Solar Energy Materials & Solar Cells 128 (2014) 166–177

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

# Comparison of electrochromic devices with V- and Sn/Mo-oxide counter electrodes and (3-glycidoxypropyl)trimethoxysilane-based ormolytes with three different lithium salts

A. Šurca Vuk*, M. Koželj, B. Orel

*National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*

## ARTICLE INFO

*Article history:*
Received 4 December 2013
Received in revised form
5 May 2014
Accepted 7 May 2014
Available online 4 June 2014

*Keywords:*
Electrochromics
V-oxide
Films
Sn/Mo-oxide films
Ormolyte
Lithium salts

## ABSTRACT

Electrochromic (EC) devices represent an effective way to modulate the intensity of incoming solar radiation in buildings or through the sun roofs of cars, but can also be used in helmets, sunglasses and home appliances. Herein we report on the development of all sol–gel $WO_3$-based EC devices of a battery type, in which all three internal layers were prepared via sol–gel processes. A comparison of the performance of EC devices assembled with two different counter electrode films, i.e. V-oxide (150 °C) and Sn/Mo-oxide (500 °C) films deposited on fluorine dopped tin oxide (FTO) glass, is presented. The applicability of both types of counter electrodes for flexible polymeric substrates is also demonstrated. The sol–gel electrolyte (ormolyte) based on (3-glycidoxypropyl)trimethoxysilane was applied in EC devices; additionally, three different lithium salts were introduced, i.e. lithium perclorate ($LiClO_4$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and lithium bis(oxalato)borate (LiBOB). The spectroelectrochemical characterisation of the EC devices revealed that the optical modulation at 634 nm increased when electrolytes with $LiClO_4 < LiCF_3SO_3 < LiBOB$ were used.

## 1. Introduction

EC devices, sometimes also called smart windows, change their optical properties (transmittance or reflectance) reversibly under the action of electric field [1–6]. They are interesting mostly from the architectural point of view, since they enable influencing the energy balance of buildings, for instance to lower the costs of ventilation due to reduced throughput of solar radiation [3–7]. Smart windows are currently commercially available (EControl glass, Germany), but their cost remains too high (a factor of ten higher than the price goal of 100–250 USD/m² [3,4]), the switching between coloured and bleached states is slow and does not suffice for some other applications. The homogeneity and contemporaneity of the colouring/bleaching of larger surfaces also represents a characteristic problem. The interest for other products has been directed to the production of EC visors on motorcycle helmets (Chromogenics, Sweden), EC sun roofs for cars and cabin windows for aircrafts (Saint Gobain, France; EADS, Germany; Maser, Spain), doors of home appliances (refrigerators (Gorenje, Slovenia) and ovens (Arcelik, Turkey)). The attempt to make EC spectacles (Essilor, France) also represents a special challenge because of the high demands for transmittance in their bleached state which is difficult to achieve with the current existing materials. The previous four products are being developed under the Innoshade EU project (www.innoshade.eu).

To reduce the price of EC devices producers are investigating the assembly of flexible EC devices [4,8], which can be fabricated with roll-to-roll processes, but impose the necessity of production of low-temperature electrodes. Among optically active electrodes, $WO_3$ remains the key material [9], but electroactive polymers like poly(3,4-ethylene-dioxythiophene) (PEDOT) [10] have also emerged as another promising option due to their high mechanical flexibility, low weight and remarkable ease of deposition techniques that do not require high temperatures. A combination of either $WO_3$ [7] or PEDOT [11] with Prussian blue [12], which is an anodic colouring material, offers effective blue-coloured EC devices. However, when other colour shades are required, nickel oxide coatings can be applied as an optically active material or counter electrode, i.e. sputtered [5] or produced as “electrochromic paints” [13,14] when deposited on flexible substrates. The applicability of low-temperature V-oxide coatings (150 °C) as counter electrodes was demonstrated in flexible EC devices with optically active PEDOT and electrolyte based on organic-inorganic hybrid *N*-(triethoxysilylpropyl)carbamatoil PEO 400, ionic liquid co-solvent and lithium bis(trifluoromethanesulfonyl) imide [15].

---

* Corresponding author. Tel.: 386 1 4760 254; fax: 386 1 4760 300.
*E-mail address:* angela.surca.vuk@ki.si (A. Šurca Vuk).

http://dx.doi.org/10.1016/j.solmat.2014.05.028
0927-0248/

Development of electrolytes is another challenge, since the electrolyte is often the weakest point of the EC devices. Due to the difficulties connected with the reliable sealing of the devices containing liquid electrolytes, various solid/polymeric electrolytes were investigated. Among those, sol–gel electrolytes (ormolytes), prepared on the basis of organic-inorganic hybrids [16], have been given considerable attention. Organic–inorganic hybrids are differently functionalised trialkoxysilanes that can, in the processes of hydrolysis (solvolysis) and condensation, build sol–gel polymeric networks in the form of gels or thin films [16]. They combine in their structures the flexibility of the organic phase and the mechanical hardness of the inorganic phase at the nano-scale. However, the electrolytes for electrochemical devices should enable the transport of the ions through the cross-linked network [17], which also can be achieved with the addition of co-solvents [18].

Investigation of ormolytes started with simple mixtures of tetraalkoxysilanes with ethylene glycols of various chain lengths and lithium salts [19,20]. The systems were catalysed with acidified water and dried to monolithic gels. The conductivities were $10^{-6}$ and $10^{-5}$ S/cm, but reached up to $10^{-3}$ S/cm. The use of di-ureasils, in which alkoxysilyl groups are bounded via urea bond (–NH–C(=O)–NH–) to poly(ethyleneoxide) (PEO) or poly(propyleneoxide) (PPO) chains of different lengths, while as lithium salts lithium perchlorate [21], lithium triflate [22] and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) [17] were applied, did not lead to significant changes in conductivity. It was $10^{-5}$ to $10^{-4}$ S/cm in the electrolyte with LiTFSI, which enabled its application in EC devices with optical modulation up to $\Delta T \sim 60\%$ at 634 nm [17]. Exchange of urea groups with urethane ones (–NH–C(=O)–O–) led first to the development of single end-capped alkoxysilyl-functionalised uretanosil-based electrolyte with lithium triflate salt, the conductivity of which was of the order of magnitude $10^{-6}$ S/cm [23]. However, the conductivity of such electrolytes can be improved to $10^{-4}$ to $10^{-3}$ S/cm if a bis end-capped di-uretanosil is mixed with a non-reactive ionic liquid co-solvent [15].

It should be emphasised that together with the intensive breakthrough of ionic liquids in the field of electrolytes, studies of the possibility of confinement of ionic liquids into sol–gel matrices (ionogels) have also begun [24]. In these cases, the tridimensional sol–gel matrices were usually prepared from tetraalkoxysilanes, such as tetramethoxysilane (TMOS) [25] and tetraethoxysilane (TEOS) [26]. Mostly the structure and conductivity of ionogels were considered [25]; their application in practical devices has not been reported frequently. However, application of TEOS-based ionogel with 1-ethyl-3-methylimidazolium bis (pentafluoroethanesulfonyl)imide in EC device with $WO_3$ and Prussian blue resulted in optical modulation $\Delta T$ of above 50%, which faded to 40% after 1000 colouring/bleaching cycles [26].

A study of di-ureasil sol–gel electrolytes [17] revealed that the high cost and water sensitivity/hydrolysis of LiTFSI salt could have considerable drawbacks in building applications; in contrast, $LiClO_4$ is not expensive, but it is a strong oxidant, so its use should be avoided for safety reasons (Fig. 1A and B). Nevertheless, properties and conductivity of electrolytes are crucially dependent on the amount and kind of applied lithium salt. The need for new lithium salts that are soluble, electrochemically stable, non-toxic and cheap have been raised mainly in the field of lithium batteries. This need led to the synthesis of new lithium salts, one of which is lithium bis(oxalato)borate (LiBOB in Fig. 1C) [27–29]. The associating properties of $BOB^-$ anion were found the weakest within the orthoborate-based salt family, and the synthesis of LiBOB is also relatively simple [29]. Chemically, LiBOB is stable in organic electrolytes and also thermally stable up to 300 °C, but may slowly decay due to hydrolysis. In contrast, LiBOB was reported to be the salt of choice for some non-polymeric siloxane electrolytes, because the conductivity of 0.7 M LiBOB was as high as the conductivity of 1.0 M LiTFSI [30].

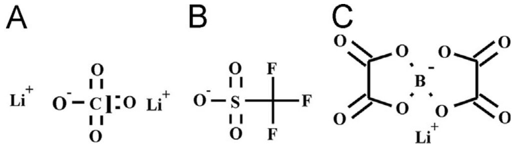

**Fig. 1.** Lithium salts that were used for the preparation of electrolytes on the basis of organic–inorganic hybrid (3-glycidoxypropyl)trimethoxysilane: (A) lithium perchlorate ($LiClO_4$), (B) lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and (C) lithium bis(oxalato) borate (LiBOB).

The aspect, often considered in the study of ormolytes, was the removal of solvent and water to obtain monolith gels. In contrast, the systematic investigations regarding the influence of water on the conductivity of electrolytes or performance of EC devices are usually not studied. Moreover, this is despite the fact that the assembling of EC devices at atmospheric conditions remains a viable option that would significantly contribute to lowering the prices of the EC commercial windows. Application of ormolytes in EC devices, anyhow, demands the right moment during electrolyte preparation. The most suitable for the application is highly viscous consistency of electrolytes just before solidification (gelling) to enable its penetration into pores of thin films. In some cases "open-time" is at least few hours or even days. After application the electrolytes solidify in the device and glue the electrodes together. This, on the other side, prevents its drying and complete removal of solvents, influencing also the conductivity values. Among the reported studies, concerning also the presence of water in electrolytes, the DSC analysis of ormolytes prepared from triethoxysilane-functionalised PEG 2000, TEOS, $LiClO_4$ and 2 M $HCl_{aq}$ catalyst revealed that 7–8 wt% of water remained in the structure of gels when thermally treated at 120 °C for 40 min [31]. Even more interesting is the work of Heusing et al. [32], who compared the performance of EC devices comprising the (3-glycidoxypropyl)trimethoxysilane (glymo)-based ormolyte without and with 3 wt% of intentionally added water. They revealed that the effect of water addition depended on the type of the EC film. The optical modulation of EC devices with $Nb_2O_5$/Mo-oxide films increased with the addition of water to ormolyte and the response was more stable. In contrast, when $Nb_2O_5$/Li-oxide electrodes were applied, the optical modulation slightly decreased after addition of water. Such results indicated that every EC device has a unique system significantly depending on all layers, which can drastically influence the optical response, speed of coloration/bleaching and stability.

Since the assembly of EC devices under ambient conditions is still not abandoned by producers, we decided to prepare a series of battery-type $WO_3$-based EC devices applying similar glymo-based ormolyte as used in Ref. [32]. All EC devices were assembled under atmospheric conditions, applying two different counter electrodes: the high-temperature Sn/Mo-oxide films (500 °C) [33] and the low-temperature V-oxide films (150 °C) [15], the latter also appropriate for flexible substrates. The ormolyte was prepared with three different lithium salts, i.e. $LiClO_4$, $LiCF_3SO_3$ and LiBOB (Fig. 1). Electrochemical and optical performance of assembled EC devices were evaluated, also from the point of view of colour coordinate changes.

## 2. Experimental section

### 2.1. Preparation of materials and EC devices

V-oxide thin films were prepared from a precursor vanadium (V) oxytriisopropoxide (ABCR) in isopropanol [15,34,35]. The films