



Electrochromics and polymers

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Abstract

Polymers are used in commercial and proposed electrochromic devices as everything from the electrochromic materials themselves to solution thickeners, the matrix or solid phase of gels, solid polymer electrolytes and sealants. Each type of application of polymers in electrochromics is discussed and several definitions are compared with regard to gels and solution-based electrochromic redox systems. A review of electrochromics and polymer gels, especially from the perspective of the extensive patent literature on the subject, is given. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymers and electrochromic (EC) technology and EC devices are intimately linked, with a few exceptions. Polymers can be EC materials themselves such as in the well-known systems: polyaniline and polythiophene in which case the EC redox material *is* the polymer forming monomer. Also, the formation of the EC redox materials can be a polymer forming reaction such as with certain polyviologens. An EC redox material can be reacted with another monomer to form a polymer or can be reacted with functional groups on an already formed polymer such as with certain other polyviologens. If the polymer in these systems is immobilized, say for example by being surface confined on an electrode surface, then the EC redox materials are immobilized by the covalent bonds that form the polymer or attach the redox materials to the polymer.

A polymer film can contain physically immobilized redox materials in a fairly high concentration (in some cases also containing a little solvent) and can function as an EC material when the film is in contact with an

electrode. The solvent in this case can be referred to as a plasticizer, although this term is sometimes misused in descriptions of EC devices in an attempt to mask the fact that mobile, solution phase materials are present. These polymers might or might not be crosslinked. A polymer, either organic, inorganic or a hybrid, can form a gel with a solvent or solution and this type of EC layer can contain one or more mobile EC redox materials. As will be discussed below the gel can be a physical gel without chemical bond formation between the polymer chains or the gel can be a chemical gel in which the chemical bonds (usually covalent bonds) are formed between the polymer chains. The chemical bonds can be formed directly by reaction of functional groups on the polymer or by added crosslinking agents that tie polymer chains together by reacting with functional groups on more than one polymer chain. In a chemical gel, a solution phase EC system may be interspersed in a matrix phase formed by the polymer. Often, an EC redox material is free to diffuse and/or migrate in the solution phase of a gel almost as if it was contained in a free solution.

In a more simplistic case, a polymer can be added to a liquid solution simply to provide thickening or increased viscosity of the liquid solution. Thickening can

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be valuable if the device leaks or is broken and can help counteract the effects of natural convection in solution phase EC devices. Obviously, as the amount of polymer thickener is increased in a liquid solution, the viscosity increases. As the addition of polymer is continued, the viscosity increases to the point eventually where the solution is self-supporting or free standing and can be considered a physical gel.

When EC redox systems, like metal oxide films, are confined on electrode surfaces, a polymer containing electrolyte can provide for mobile ions to charge compensate the confined redox systems when they are electrochemically oxidized or reduced. These polymer containing electrolytes range from pure polymer–salt combinations to thickened salt solutions. A basic polymer electrolyte is a polymer–salt combination in which one or more ions from the salt is mobile and can be transported through the electrolyte like for example in poly(ethylene oxide) containing a lithium salt. The addition of some solvent/plasticizer often increases ionic conductivity in polymer electrolytes. Salts dissolved in the solution phase of physical and chemical gels can achieve ionic conductivities approaching those of liquid electrolytes.

Polymeric sealant materials are often critical to the life of an EC device and may represent as big a R&D challenge as the EC system itself in a device commercialization effort. Even an all solid state EC system consisting of multiple thin film ‘ceramic’ coatings on glass that has been proposed for use in a double pane, insulated glass unit configuration, may have to rely on polymeric sealant materials for a portion of its life expectancy [1,2].

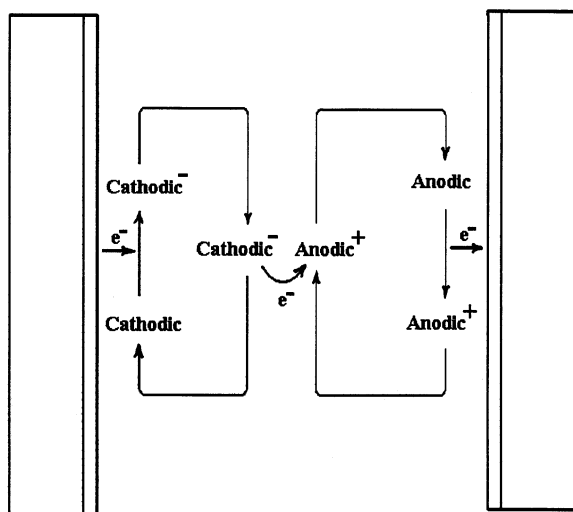


Fig. 1. Single compartment, self-erasing EC device with two solution-phase EC redox materials.

2. Solution phase electrochromics

The vast majority of EC devices manufactured today involve at least one and in most cases more than one solution-based EC redox material. These materials are free to diffuse and/or migrate to the surface of the electrodes and undergo oxidation or reduction. In the preferred systems, both materials change from colorless to colored when the device is activated. In self-erasing devices with solution-based anodic and cathodic EC redox materials, the colored redox materials diffuse from the electrode surface to the bulk of the solution and meet each other. Upon meeting, they undergo homogenous electron transfer to reform the colorless form of the redox materials and they then can be transported back to the electrode to again participate in the color forming electrochemical reaction. This process is illustrated in Fig. 1. The self-erasing process requires continuous passage of current to maintain the colored state of the device. However, for a large EC window with a slow switching time, the current required to maintain deep coloration can be less than $5 \mu\text{A}/\text{cm}^2$. In addition, self-erasing helps to make certain EC devices, like automatic dimming rearview mirror, fail safe since they spontaneously go to the clear condition in the case of power failure.

Some examples of cathodic solution-based EC redox materials are shown in Fig. 2 and a number of specific materials are given in Refs. [3–5]. These materials generally undergo two reductions of one electron each. The reductions take place at different redox potentials and the first reduction is used in EC devices to provide color formation. The fact that the product of the second electrochemical step is chemically stable (at least to a reasonable extent) means that the product of the first reaction can be highly stable, chemically. The author has observed no perceptible change in coloration of solutions for electrochemically formed viologen cation radicals of some viologens in sealed glass tubes at room temperature over a period of more than 12 years.

Some examples of anodic solution-based EC redox materials are shown in Fig. 3 and a number of specific materials are again given in Refs. [3–5]. These materials generally undergo two oxidations of one electron each. The oxidations take place at different redox potentials and the first oxidation is used in EC devices to provide color formation. Again, the fact that the product of the second electrochemical step is chemically stable (at least to a reasonable extent) means that the product of the first reaction can be highly stable, chemically.

With the proper choice of cathodic and anodic EC redox materials, devices have been constructed that cycle through full charge/discharge cycles at 70°C for many millions of cycles.

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