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All solid-state electrochromic device consisting of a water soluble viologen dissolved in gelatin-based ionogel



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ABSTRACT

An all solid-state electrochromic system made of a viologen dissolved in a gelatin-based ionogel called Ion Jelly is presented. The obtained Ion Jelly possesses higher ionic conductivity than the constituent ionic liquid, which is ascribed to the broken ionic aggregates caused by the presence of water. Spectro-electrochemical studies carried out with the solid-state cell show that the kinetics of the reduction process is slower than that of the oxidation process, as denoted by the calculated time constants obtained from current vs. time plots. This may be owing to formation of an insoluble reduced species, which remains at the surface of the current collector, facilitating its oxidation process. The kinetics studies also show that the color change in response to the charge transfer process is faster during the reduction step. Both reversibility and durability of the device, upon successive oxidation/reduction steps, are related with the employed reduction potential, being the best compromise with the color contrast achieved at -0.25 V vs. Ag/Ag⁺, where 30% of transmittance change is observed up to 75 switching cycles.

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1. Introduction

Electrochromism is the phenomenon associated with electroactive species that change their color upon changing their redox state [1]. These species can be deposited onto a conducting and transparent substrate or be dissolved in an electrolyte, being applied in devices, such as rearview mirrors, windows and displays, among others [2].

Several types of electroactive materials are electrochromic as, for instance, oxides (WO₃, V₂O₅, TiO₂), inorganic complexes (Prussian blue and its analogous) and organic materials (phthalocyanines and conducting polymers) [3]. Another class of organic electrochromic materials comprises the viologens, which are 4,4'-bipyridinium salts containing substituents at the 1,1' positions [4]. These compounds are colorless in the di-cation form, which is their most stable oxidation state. When one electron is transferred to the material, the resulting radical cation acquires an intense color that depends on the nature of the substituent. The irreversible insertion of a second electron forms a less colored di-reduced

specie. For construction of the electrochromic devices, these materials can be either immobilized on the conducting substrate through functionalization of different materials – such as TiO₂ nanoparticles [5–7] and conducting polymers [8–10] – or directly mixed with the electrolyte [11–13]. Alternatively, they can be obtained as polymers, the so-called poly(viologen)s [14,15].

For practical applications, it is interesting to construct all solid-state electrochromic devices. In this sense, the ionogels deserve special attention due to their interesting properties [13,16–18]. Ionogel is the term employed to described electrolytes in which an ionic liquid (IL) is encapsulated into a solid matrix, such as polymers or silica, resulting in a gel with very interesting ionic conductivity values for electrochemical applications [19–21]. However, considering an electrochromic device in which a viologen must be mixed with the electrolyte, there may be difficulties related with the solubility of the electrochromic material. For the purpose of this work we have chosen Ion Jelly. This particular combination of ILs with gelatin has been shown to be an interesting and promising strategy not only to prepare transparent, flexible and conducting materials for different electrochemical devices [22–25], but also as an enzyme immobilization matrix [26], separation membrane [27] and even a drug delivery system [28]. Moreover, gelatin is soluble in water above 35 °C being jellified upon cooling. As both gelatin and ionic liquid possess ionic character, they are strongly attached to each other during

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this process [22]. Finally, the presence of water in the Ion Jelly should help dissolve small viologens.

Thus, this contribution presents the preparation and spectro-electrochemical characterization of a solid-state electrochromic device based on 1-butyl-3-methylimidazolium dicyanamide (BMIMDCA), Ion Jelly and 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium bromide viologen (Fig. 1). As far as we are concerned, this is the first time that a gelatin based ionogel containing a dissolved viologen is studied for electrochromic applications.

2. Experimental

2.1. Synthesis of 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium bromide viologen

For the viologen preparation, 1.00 g (6.40 mmol) of 4,4'-bipyridine (Aldrich) and 2.75 g (12.8 mmol) of 4-(bromomethyl)benzoic acid (Aldrich), both dissolved in 30 mL toluene, were kept at 70 °C under stirring overnight. Then, the solvent was evaporated and the obtained pale yellow solid was washed several times with small amounts of acetone and dried under vacuum at 65 °C for 12 h. (Yield: 80%). ¹H NMR (D₂O) δ 6.00 ppm (s, 4H), δ 7.58 ppm (d, J=8.6 Hz, 4H), δ 8.03 ppm (d, J=8.6 Hz, 4H), δ 8.55 ppm (d, J=7.0 Hz, 4H), δ 9.18 ppm (d, J=7.0 Hz, 4H)

2.2. Ion Jelly preparation

Initially, 300 μL of BMIMDCA (Aldrich), 20 mg of the obtained viologen and 60 mg of gelatin (Panreac Cultimed) were kept under slow stirring for 2 h at 40 °C for homogenization. Subsequently, 500 μL of deionized water at 40 °C were added to the system.

For the conductivity calculation, 200 μL of the mixture were placed inside a rubber cylinder and after jellification, pressed between two platinum electrodes of known surface area. The resistance of the gel at room temperature was then measured by Electrochemical Impedance Spectroscopy (EIS) with an Autolab PGSTAT 30 potentiostat. It was done by applying a potential of 0.0 V and superimposing an alternate signal with an rms amplitude of 10 mV between the two platinum electrodes of known surface area sandwiching the ionogel. The frequency range of the applied alternate signal was between 10 kHz and 1 Hz. From the obtained resistance value, the Ion Jelly conductivity was calculated

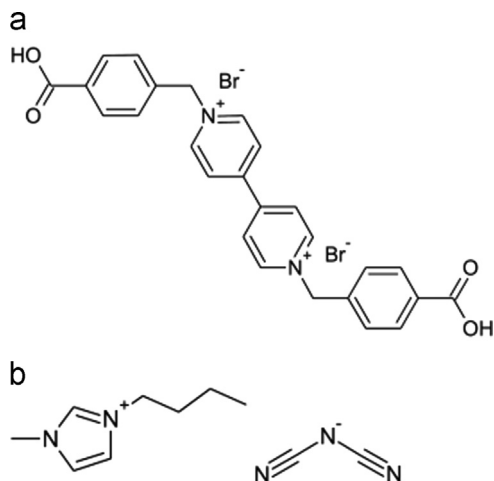


Fig. 1. Structures of the viologen 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium bromide (a) and the ionic liquid BMIMDCA (b).

accordingly to Eq. (1).

$$\sigma = \frac{L}{A \times R} \quad (1)$$

where σ is the conductivity (S cm⁻¹), L is the distance between the two platinum electrodes (cm), A is the electrodes surface area (cm²) and R is the resistance (Ω).

2.3. Solid-state device preparation

For preparation of the solid-state electrochemical cell, a glass covered with indium-tin oxide (ITO – 9–15 Ω sq⁻¹ – Luminescence Technology Corp.) with dimensions of 25 × 15 mm was used as substrate. The substrate was previously covered with a mask (see Fig. 2) made of acrylated varnish and then subjected to a treatment with sulfuric acid (6 mol L⁻¹) for 30 min at 60 °C in order to remove the ITO from the uncovered regions. Each of the different regions in which the ITO remained was then covered with the appropriate metal (silver for the reference electrode and platinum for the counter (thickness=10 nm) and the working (thickness=0.3 nm) electrodes. The silver was deposited by applying –5 mA for 30 s using a 0.1 mol L⁻¹ aqueous solution of AgNO₃ and the platinum was deposited by sputtering with a Cressington sputter coater, model 208HR. The purpose of depositing 0.3 nm of Pt over the working electrode is to increase the conductivity, however, keeping its transparence for the spectro-electrochemical experiments.

While still warm, the Ion Jelly containing viologen was applied over the cell: 200 μL of the mixture was placed on the top of the cell and then gently spread with the aid of a glass rod, previously heated at 40 °C, in order to prevent premature jellification or the formation of air vesicles, which could affect the electrochemical performance. For determination of the film thickness, the sample was lyophilized before the cross-section measurement by field-emission scanning electron microscopy (FESEM) using a Jeol microscope, model JSM-7401F. An average thickness of (19 ± 2) μm was obtained from 32 different measurements.

2.4. Spectroelectrochemical characterization

The electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat. Electrochemical measurements were run simultaneously with transmittance measurements using

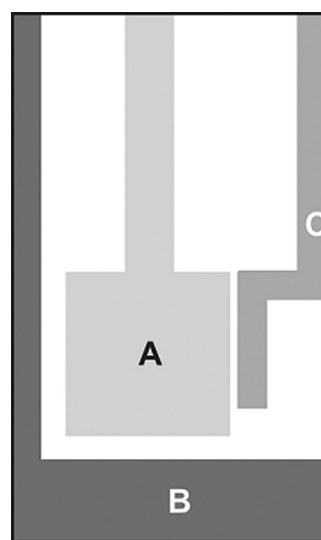


Fig. 2. Solid-state cell configuration. Working electrode covered with 0.3 nm of platinum (A), Counter-electrode covered with 10 nm of platinum (B) and reference electrode covered with silver (C).

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