Electrochromic thin-film components for information representation systems

V A Shakhnov, A I Vlasov and S V Tokarev

Bauman Moscow State Technical University, 2-ya Baumanskaya st. 5/1, 105005
Moscow, Russian Federation

Corresponding author e-mail address: shakhnov@iu4.bmstu.ru

Abstract. The solutions in the sphere of energy efficient technologies of information representation systems development are overviewed in this paper. The main emphasis is on “electrochromism” phenomenon, which is a reversible change of material optical characteristics during the application of an external electrical potential. The possible use of electrochromism phenomenon in energy-efficient electromagnetic radiation modulation systems is shown. The generalized model of the universal electrochromic cell construction is presented. The materials with electrochromic characteristics, the field of electrochromes use and the developments in the sphere of electrochromic technologies are analyzed.

1. Introduction

Energy efficient information representation systems development is a real challenge to modern science. A promising possibility in this sphere is a technology based on “electrochromism” phenomenon. This phenomenon is reflected in thin-films structures in the electromagnetic radiation absorption spectrum change during the application of an electrical potential. The electrical potential is a result of electrons transmission in oxidation-reduction chemical reaction during the application of an external electrical field [1,2]. The absorption spectrum could be located in the visible, infrared or ultraviolet scope. The spectrum location depends on the used electroactive material. Electrochromic device principle of action is based on oxidation-reduction chemical reaction. The electrochromic device contains electrochromic (electroactive) material which consists of electroactive particles. The electroactive material is directly involved in oxidation-reduction chemical reaction. It also changes the adsorbing power during the application of an external electrical potential. The electrochromic material is an electroactive thin film or electroactive solution so that it can be in the solid or liquid state. The term “chromism” means the ability of the substance to change the color reversibly during different external exposures [3,4].

The first reference to electrochromic materials dates from 1706. The first material with electrochromic characteristics (color change from dark blue color to the discolored state during the application of the external voltage) was Prussian blue (Heinrich Diesbach). Wolfram oxide electrochromic characteristics showed up in experiments conducted by Jacob Berzelius (1815). The experiment showed wolfram oxide color change in reduction chemical reaction in gaseous hydrogen. The electrochromism phenomenon in thin films of wolfram oxide was first described by Craus in 1953. The starting point to electrochromism phenomenon studying was the publication of S.K. Deba (1969). In his paper, he presented the first controlled electrochromic device based on the wolfram oxide. The application interest in electrochromism phenomenon is related to the use of this effect in...
the smart glass, windows and displays [5,6]. The use of photochromic and thermochromic technologies is energy efficient during the room lighting or cooling respectively [7,8].

The advantage of the electrochromic display is low power consumption because energy consumes only at the moment of information updating. Forward-looking electrochromic displays are retro-reflective as well as LCD displays (unlike light-emitting OLED displays). A static image doesn’t consume any power because the electrochromic material has a memory effect. The main disadvantage which limits the use of electrochromic displays is long response time. Big electrochromic display panels may have uneven color because the electrodes near the external contact have a higher voltage than the other electrodes.

2. The concept of the universal electrochromic cell construction

Electrochromic devices may have different configurations, but the base configuration is similar to universal electrochemical cell configuration.

Electrochromic devices usually consist of seven layers which are shown in figure 1 [2]. Three inner active layers (counter electrode, ion conducting layer or electrolyte, working electrochromic layer) are located between two conductive transparent electrodes. These five layers are located between protective layers, which are usually made of glass or flexible polymeric material. Oxidation-reduction chemical reaction proceeds between two electroactive materials - counter electrode and working electrode in the electrolyte.

![Figure 1. Universal electrochromic cell construction. (a) – a variant of an electrochromic indicator construction; (b) – a variant of an electrochromic cell construction.](image)

There are four types of electrolytes for electrochromic devices – aqueous electrolytes, organic liquid electrolytes, ionic liquid electrolytes, solid polymer electrolytes [3,4]. Aqueous and organic liquid electrolytes are durable and easy to manufacture. Due to these advantages, these electrolytes are often used in electrochromic smart glass. The disadvantages of these electrolytes are the possibility of their leakage and low chemical stability. Organic liquid electrolytes contain propylene carbonate or ethylene carbonate with the addition of salts such as lithium perchlorate (LiClO₄) or sodium perchlorate (NaClO₄) to improve their electrochemical characteristics. Ethyl ammonium nitrate (EtNH₃NO₃) is related to ionic liquid electrolytes [9].

Solid polymer electrolytes are matrixes of polymer or gel with absorbed liquid electrolyte solution, where only one type of ions can move in the polymer matrix. Another realization of solid polymer electrolytes is an ion-related system consisting of the mixture of ion-containing polymer and salt, where cations and anions can move in the polymer structure.

Counter electrode in electrochromic device structure is used as a layer for ions keeping. The counter electrode layer can be made from any material which has a proper electron and ion conductivity similar to the working electrode. The counter electrode may also have electrochromic characteristics as well as the working electrode with the only difference in the type of colouration (cathode/anode).
Glass or polyethylene terephthalate (PET) substrates can be the base of multilayer electrochromic device structure. Both substrates should be transparent to electromagnetic light emission to be used in smart glass technology. For electrochromic displays and mirrors, only one transparent substrate is needed.

The high light transmitting ability and low resistance allow using transparent conductive materials as an electric current collector in solar panels and as electrodes in the smart glass, electrochromic and LCD displays and sensor panels.

Today the best combination of light transmitting and conductive characteristics has indium oxide doped with tin (ITO) at a ratio of 90% indium oxide In$_2$O$_3$ and 10% tin oxide SnO$_2$. ITO cover is non-organic which combining with low resistance coefficient (0.001 Ohm/sm), the high light transmitting coefficient (more than 90%) and infrared radiation reflection makes it suitable for use in different devices and systems. The disadvantage of ITO is relatively high cost because indium is rare earth element. As an alternative to ITO cover other high-alloy conductive materials oxides can be used, e.g. fluorine-tin oxide SnO$_2$:F (FTO), zinc-aluminum oxide ZnO:Al (AZO), zinc and gallium oxide ZnO:Ga (GZO) and titanium-niobium oxide TiO$_2$:Nb (TNO). It is expected that 90% of capacitive sensor panels and smartphones market will use ITO and its alternatives in 2016 [10]. Other alternatives to transparent conductive oxides are organic polymers and nanomaterials.

PEDOT or poly(3,4-ethylenedioxythiophene) is an organic conductive polymer. This polymer has several advantages over ITO covers such as flexibility, low cost and ability to use PEDOT in printing processes. PEDOT chemical compounds polyaniline PAN1 and polypyrrole PPy have required physical characteristics to use them as a transparent conductive layer.

Carbon nanotubes usage is a forward-looking alternative due to their high conductivity and light transmitting coefficient about 90% at wavelengths from 440 nm to 22 μm. Carbon nanotubes have been already used as a conductive material in electrochromic devices instead of ITO cover. Carbon nanotubes use helped to improve the electrochemical stability of the device, increase the contrast and decrease the response time. Graphene also can be used as a transparent conductive material due to the high mobility of charge carriers and absorption of only 2.3% of visible light.

3. Electrochromic materials classification

Electrochromes are classified by a phase condition of a substance before and after the process of an absorption band change. The phase condition defines the time current characteristic of the electrochromic device. This characteristic is related to substance coloring time characteristic. There are three types of electrochromes: Type I – Liquid-phase, Type II – Transitional, Type III – Solid-phase.

Electrochromic devices of the first type use the electrochromic substance in the liquid phase. The substance stays in this phase throughout the device working period (e.g. liquid methyl viologen (1,1'-dimethyl-4,4'-bipyridyl)).

Electrochromic devices of the second type – initially electrochrome is in the liquid phase and then changes to solid phase precipitating on the electrode in the process of electron charge transfer. This phase change increases the efficiency of write-erase cycles and reduces the response time during discoloration. The examples of second type electrochromes are heptyl or benzyl viologen [11], methoxyfluorane in a solution of acetonitrile [12]. The examples of non-organic second type electrochromes are bismuth, lead or silver that recover on the electrode from the liquid solution of ions or cations in combination with joined organic or non-organic molecules (ligands).

Electrochromic devices of the third type are characterized by a solid phase of the electroactive substance throughout the whole working period. The most of the non-organic electrochromic materials are materials of the third type. Non-organic electrochromic materials of the third type are phthalocyanine complexes and metal hexacyanoferrates (“Prussian blue”). Organic electroactive conductive polymers are polypyrrole, polypyrrophene, polyaniline which are monomers and form a solid electrochromic structure in polymerization reactions. The most important electrochromic substances are transition metal oxides (TMO), materials on the basis of Prussian blue (Prussian blue).
that is a mixture of hexacyanoferrates, viologens, lanthanides complexes, metal-polymers and metal-phthalocyanines.

The researches in the sphere of electrochromism phenomenon are continuing. Electrochromic materials are promising for energy-efficient electromagnetic radiation modulation systems constructing [13-17].

4. Experiments analysis, conclusions and recommendations
For universal electrochromic cell prototype forming a conductive layer of ITO was formed on a glass substrate by constant current sputter deposition [2,15]. The source for each prototype was a sputter target from indium and tin oxides alloy at a ratio of 90% and 10% respectively. Sample 1 was not annealed after sputter deposition. Samples 2, 3 and 4 were annealed for 20 minutes at 200, 300 and 400 °C respectively. The resistance of thin-film conductive surface was measured by van der Pauw method with Signatone 1160 scanning probe station. Figure 2 is a plot of a surface layer resistance and the annealing temperature.

The graph on fig. 2 shows that the smallest resistance is achieved after prototypes with ITO cover annealing at the temperature close to 200 °C. The bigger resistance in different annealing conditions is a result of the big number of structural defects.

Prototypes light transmitting coefficient in visible scope was measured by a spectrophotometer. The results are presented on fig. 3. The graph on fig. 3 shows that the increase of the annealing temperature leads to the increase of glass with ITO cover transmitting coefficient. For further experiments prototypes with conducting coating annealed at 200 °C were used. The resistance of the conductive coating layer should be minimized to improve the working parameters of electrochromic indication systems. The results of the experiments are shown on voltammogram of electrochromic cover prototype without annealing (fig.4) and on cyclical voltammogram of the annealed prototype with electrochromic cover (fig.5) [2,15].

![Figure 2](image1.png)

**Figure 2.** The resistance of ITO thin-film conductive surface on the glass substrate at different annealing temperatures.

![Figure 3](image2.png)

**Figure 3.** Prototypes with ITO cover transmitting coefficient in visible scope. 1-4 – sample number.
Graphs on fig.4 and fig.5 have two current peaks – one towards the external voltage increase and one backward. These peaks demonstrate that reduction and oxidation processes proceed towards and backward respectively. The number of peaks suggests that the system consists of only one oxidation-reduction pair without any impurities. Voltammogram of electrochromic cover prototype without annealing also shows the dispersion of the measured values after 10 cycles of measurements. Voltammogram of the annealed prototype with electrochromic cover shows smaller measurements dispersion. In addition, the annealed prototype has more pronounced current peaks than the cover.
prototype without annealing. This difference reveals that the annealed prototype structure is more homogeneous comparing to amorphous structure of the non-annealed prototype.

The research on optical characteristics of the formed electrochromic cell was undertaken using the annealed cover prototype. An electrochromic cell with wolfram oxide cover transmission spectrum is shown in fig.6. Generally, the prototype in the discolored state is transparent in the whole visible scope. The average transmitting coefficient is 82%.

The advantages of electrochromism phenomenon are low power consumption due to color saving effect (saving color without applying any external voltage), low cost of the basic materials, an opportunity to use simple printing technologies to manufacture electrochromic devices and integrate them with other printed electronics and an extensive palette of color materials which simplify color devices construction by eliminating color filters. The disadvantages of electrochromic devices are relatively long time for optical characteristics switching and a possible degradation of some materials.

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