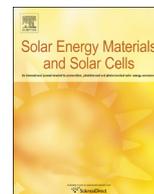




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Room temperature processing for solid-state electrochromic devices on single substrate: From glass to flexible plastic

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ABSTRACT

Herein, we present, for the first time, the features of a full solid-state electrochromic (EC) device fabricated on a single substrate, made of glass as well as flexible plastic, adopting a low-cost, eco-friendly, and facile fabrication process. By combining a solution processing of Nafion electrolyte film and RF sputtering deposition at room temperature (RT) on Nafion, we obtained monolithic systems with a simplified architecture (substrate/ITO/WO₃/Nafion/ITO) in which a suitable Nafion film (8 μm thick) tightly shares its interfaces with the WO₃ layer and the highly transparent and conductive RF-sputtered ITO film. Compared to conventional sandwich-type EC devices using semi-solid or liquid electrolytes, the resulting devices exhibited a strong enhancement in terms of interface properties, robustness, cyclic stability, and long-term durability (at least 1000 chronoamperometric cycles). Moreover, electro-optical characterizations highlighted high transmittance modulation (49% at 650 nm), astonishing results in terms of coloration efficiency (139 cm²/C), and low energy absorption (80 mW s/cm²).

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1. Introduction

In the last decades, there has been a large interest in electrochromic (EC) devices [1]. Since early works reported by Granqvist and Deb [2,3], different technological solutions have been proposed in order to improve their key parameters such as visual contrast and coloration efficiency. However, despite their limited commercial applications, they are promising candidates for different practical solutions, such as rearview mirrors for cars, smart windows for building integration, displays and other electro-optical devices [4,5]. EC devices are based on chromogenic materials that change their color by a reversible variation of the optical properties and electronic structure (coloration and bleaching processes) in response to external electrical biasing. For example, the operation of an inorganic EC device based on a transition metal oxide like tungsten trioxide (WO₃) is characterized by the simultaneous injection of electrons into the conduction band and the intercalation of small cations, such as H⁺, Li⁺ or Na⁺ from the electrolyte into the typical octahedral structure of the chromogenic material. Because of the electron injection and cation intercalation, it is possible to modulate the color of the chromogenic active layer, which depends on the doping concentration and size

of the intercalated cation. WO₃ thin films, prepared by vacuum techniques or the sol-gel method, have been extensively explored and represent the ideal cathodic material due to its superior electrochemical performance (cyclic durability), better environmental stability and higher coloration efficiency than other inorganic oxides or polymer chromogenic materials [6–11]. To date, numerous aspects regarding the fabrication methods, the selection of electrode and electrolyte layers significantly restrain the development of an effective full solid-state EC device and its potential exploitation. The conventional liquid or gel electrolytes, usually placed or sandwiched between the two active materials, represent one of the most critical limitations. These systems suffer from numerous drawbacks due to a poor structural stability, tendency to leak and evaporate, determining a non-uniform coloration and a strong irregularity of EC response [12–15]. Thus, a substantial effort has been made worldwide to prepare and synthesize innovative solid electrolytes with the aim to overcome these major drawbacks. Solid polymer electrolytes (SPE) are among the most promising materials due to their low processing costs, electrochemical stability, flexibility and easy scalability [1,16–18]. However, good ionic conductivities (10⁻⁴ to 10⁻³ S cm⁻¹), suitable for practical applications, including electrochromism, is gained at the expense of an overall reduction of their structural and mechanical properties [19–26], compromising the long-term device durability. Furthermore, these lithium salts based polymer electrolytes are usually sticky, toxic and react strongly with air and moisture constituting an obstacle in view of

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the industrial development. In the meantime, proton-based EC devices based on highly proton-conductive polymer ionomers, usually referring to the trade name Nafion[®], have represented a potential alternative to the SPEs for the fabrication of quasi-solid state EC devices [11,27,28]. Nafion has been exploited in membrane fuel cells (50–250 μm thickness), and it is the most widely used material for other electrochemical applications requiring an ion conducting polymer [30–32]. Its chemical structure consists of a tetrafluoroethylene (TFE) backbone, responsible of both mechanical and chemical stability, and perfluoroether side chains end-capped with sulfonic acid groups that are responsible of its exceptional proton conduction properties [31]. Furthermore, this polymer exhibits good optical properties and it can be easily processed in transparent and homogeneous membranes. However, despite the above mentioned advantages, Nafion membranes suffer from several drawbacks related to their strong acidic character, hydration degree and interface properties, which have strongly limited its use in only a few EC devices [11,27–29]. In details, the acidic character of hydrated membranes could lead to the deterioration of transparent conductive oxides such as indium tin oxide (ITO), resulting in a sheet resistance increase [33]. It is also well known that Nafion's proton conductivity is strongly dependent on its hydration degree, so that an operating temperature above 80 °C or a dehydration process, e.g. a prolonged vacuum drying treatment, could cause a decrease of its ionic conductivity [31,34–36]. Moreover, interfacial properties may also affect the device performance in terms of coloration and bleaching kinetics [11]. Another critical aspect in developing effective solid-state EC device lies in complex and very expensive manufacturing processes. Until now, to the best of our knowledge, all solid-state EC device architectures reported in literature were characterized by a multilayer structure with a gel or quasi-solid electrolyte interposed between two conductive substrates (glass or plastic), typically laminated by clamping, using a few drops of liquid or sticky electrolyte. These common procedures, carried out to assembly an EC device, complicate the sealing, and increase both the amount of layers and waste of raw materials. Unfortunately, for the most part of the devices this is often an inevitable choice due to the difficult low temperature deposition processing of high transparent and conductive oxide (TCO) thin film on top of the organic active layers such as solid polymer electrolyte or chromogenic polymer.

Nevertheless, novel approaches to simplify the device architectures or to combine the electrolyte and the chromogenic material in a single film have been pursued to increase the stability of the device and reduce the deposition steps to avoid the electrolyte leakage. However, up to now very few examples of EC devices fabricated on a single substrate have been reported in literature. Recently, more compact all-organic chromogenic film were fabricated by blending EC polymer with the electrolyte in one single layer [37–39]. Niwa et al. and Subrahmanyam et al. have demonstrated a full solid state device processed at high temperature containing two EC inorganic films having a complementary mechanism of coloration (anodic/cathodic) and an inorganic Ta₂O₅ solid state layer, acting as an electrolyte [40,50]. Recently, LiPON was effectively adopted as highly suitable solid electrolyte for all inorganic thin film EC device [41]. On the other hand, Huang et al. reported a complex device architecture that consists of an unsealed silicon-based photovoltaic device driving the color tuning of EC films, using a liquid electrolyte [42]. In the meantime, a single substrate EC polymer film, has been shown by Jensen et al. by using a photo-curable acrylate-based electrolyte and a silver grid electrode deposited by flexographic printing [43].

In the light of what reported in literature, we fabricated a simplified full solid-state EC device, entirely on a single substrate, by adopting a facile, low-cost, non-toxic, eco-friendly, and room temperature (RT) fabrication process. On taking advantages of a

suitable solvent-processing of Nafion film thickness and the optimization of ITO films deposited at ambient temperature on the solid polymer electrolyte by radio-frequency (RF) sputtering technique, we were able to “grow” the active layers on any conducting substrates including glass and flexible plastic, polyethylenenaphthalate (PEN), and, potentially, fabric or paper. This result paves the way towards ultra-thin, compact, light-weight and stable solid state EC devices of any shapes. This simple, single substrate fabrication method does not require a lamination process with a secondary electrode since all the layers deposited at RT are solid, dry to the touch and non-sticky without any extra curing treatment of the electrolyte. Furthermore, this monolithic system allows a robust operation due to the strong interface of solid electrolyte layer with both the counterelectrode and the chromogenic film.

2. Experimental

2.1. Fabrication of solid electrolyte Nafion films

Concentrated (20–22 wt%) and diluted (5–5.5 wt%) Nafion[®] solutions in alcoholic solvents were purchased from Ion Power, GmbH, Germany. The electrolyte used for the proton charging process of the WO₃ was an aqueous sulfuric acid (H₂SO₄) solution (0.01 M, pH=2). High quality uniform and transparent polymer thin films of 0.5 μm , 1 μm , 5 μm , 8 μm , 10 μm and 30 μm were prepared by spin-coating technique. The films were deposited on WO₃ substrates in colored state with various spinning velocity, ranging between 4000 rpm and 300 rpm, from concentrated and diluted Nafion solutions. The thickness of deposited films was examined by means of a profilometer (Veeco Dektak 6 M). In order to avoid the diffusion of protons and hydronium ions (H₃O⁺) in the surrounding environment we removed the dry layer of the polymeric film deposited on the glass-ITO/WO₃ substrate, confining the thin Nafion film exclusively on the chromogenic active area in colored state (dark blue tint). Further, to maintain the EC electrode fully charged with protons, we stored it in vacuum chamber before the counter electrode sputtering deposition.

2.2. Physical vapor depositions of WO₃ and ITO thin films

Tungsten oxide layers (300 nm thick WO₃) were deposited by electron beam (Temescal Power source) on L-shape patterned ITO coated glass substrates (VisionTek Systems Ltd, 12 Ω /square). Since each commercial ITO coated glass has two L-shaped conducting patterns, two identical EC devices were obtained. The vacuum chamber was initially evacuated up to 10⁻⁶ mbar, and then pure dry oxygen was admitted through a needle valve (20 sccm). The pressure was maintained at 10⁻⁴ mbar throughout the process. The deposition rate was about 1.5 $\text{\AA}/\text{s}$, and the e-beam power was about 6%. During the deposition process, the chamber reached a temperature of about 215 °C. The process temperature was kept at RT when conductive plastic substrates were adopted. After the deposition of WO₃ thin films, a proton charging process was performed in a H₂SO₄ solution (0.01 M, pH=2) in a standard three-electrode electrochemical cell. Such post-treatment of the WO₃ film allowed a full proton charging of the WO₃ layer determining a blue tinting *via* reduction of W⁶⁺ sites to W⁵⁺. Gold (Au) deposition was performed by using the same electron beam technique, at RT conditions (pressure: 10⁻⁶ mbar; deposition rate was about 0.5 $\text{\AA}/\text{s}$; e-beam power was about 9%). These parameters refer to the processes carried out to deposit the thin Au interlayer (20 nm thick) in Device B and the reflective electrode (70 nm thick) in Device C.

High vacuum non-reactive RF sputtering deposition was

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