



Highly stable ion gel-based electrochromic devices: Effects of molecular structure and concentration of electrochromic chromophores



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ARTICLE INFO

Keywords:

Electrochromism
Ion gel
Electrochemical device
Copolymer
Viologen

ABSTRACT

We fabricated electrochromic devices (ECDs) based on ion gels consisting of copolymers and room temperature ionic liquids (RTILs). Two electrochromic (EC) chromophores of diheptyl viologen (DHV²⁺) and monoheptyl viologen (MHV⁺) were employed in this work. A unique magenta (reddish)-colored state can be induced in contrast to typical alkyl viologens exhibiting only bluish-colored states. The ECDs with DHV²⁺ displayed various coloration behaviors according to the concentration of viologens. While only the blue-colored state was present at low concentrations, a sequential transition from blue to magenta was observed as the concentration increased. However, the resulting magenta color was not suitable for practical applications due to its instability. On the other hand, stable magenta-colored states were achieved from the MHV⁺-containing ECDs, irrespective of viologen concentration. In addition, the devices based on MHV⁺ exhibited high color purity, large transmittance contrast, and good cyclic coloration/bleaching stability. Overall, this result implies that MHV⁺ can serve as a simple but effective EC chromophore for ECDs displaying magenta-colored states.

1. Introduction

Electrochromic (EC) materials change their optical characteristics (namely, transmittance or absorbance) via redox reactions triggered by an applied voltage [1–5]. Therefore, EC materials have been widely used in electrochemical applications including smart windows, anti-glare rear-view mirrors, and electrochemical displays [6–35]. Among these materials, small organic molecules such as 1,1'-substituted-4,4'-bipyridinium salts (dialkyl viologens, DAV²⁺) are suitable for ion gel-based ECDs because of their compatibility [24–28]. Ion gels, composites of copolymers and room-temperature ionic liquids (ILs), have many advantages including high ionic conductivity, tunable mechanical strength, and outstanding thermal and electrochemical stability [36,37]. Thus, they are suitable for low-voltage, flexible device applications [24–29,38–41].

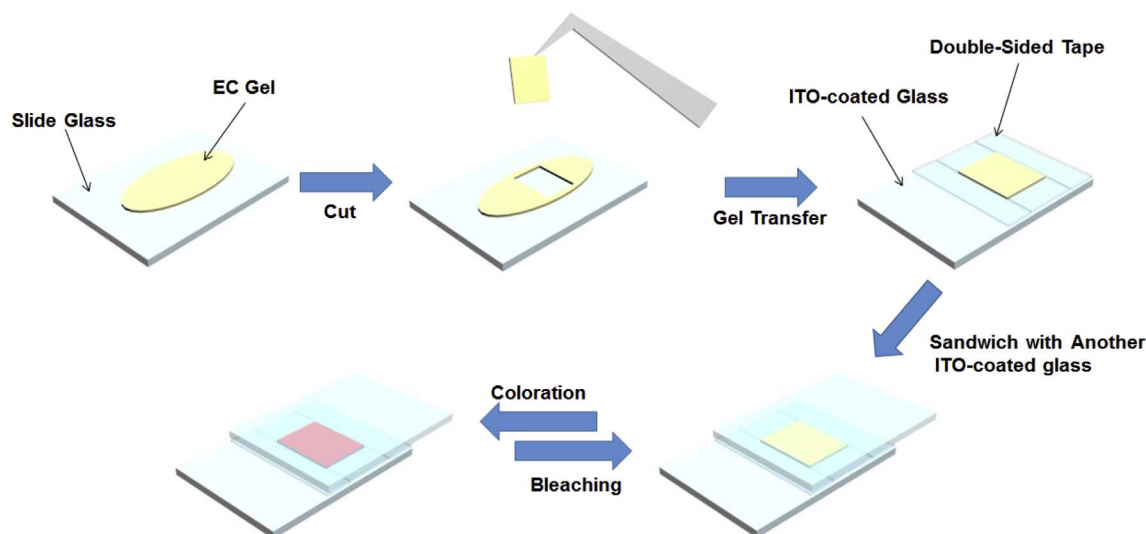
One important challenge for display applications of ECDs based on ion gels is the demonstration of various colors. Unfortunately, most DAV²⁺s with short alkyl chains (e.g. dimethyl viologen [26,30], and diethyl viologen [31,32]) exhibit only a bluish-colored state. In general, alkyl substituents must be replaced with functionalized phenyl groups in order to achieve other green or red colors. This means a relatively complex synthetic procedure such as the Zincke reaction is required

[33–35]. On the other hand, the reddish-colored state of DAV²⁺-containing ECDs has been demonstrated, when the alkyl group is longer than heptyl ($n = 7$) and the electrolyte is hydrophilic. This phenomenon originates from the dimerization of the colored species (viologen cation radicals) due to dominant spin-pairing [1,42]. However, such a reddish-colored state of DAV²⁺ exhibited low coloration/bleaching cyclic stability because of the quasi-reversibility of the dimer-to-monomer dissociation [1,43]. Recently, a magenta color was obtained from mono heptyl viologen (MHV⁺)-containing ECDs based on ion gels [28]. However, further systematic characterization is necessary for a full understanding of the EC behaviors.

In this study, we investigated the effect of EC gel composition on ECD performance including color purity, transmittance contrast, and operational stability. We chose two alkyl-substituted viologens that can provide reddish (i.e. magenta) colored states: DHV²⁺ and MHV⁺. These EC materials were combined with anodic species of dimethyl ferrocene (dmFc) in ion gels composed of poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) and room-temperature ionic liquids. The resulting gel was mechanically robust, so we fabricated the device by the 'cut-and-stick' method [27,44]. All ECDs having either DHV²⁺ or MHV⁺ showed a distinct compositional dependence in applied voltage response, color purity, and transmittance contrast between colored and

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Scheme 1. Schematic diagram of the fabrication process for ECDs based on EC gels by the “cut-and-stick” strategy.

bleached states. Moreover, the magenta-colored state of the MHV^{+} -containing device was more stable, in comparison with the ECD based on DHV^{2+} . Because MHV^{+} is more suitable for practical applications, we further examined the dynamics (coloration/bleaching response time) and coloration efficiency (η) of ECDs at three different MHV^{+} concentrations. Overall, a higher concentration of MHV^{+} induced a quicker coloration response and higher coloration efficiency, whereas the bleaching speed was slower due to larger amount of colored species to be re-oxidized. The operational stability of DHV^{2+} -containing ECDs deteriorated rapidly during coloration/bleaching switching, and eventually failed after $\sim 20,000$ s. On the other hand, the devices with MHV^{+} exhibited much better stability: a transmittance contrast of $\sim 50\%$ was maintained even after $\sim 30,000$ s operation. These results indicate that MHV^{+} is an attractive EC material for the realization of magenta (reddish) pixels for ECDs based on ion gels.

2. Experimental section

2.1. Materials

All materials were purchased from Sigma-Aldrich and used without purification unless otherwise noted. Two electrochromic materials employed in this study, diheptyl viologen bis(hexafluorophosphate) [$DHV(PF_6)_2$] and monoheptyl viologen hexafluorophosphate [$MHV(PF_6)$], were prepared by an anion exchange reaction as described in previous work [28]. To obtain a room-temperature ionic liquid of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMI][TFSI]), an aqueous solution containing 1-butyl-3-methylimidazolium chloride [BMI][Cl] and excess [Li][TFSI] was stirred at 30°C for 24 h, followed by column chromatography for purification [39]. The ITO-coated glass (sheet resistance: $10\ \Omega/\text{sq}$, Asahi Glass Co.) was washed with acetone (10 min), methanol (10 min), and 2-propanol (10 min) under sonication. Then, UV/ozone treatment was conducted for 10 min before use.

2.2. Device fabrication

First, a homogeneous acetone solution of EC gels comprised of a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMI][BF₄]) or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMI][TFSI]), $DHV(PF_6)_2$ (or $MHV(PF_6)$) and dmFc was prepared. It is noted that a copolymer of PVDF-co-HFP provided two important functions. The “cut-and-stick” strategy became available based on high mechanical

strength of ion gels with PVDF-co-HFP, so we could fabricate ECDs conveniently. In this work, we employed two ionic liquids of [BMI][BF₄] and [BMI][TFSI] for DHV^{2+} - and MHV^{+} -based ECDs, respectively. When we utilized a typical copolymer of polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene (SMS), only [BMI][TFSI] can produce uniform ion gels. However, homogeneous ion gels could be prepared with both ionic liquids, when we employed PVDF-co-HFP. The resulting solution was dropped onto the slide glass, and dried at room temperature for 1 h. Next, the gel was cut into the desired shape with a razor blade. Then, using tweezers, the EC gel was transferred onto the target ITO-coated glass. Finally, another ITO-coated glass was placed on top of the gel with an $88\ \mu\text{m}$ -thick spacer (double-sided tape) (Scheme 1). The various compositions of the gels employed for ECDs are summarized in Table 1.

2.3. Characterization

The DC voltage was supplied by a source meter (Keithley 2400, Tektronix). The UV-vis spectra of the ECDs were recorded on a UV-vis spectrometer (V-730, Jasco) from 380 nm to 1100 nm at a scan rate of 400 nm/min. The CIELAB color coordinates of the ECDs in the colored state were estimated from UV-vis absorption spectra using the Spectra Magic NX software (CM-S100w, Konica Minolta), for which spectra at a wavelength range of 380–780 nm were used. The L*, a*, and b* correspond to the color lightness, color opponents of green (negative a*)/red (positive a*), and blue (negative b*)/yellow (positive b*), respectively. To examine the operational stability of the device, transmittance change profiles of the ECDs were obtained at a fixed wavelength (545 nm) upon

Table 1
Summary of weight ratio of gel components employed in this work.^a

	DHV^{2+} or MHV^{+}	dmFc	P(VDF-co-HFP)
DHV-L	3	1	36
DHV-M	9	3	36
DHV-H	27	9	36
MHV-L	1.9	1	36
MHV-M	5.7	3	36
MHV-H	17.1	9	36

^a In this work, the amount of ionic liquid ([BMI][BF₄] or [BMI][TFSI]) was 9-times larger than copolymer P(VDF-co-HFP), in which typical copolymer mass was ~ 40 mg. Also, irrespective of the composition, the molar ratio between DHV^{2+} (or MHV^{+}) and dmFc was fixed as 1:1.

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