



ELSEVIER

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Reversible electrochromism between transparent and white using aqueous systems of tetrabutylammonium/bromide and tetrabutylphosphonium/bromide



Katsuyoshi Hoshino^{a,*}, Mai Ando^a, Yosuke Oikawa^a, Masafumi Okuma^a, Katsuyuki Murashiro^b

^a Graduate School of Advanced Integrated Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

^b Ichihara Research Center, JNC Petrochemical Corp., 5-1 Goikaigan, Ichihara, Chiba 290-8551, Japan

ARTICLE INFO

Article history:

Received 29 September 2014

Received in revised form

14 January 2015

Accepted 16 January 2015

Available online 6 February 2015

Keywords:

Smart window

Tetraalkylammonium

Tetraalkylphosphonium

Tribromide

White film

Memory effect

ABSTRACT

The electrode reactions of tetrabutylammonium bromide (TBABr) and tetrabutylphosphonium bromide (TBPBr) were investigated in the presence of LiBr. The cyclic voltammograms of TBABr and TBPBr exhibited a white-colored state (white film formation) and a transparent colorless state (film dissolution). Fourier transform infrared spectroscopic and X-ray photoelectron spectroscopic measurements of the white films revealed that TBA⁺ and TBP⁺ formed water-insoluble ion pairs with the tribromide generated by the electrooxidation of Br⁻ to produce the white-colored TBABr₃ and TBPBr₃ films, respectively. The films were reversibly decolorized electrochemically to the initial transparent state. In addition, the cyclic voltammetry with different alkylammonium salts ((C_nH_{2n+1})₄N⁺Br⁻, n=2, 4, 5, and 6) suggested that hydrophile-lipophile balance (HLB) was closely related to the white film formation, and that the HLB corresponding to the tetrabutylammonium made possible the formation of the stable white film with a long memory life time (recording) and the complete dissolution of the white film with a low applied potential (erasing). The morphological observation of the white films demonstrated that the white-colored appearance was attributed to the effect of light scattering by their coarse structures.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Smart windows are color-tunable devices with a colorless transparent mode and colored modes [1–8]. In the colorless transparent mode, we can view the outdoors and receive daylight under moderate climate conditions. Whereas, in the colored mode, solar energy can be blocked during a hot climate condition and the loss of infrared radiation from indoors can be prevented during a cold climate condition. Thus, the application of smart windows to window glazing in buildings should contribute to the reduction of cooling loads and heating loads, and thus increase the energy efficiency of the buildings [9]. Considering that a large amount of the total energy loss of the buildings comes from the windows [10], the role of smart windows is expected to be very important. Various electrochromic, electrophoretic, liquid crystal, and gasochromic devices have been proposed as promising candidates for smart windows [2,3,7]. Among them, the electrochromic smart window (ECW) is considered to be the most promising since it has

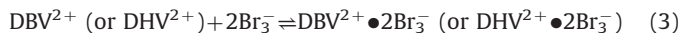
some advantages over the other devices [2,3]: The ECWs have a high transmittance modulation range; the power consumption is low since the power is only required during the switching (or the ECW has a memory effect); the stability to daylight is suitable for long-term exterior applications. Hence, the ECWs are now used in buildings and airplanes for reduced energy consumption in the United States and Europe [11].

The most applied electrochromic material is tungsten oxide, WO₃, which is colored blue and transparent in the reduced and oxidized states, respectively [12–17]. However, the blue-colored state absorbs sunlight and emits the absorbed energy as heat, therefore, its ability to block sunlight energy is limited. Thus ECWs that switched between the transparent state and the mirror state were developed [1,18–21]. The mirror state reflects sunlight and the switchable mirror is expected to be a new smart window. Recently, we developed a novel ECW that can be switched between the transparent and white states [22]. The white state was established by the electrooxidation of Br⁻ in the presence of 1,1'-dibenzyl-4,4'-bipyridinium (DBV²⁺) or 1,1'-diheptyl-4,4'-bipyridinium (DHV²⁺) ions. The electroreduction of Br⁻ produces Br₂ (Eq. (1)) which then combines with Br⁻ to give Br₃⁻ (Eq. (2)) [23,24]. The generated Br₃⁻ forms a water-insoluble complex with

* Corresponding author. Fax: +81 43 290 3478.

E-mail address: k_hoshino@faculty.chiba-u.jp (K. Hoshino).

DBV²⁺ (or DHV²⁺), DBV²⁺ + 2Br⁻ (or DHV²⁺ + 2Br⁻) (Eq. (3)). The complex is deposited on an electrode as a porous film whose external appearance was white due to its light diffusive effect.



This white-colored ECW is just like a curtained window, which is suitable for reflecting sunlight and easy on our eyes. However, its light diffusive effect is not very high and does not sufficiently prevent the penetration of sunlight energy into a building. In addition, these viologens are relatively expensive for industrial applications.

In this study, we report that the white-colored ECWs are constructed using simple aqueous tetrabutylammonium bromide (TBABr)/LiBr and tetrabutylphosphonium bromide (TBPBr)/LiBr systems. These systems show a reversible electrochromism between transparent and white, and exhibit a somewhat higher light diffusive effect than the DBV²⁺/LiBr and DHV²⁺/LiBr systems. In addition, these ammonium and phosphonium salts reduce material costs by as much as one-tenth to one-twentieth those of DBV²⁺ and DHV²⁺.

2. Experimental

2.1. Materials

As the key compounds to form white-colored deposits, tetrabutylammonium bromide (TBABr, Tokyo Chemical Industry, 99.0% <) and tetrabutylphosphonium bromide (TBPBr, Tokyo Chemical Industry, 99.0% <) were employed and used as supplied. The electrochemical behaviors of TBABr and TBPBr were investigated at an indium-tin-oxide-coated glass (ITO, 10 Ω sq⁻¹, Geomatic Co.) electrode. Prior to the electrochemical measurements, the ITO plates were cleaned by sonication in acetone for 10 min. A typical electrolyte solution was prepared by adding TBABr (or TBPBr) and a supporting electrolyte (0.1 M) to distilled-deionized water. The supporting electrolyte is a reagent grade salt, LiBr (Kanto Chemical Co., Inc., 98% <) and used as supplied. The bromide salts of tetraethylammonium (98%) and tetrapropylammonium (98%) were purchased from Aldrich. The bromide salts (98% <) of tetrapentylammonium, tetrahexylammonium, dodecyltrimethylammonium, and tetradecyltrimethylammonium were obtained from Tokyo Chemical Industry. All these bromide salts were used without purification.

2.2. Measurements

The electrochemical and spectroelectrochemical measurements were done at room temperature using a three-electrode-type cell consisting of two compartments and a potentiostat (BAS Co., model ALS 750A). All the measurements were carried out in solutions deaerated by bubbling with nitrogen gas having a normal purity (> 99.9%) for 40 min and the same gas was passed over the solution during the experiments. The ITO (10 mm × 20 mm × 1.1 mm) and the counter Pt plates (10 mm × 20 mm × 0.3 mm) were immersed in the electrolyte solution (ca. 15 ml) in the main compartment. The area of the ITO exposed to the solution was typically 10 mm × 10 mm. In the auxiliary compartment (ca. 5 ml), separated from the main compartment by a sintered glass frit, was an immersed agar bridge connected to a reference saturated calomel electrode (SCE; TOA Co.). For the measurements of the coloration efficiency and UV-vis spectra, a photoelectrochemical cell was employed in which the main compartment was designed as a rectangular prism [25,26]. The UV-vis spectra were obtained using an ultraviolet spectrophotometer (Ocean Optics, Inc., USB4000-UV-vis spectrometer and

a DH-2000 deuterium tungsten halogen light source) and an optical fiber system.

For the X-ray photoelectron spectroscopic (XPS) measurements, a Shimadzu ESCA-1000 spectrometer with Al Kα radiation was used, the absolute binding energy scale being obtained by setting the C 1 s peak to 284.6 eV. The scanning electron microscopic (SEM) and laser microscopic (LM) observations were performed using a Topcon ABT-32 microscope and a Keyence VK-9700 microscope, respectively.

3. Results and discussion

3.1. Cyclic voltammetry of TBABr and TBPBr

Fig. 1 shows the repeated cyclic voltammograms of 0.1 M TBABr (a) and 0.1 M TBPBr (b) in an aq. 0.5 M LiBr solution at the ITO electrode. The potential sweep rate and measuring temperature were 20 mV s⁻¹ and 22 ± 2 °C, respectively. When the potential was swept in the anodic direction, a steep current rise due to the electrooxidation of Br⁻ to Br₂ (Eq. (1)) was observed at anodic potentials greater than ca. 1 V in both of the voltammograms [23,24]. The generated Br₂ is combined with Br⁻ to produce Br₃⁻ (Eq. (2)). The formation equilibrium constant for Br₃⁻ is 17 M⁻¹ [24,27]. These current rises were followed by the formation of a white film on the ITO electrode surface. When the direction of the potential sweep was reversed at +1.5 V and the potential was swept toward the cathodic direction, reduction waves appeared at -0.65 V (current peak) and -0.75 V (current peak) in voltammograms a and b, respectively. The white film disappeared in response to these current flows. The above oxidation and reduction waves were also observed in the repeated voltammograms for a LiBr (0.1 M) single system (part c in Fig. 1). However, the reduction peak potential (-0.15 V) was more positive (anodic) than those of the TBABr/LiBr and TBPBr/LiBr systems, and no electrochromism was observed during the potential sweep.

In order to highlight the coloration-decoloration characteristics of the TBABr/LiBr and TBPBr/LiBr systems, in-situ UV-vis absorption measurements of the ITO electrode were carried out. Fig. 2 shows the relation between the absorbance (λ = 500 nm), A₅₀₀, and the potential that was simultaneously measured with the above-described cyclic voltammetry. Parts a and b in this figure show the results using the TBABr/LiBr and TBPBr/LiBr systems, respectively. In both of the curves, the absorbances rapidly increased from around 1 V when the potential was swept to the anodic side. This potential coincides with the potential at which the oxidation current started to increase in the cyclic voltammograms a and b in Fig. 1. Also, when the direction of the potential sweep was reversed at 1.5 V and was swept to the cathodic side, the absorbance continued to increase even 10 s after the potential reversal. This suggests that some slow events should occur during the period between the electrooxidation of Br⁻ and the deposition of white precipitates (see Section 3.3). The white film in the TBABr/LiBr system disappeared in the potential range of -0.25 to -0.8 V when the direction of the potential sweep was reversed at 1.5 V and the potential was swept toward the cathodic direction. This potential range coincides with that in which the cyclic voltammetric reduction currents occurred (see Fig. 1a). Also, in the case of the TBPBr/LiBr system, decolorization in Fig. 2b synchronously occurred with the flow of the reduction current in Fig. 1b. Based on the analogy with the previously-reported DBV/LiBr system [22], the above experimental findings suggest that the electrogenerated Br₃⁻ is combined with tetrabutylammonium cation, TBA⁺, (or tetrabutylphosphonium cation, TBP⁺) to produce water-insoluble TBA⁺Br₃⁻ (or TBP⁺Br₃⁻) and that TBA⁺Br₃⁻ (or TBP⁺Br₃⁻) deposits on the ITO electrode to produce the white film. Additionally, the Br₃⁻ anion in TBA⁺Br₃⁻ (or TBP⁺Br₃⁻) is likely to be reduced to Br⁻

Download English Version:

<https://daneshyari.com/en/article/77844>

Download Persian Version:

<https://daneshyari.com/article/77844>

[Daneshyari.com](https://daneshyari.com)