2.4 Sketch of a typical EC cell with liquid electrolyte

Protons have highest mobility as compared with other cations such as Li^+, Na^+, Ag^+ etc., and should lead to fastest EC cell. Most of the work reported is on proton insertion from acidic aqueous electrolytes. Diffusion coefficient for protons was found to increase with degree of hydration of EC films while long-term electrochemical stability against dissolution, was found to be adversely affected. Further, colour-bleach cycling increases the rate of dissolution.

2.4.2 Counter Electrode

The counter electrode is another part of 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 and life -time of an EC cell deteriorates. 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 electrolytes.

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, which are good conductors, are polarizing for ion-current flow. They show gradual decay in

current, because of depletion of cations in the electrolytes near the electrode. The current can be increased by applying higher voltages, which might be accompanied by evolution of gases, degrading the EC cell seriously.

Another commonly used counter electrode (CE) is graphite painted on conductive substrates [18]. Due to its porous structure it provides a large surface area, which is beneficial for the colouration process. The potential of graphite CE varies with long-term operation and hence subject to operation with simple constant drive voltage, non-uniform colouration between segments is observed. This demands setting of a complicated drive.

The ideal non-polarizable counter electrode is H_xWO_3 for the proton-based systems. The alkali metal bronze is used for Li^+ and Ni^+ ion systems. Platinum is another good counter electrode usually used which satisfies all the conditions for counter electrode, but it is expensive. Reports are available on the different CEs such as steel wire, SnO_2 coated glass [19], ITO doped or ZnO [20], iron graphite mixture [21]. The cation storage capacity can be increased by using high surface area carbon.

2.5 Crystal structure of bulk like niobium oxide

The basic micro structural features are of decisive importance for electrochromism and lead to electronic band structure models capable of explaining why certain materials become absorbing under ion insertion, i.e., why they can display cathodic and ionic electrochromism. The oxide has a tendency to

form sub-stoichiometric shear phases containing edge-sharing octra hedra. The crystal structure has been clearly displayed by high-resolution microscopy.

The electrochromic oxides can be categorized in different ways, for example as framework structures and layer structures. It is appropriate to make a more detailed distinction into structures with perovskite-like, rutile like, and layer type and block type configuration.

Niobium oxide shows both similarities and differences when compared with the defect perovskites and rutile-type oxides. Nb_2O_5 may be categorized as being of block type. Niobium pentoxide crystals are built, essentially, from NbO_6 octra hedra arranged so that the overall stoichiometry is Nb_2O_5. Most of the structures consists of blocks of corner sharing octa hedra with a well defined cross-section in one plane and, in principle, infinite extent in the perpendicular direction, being the crystallographic C-axis. The blocks are connected by edge-sharing octa hedra, yielding two sets of columns with different bases.

The simplest structure, referred to as $R-Nb_2O_5$, comprises blocks with cross sections being 2x2 octa hedra. Figure 2.5(a) shows structural units characteristic of $R-Nb_2O_5$. The $M-Nb_2O_5$ and $N-Nb_2O_5$ comprises blocks with cross-sections being 4x4 octa hedra. Figure 2.5 (b) and figure 2.5(c) show ideal structures of $M-Nb_2O_5$ and $N-Nb_2O_5$. Another more complicated, structure exists in $H-Nb_2O_5$ (also called $\alpha-Nb_2O_5$), shown in figure 2.5(d), with blocks having cross sections of 3x4 and 3x5 octa hedra, as well as tetragonally

coordinated Nb atoms. A high-density oxide, known as B- Nb_2O_5 , can be thought of as built from corner-sharing rutile blocks. M- Nb_2O_5 is tetragonal, whereas the other varieties are monoclinic.
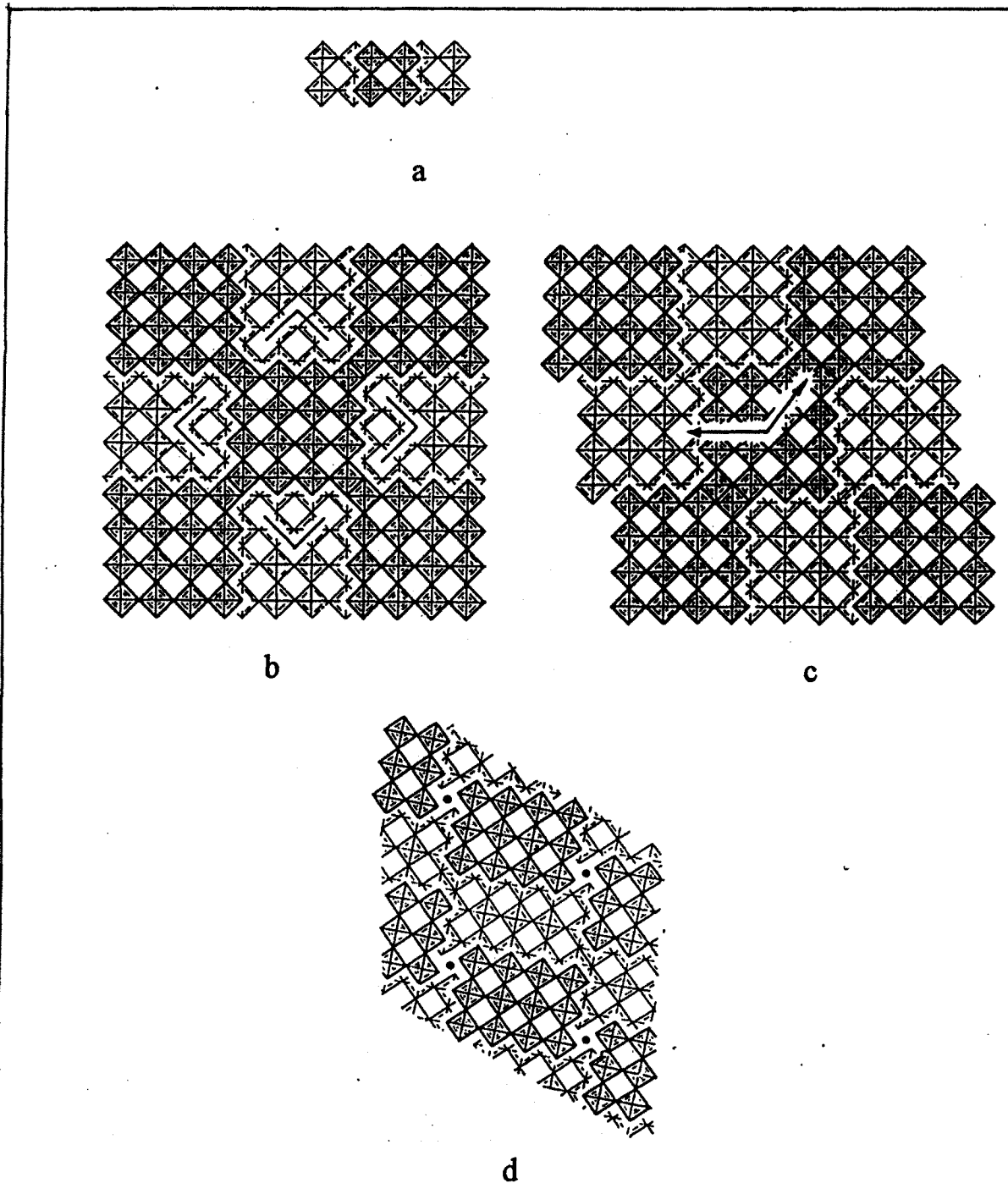
Fig. 2.5 a) Structural units characteristic of R-Nb$_2$O$_5$.
   b) Ideal structure of M-Nb$_2$O$_5$.
   c) Ideal structure of N-Nb$_2$O$_5$.
   d) Ideal structure of H-Nb$_2$O$_5$.

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