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ORIGINAL ARTICLE

Chromophore doped DNA based solid polymer electrolyte for electrochromic devices

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Abstract The paper presents the main results of our study on preparation and characterization of conducting biomembranes to be used as solid polymer electrolytes (SPEs). It bases on deoxyribonucleic acid (DNA), glycerol (GLY) and photosensitive chromophores, like Prussian Blue (PB). Its primary application is in fabrication of electrochromic windows. The new SPEs were characterized by UV-VIS and FTIR spectroscopy. They were used in preparation of small electrochromic devices (ECDs). The obtained devices were evaluated by cyclic voltammetry and also by spectroscopic methods. The results show their color change from blue pale to intense blue after application of a direct current (DC) electric field, making the composites very interesting for industrial applications in smart windows.

1. Introduction

Nowadays, the electrochromic cells find increasing interest because of their important potential for practical applications. It concerns, particularly, display (Oh et al., 2011), photovoltaic cells for solar energy conversion (O'Reagan and Grätzl, 1991) and electrochromic smart windows (ECWs) (Macedo et al., 1992). Although all these applications are important the ECWs technology attracts a particular attention because of its high potential for practical applications: for example, in security (conductor blindness by reflected light from rear car mirrors, aircrafts pilot protection against dazzling by the sun light, electrically controllable light attenuators, optical power limiting), and more particularly for energy conservation in buildings and a better inhouse comfort. In the last applications the transmitted light intensity is controlled by the applied electric field (Lee and DiBartolomeo, 2002; Granqvist, 2014).

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The principle of ECWs operation bases on switching their states between colored and bleached ones by varying the applied electric field (Granqvist, 1995). The widely accepted explanation of the absorption change, or in other words, coloration in electrochromic thin films bases on the change of metal ions oxidation by the applied electric field, and as consequence, a modification of their absorption band. It is connected with the charge balance: electrochromic window is colored when electrons and ions meet in cathodic electrochromic layer, and is bleached when electrons and ions come together in anodic electrochromic layer (Pehliva, 2013). The ECD has a color memory, high contrast ratio, long lifetime, and an ability to adjust the transmittance through varying the applied electric field.

The ECD consists, generally of multilayers sandwiched between two electrons charge collectors coated glass substrates composed as following: an active electrochromic material; a counter-electrode; and separated by a liquid or solid polymer electrolyte (SPE) (Şenel et al., 2007). Good electrolytes for electrochromic devices (ECDs) are those in which the ions exhibit a high mobility and an ability to be intercalated or extracted from the electrochromic layer when a potential is applied.

Usually one uses the electrolyte layer in liquid-state electrolyte (LSE) (Monk et al., 2007) with high ionic conductivity. However, despite their good ionic conductivity, LSEs are not suitable for practical applications due to their tendency to leak (Gray, 1991) and difficulties related to a non-homogeneous response during the coloration process (Reiche et al., 1995). Polymer electrolytes present a particular interest, compared to other types of electrolytes used for electrochromic applications because of their long open circuit memory and uniform color changes they provide (Granqvist, 2012). Therefore they are frequently used as SPEs for ion-conducting layer.

In recent years, due to the environmental protection concerns (Florjanczyk et al., 2009), a new approach in the synthesis of polymer electrolytes was imposed through the use of biomaterials originating from renewable sources (Nogi and Yano, 2008). Thus, new SPEs for electrochromic devices were prepared from different polysaccharides (Pawlicka et al., 2008; Fuentes et al., 2007) and also from proteins as well as from deoxyribonucleic acid (DNA) (Singh et al., 2010; Pawlicka et al., 2010). The last one is one of the oldest naturally occurring polymers (Kwon et al., 2009). It attracted a special attention for applications in optoelectronics because of its particular structure consisting of double stranded helix (Samoc et al., 2006; Steckl, 2007). The important characteristics that make DNA both attractive and successful for a wide variety of applications are abundance, low extraction cost and biodegradability. Due to its ability to induce orientation of chromophores, the interaction between DNA and other molecules plays important roles in life science. Manipulating DNA molecules by physical and chemical means can lead to a variety of structures.

These materials present a unique and important practical applications property which is solid-state electrolytes. However, the ionic conductivity of SPEs made from biomaterials is relatively low. To improve it, different approaches, such as plasticization, grafting and crosslinking were utilized (Cha et al., 2004). In the previous work (Mîndroiu et al., 2014) we have shown that the ionic conductivity of DNA based membranes can be improved by doping them with different amounts of photosensitive chromophores, e.g. Nile Blue (NB). The NB molecules are intercalated between DNA double helix and cause important structural transformation of DNA (Ju et al., 2005), improving the ionic conductivity of membrane electrolytes.

The Prussian Blue (PB) molecule $\{Fe_4[Fe(CN)_6]_3]\ nH_2O\}$ is another photosensitive chromophore which is also used for a variety of applications (Somani, 2010). It is the first synthetic pigment, discovered in 1704 by Disbatch. Its chemical structure is shown in Fig. 1. Prussian Blue, also called ferric ferrocyanide is a mixed valence compound with zeolite type structure.

Due to its particular structure, and to redox, spectroscopic, charge transfer and physico-chemical properties, the large interest PB presents is for electrochromic applications. PB has a blue color in its original state, but under a negative potential can be bleached to a colorless one (reduced state). Under a positive potential PB returns to its original color state (oxidized state).

In this paper we describe the fabrication and characterization of a novel DNA–PB chromophore based solid polymer electrolyte to be used as biomembrane in electrochromic devices. The main purpose is obtaining a processable material with high ionic conductivity, good transmittance and applicable in electrochromic devices. The targeted new materials were obtained in the form of membranes, and were evaluated by various modern characterization techniques.

2. Materials and methods

2.1. Materials

Highly purified deoxyribonucleic acid (DNA), extracted from the waste produced by salmon processing industry was purchased at Ogata Research Laboratory, Ltd., Chitose, Japan. The average molecular weight (M_w) of the DNA used was $2 \times 10^7\ g\ mol^{-1}$. The chromophore used, Prussian Blue was purchased from Fluka Analytical ($M_w = 306.89$ – anhydrous).

For *electrochromic smart windows* as electrodes WO_3/ITO/glass (Solarska et al., 2006) and CeO_2–TiO_2/ITO/glass were used (Mîndroiu et al., 2014).

2.2. Experimental techniques

The infra red (IR) measurements were performed in the attenuated total reflection mode (ATR) using a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. The studied samples were placed on a Diamond crystal. The investigated spectral

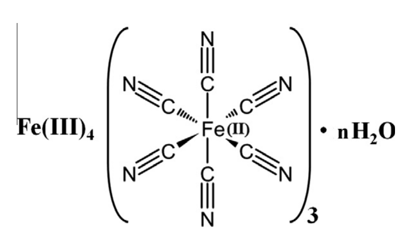

Figure 1 Chemical structure of Prussian Blue.

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