Electrochimica Acta 159 (2015) 227–233

Contents lists available at ScienceDirect

Electrochimica Acta

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

Hydroxypropyl cellulose-based gel electrolyte for electrochromic devices

Przemyslaw Ledwon [a,*], Juliana R. Andrade [b], Mieczyslaw Lapkowski [a,c,1], Agnieszka Pawlicka [b,1]

[a] Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, Strzody 9, 44-100 Gliwice, Poland
[b] IQSC, Universidade de São Paulo, Av. Trabalhador Saocarlense 400, 13566-590 São Carlos-SP, Brazil
[c] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 41-819 Zabrze, Curie-Sklodowskiej 34, Poland

ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 26 January 2015
Accepted 27 January 2015
Available online 29 January 2015

Keywords:
polysaccharide derivative
HPC
polymer electrolyte
electrochromic device

ABSTRACT

Hydroxypropyl cellulose-based polymer (HPC) electrolytes were prepared and characterized. A gel electrolyte was tested in electrochromic devices. The membranes were obtained by casting method from dichloromethane solution. The best samples displayed ionic conductivity values of 3.5×10^{-5} and 1.1×10^{-4} S cm^{-1} at 25 and 50 °C, respectively. The DSC analyses evidenced glass transition temperature of -37 °C and the TGA showed three stages degradation of the sample starting at 130 °C. The 3.5 V electrochemical stability of the samples using SnO_2:Sb/glass (ATO) electrodes was determined by cyclic voltammetry in the −2 to 1.5 V interval. Moreover, the samples displayed transparency and excellent adhesion to different surfaces. Small electrochromic devices were assembled with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) as primary and polyaniline or Prussian blue (PB) as complementary electrochromic layer. Performance of the devices was analysed by cyclic voltammetry at different scan rating. UV–vis transmittance results revealed 35% of colour change at 650 nm for electrochromic device (ECD) with glass/ITO/PB/HPC/PEDOT:PSS/ITO/glass configuration. Twenty repetitive colour/bleaching cycles showed absorbance value change of about 0.22. The obtained results confirmed that HPC-based electrolytes are good candidates to be applied in ECDs with conducting polymers as primary and secondary electrochromic coatings.

1. Introduction

In the past years, there has been a growing interest to use the natural macromolecules as solid or gel electrolyte for electrochromic windows [1] and solar cells [2]. Among different polymer electrolytes those based on natural macromolecules such as chitosan [3], starch [4], pectin [5], agar [6], gelatin [7] and DNA [8] have been also reported. Cellulose and its derivatives [9,10] are very attractive natural polymers due to cellulose abundance in nature. Most of cellulose derivatives are soluble in water; however, some of them, such as hydroxypropyl cellulose, methyl cellulose, ethyl cellulose, cellulose acetate are soluble in organic solvents [11]. Cellulose derivatives soluble in organic solvents are essentially used as semipermeable membranes, for drug delivery, in coating materials for reservoir or osmotic systems and excipients for matrix systems [12].

Conjugated polymers are intensively investigated as active materials for electronic devices applications due to their electroluminescent, phosphorescent, electric conductivity, electrochromic or photoelectric properties. They are proposed to be used in organic light emitting diodes [13], solar cells [14], electrochromic devices [15], sensors [16] and organic thin-film transistors [17].

Poly(ethylene dioxythiophene) (PEDOT) is one of the most popular soluble conjugated polymers. PEDOT is also used as a model compound to the wide range of applications due to its excellent environmental and electrochemical stability, electric conductivity [18] and solubility in water when complexed with poly(styrene sulphonate) (PSS). Moreover, its colour change from transparent to deep blue when passing by different oxidation states is widely studied as electrochromic layer for electrochromic devices [19–22]. Polyaniline is another well-known conjugated polymer for use in electrochromic application owning to good electrochemical and optical properties. [23–26]

* Corresponding author. Tel.: +48 322 371 305; fax: +48 322371925.
E-mail addresses: przemyslaw.ledwon@polsl.pl, przemekled@gmail.com (P. Ledwon).
[1] ISE member.

http://dx.doi.org/10.1016/j.electacta.2015.01.168
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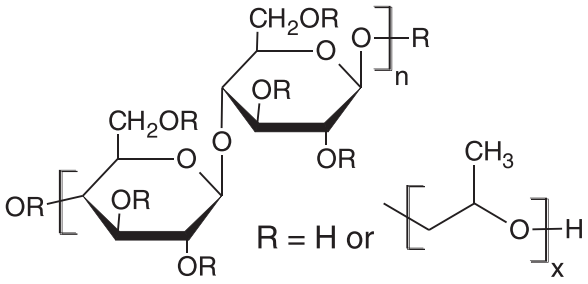

Fig. 1. The molecular structure of hydroxypropyl cellulose.

Electrochemical device with conjugated polymer, similarly to traditional one has a sandwich structure with two electrodes and an electrolyte between them [27]. The electrolyte should have appropriate counter ions that provide the neutrality of polymer film during doping as well as good conductivity [28]. Solid and gel polymer electrolytes have several advantages when compared with liquid ones. They are relatively easy to obtain and free from leakage thus safe for user. The main disadvantages are low conductivity and solubility of salts and poorer contact at electrode/electrolyte interface when compared with liquid electrolytes [29].

The present report describes a new anhydrous gel electrolyte based on hydroxypropyl cellulose (Fig. 1). The electrolyte in the membrane form was tested in small electrochromic windows (ECDs) containing PEDOT:PSS films and complementary coatings of polyaniline (PANI) and/or Prussian blue (PB). Thus, two ECDs with glass/ITO/PB/HPC/PEDOT:PSS/ITO/glass and glass/ITO/PANI/HPC/PEDOT:PSS/ITO/glass configuration were assembled and characterized.

2. Experimental section

0.25 g of hydroxypropyl cellulose (HPC; Sigma Aldrich; M_w = 100,000), previously dried at 120 °C for 12 h was dissolved in 12 ml of dichloromethane (CH_2Cl_2, Cinetica 99.98%) and stirred in room temperature to complete dissolution. 0.15 g of polyethylene glycol (PEG 300; Synth), 0.05 g of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4; Sigma Aldrich), and 0–0.25 g (0–36 wt.%) of 4-dodecylbenzenesulfonic acid (DBSA; Fluka) were added to the solution at room temperature, and stirred. The membranes were obtained by pouring of the electrolyte solution on Petri plates followed by pre-evaporation of CH_2Cl_2 at room temperature for 5 min, and subsequent drying at 40 °C for 4 h. The impedance, DSC and TGA measurements, and ECDs characterization refer to the electrolyte composition with 0.2 g (31 wt.%) of DBSA.

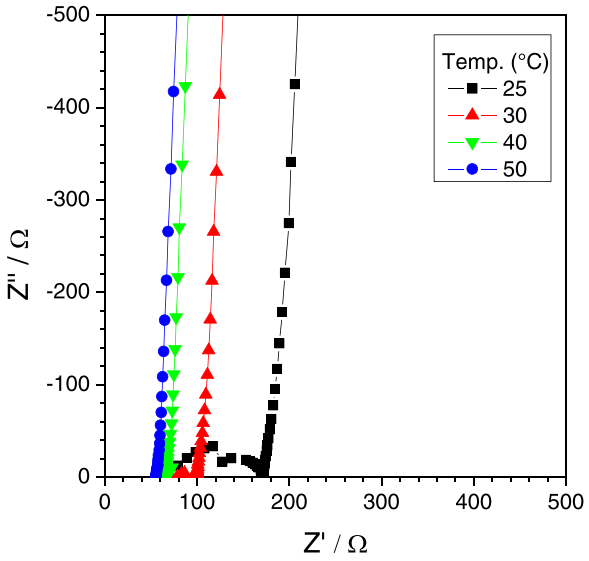

Fig. 3. Nyquist plots of HPC-based electrolyte with 31% of DBSA at different temperatures.

The impedance measurements were performed by sandwiching the 1.54 cm round and about 50 μm thick membranes between two steel electrodes. The measurements were performed in vacuum using a home-made Teflon® sample holder, and Solartron SI 1260 Impedance/Gain Phase Analyzer coupled to a computer. The frequency range was of 10^6 to 10 Hz, amplitude of 5 mV and temperature range from 25 to 50 °C in an EDG 5P oven.

The conductivity σ was then estimated from the resistance R_b. The formula $\sigma = l/R_bA$ was used, where l is the thickness of the electrolyte sample and A is the contact area between the electrolyte and the electrode [6].

The glass transition temperature of the materials was obtained from Differential Scanning Calorimetry (DSC) using DSC-50 TA Instruments apparatus. The analyses were performed in duplicate in nitrogen atmosphere at 20 mL min^{-1} flow rate and in the temperature range from −120 to 300 °C. The thermal gravimetry (TGA) were performed with TGA-50 TA Instruments in the temperature range from room to 400 °C under nitrogen atmosphere; at flow rate of 60 mL min^{-1} and a heating rate of 10 °C min^{-1}.

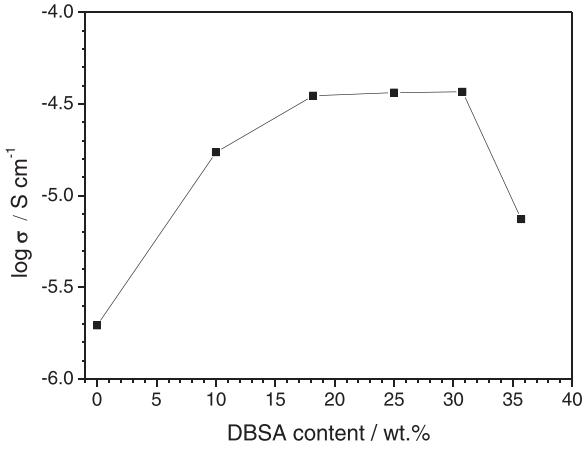

Fig. 2. Effect of DBSA content on the ionic conductivity of the HPC-based electrolyte measured at 25 °C.

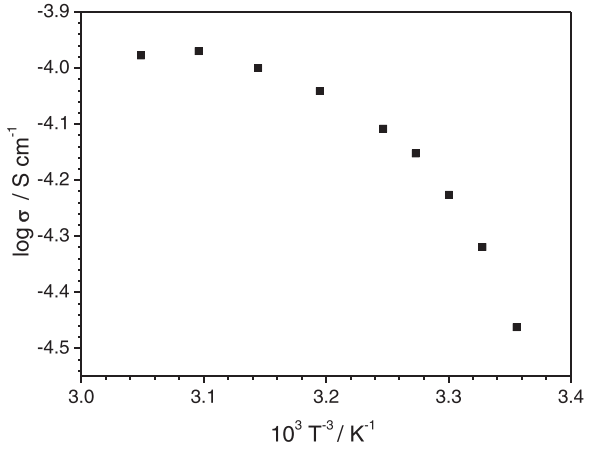

Fig. 4. Temperature-dependence ionic conductivity of the HPC-based electrolyte with 31% of DBSA.