# Conducting polymer based solid electrochromic devices: effect of polymeric electrolytes.

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Conducting polymers (CPs) have shown a variety of color and relatively low optical switch voltage in electrochromic devices (ECDs). In previous works [1-3] polyaniline (PANI) and poly3-methylthiophene (P3MT) thin films have been used as electrochromic active materials in solid ECDs. During the device preparation two types of polymeric electrolytes were used: an ionic conductor consisting in $LiClO_4$ dissolved in polymethyl methacrylate (PMMA-$LiClO_4$) and an acidic protonic conductor made from a mixture of concentrated $H_2SO_4$ and polyethylenimine (PEI-$H_2SO_4$). Optical kinetic measurements show a faster switch speed in the case of protonic electrolyte than that of the ionic one, whereas the latter gives a better device stability. The instability of PANI based EDCs is improved if a complementary electrochromic active thin film, in this case P3MT, is introduced into the PANI based ECDs to avoid the direct contact between ITO and the acidic electrolyte (Fig.1). On the other hand a composite PANI film with a polyacid, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), gives a better device stability than that of unmodified PANI film (Fig.2). This composite material can even keep its electrochromic activity in a solid ECD with a higher pH value of PEI-$H_2SO_4$ electrolyte, leading to a weak acidic or neutral ambient for ITO. A parametric analysis of optical kinetic curves of the conducting polymer based ECDs is carried out to estimate the charge transfer parameters of the systems as a function of device preparation conditions (Eq.1).

**References**
1.  H.Hu, L.Hechavarría and J.Campos, "Optical and electrical responses of polymeric electrochromic devices: the effect of polyacid incorporation in polyaniline film", submitted, July, 2002.
2.  H.Hu, L.Hechavarría and M.E.Nicho, "Optical responses of conducting polymer thin films in gas sensors and electrochromic devices", submitted, September, 2002.
3.  L.Hechavarría, H.Hu and M.E.Rincón, "Polyaniline – poly(2-acrylamido-2-methyl-1-propanosulfonic acid) composite thin films: structure and properties", submitted, November, 2002.
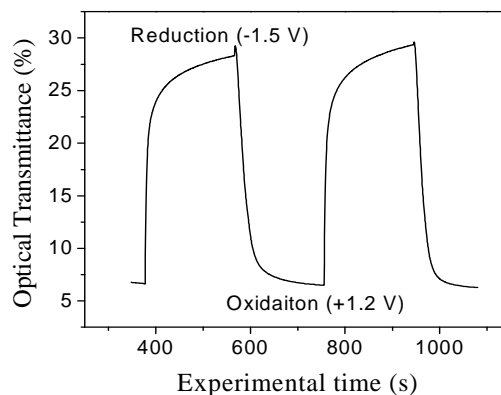
Figure 1. Optical response of a solid electrochromic device consisting on glass/ITO/PANI/PEI-$H_2SO_4$/ P3MT/ITO/glass.

Figure 2. Optical responses of solid electrochromic devices consisting on glass/ITO/PANI or PANI-PAMPS/PEI-$H_2SO_4$/ ITO/glass.
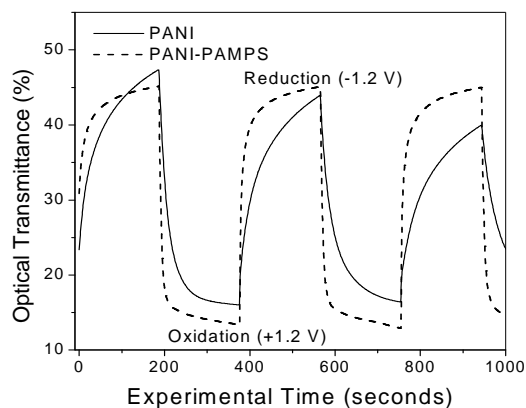
$$Y = A_1(1 - \exp(-t/\tau_1)) + A_2(1 - \exp(-t/\tau_2)) \quad (1)$$

with
$$A_{1,2} = \frac{1}{1 + \exp(nF\Delta E / RT)}$$

and
$$\tau_{1,2} = \frac{1}{\kappa_E} A_{1,2} \exp(-\alpha nF\Delta E / RT)$$



where $\Delta E = E - E^0_{A/B}$ with E as the applied voltage and $E^0_{A/B}$, the formal potential of the redox couple; $\alpha$ is the coefficient of charge transfer across the



conducting /nonconducting boundary; $\kappa_E(s^{-1})$ is the charge extraction rate at metal/polymer interface; and the rest symbols have their usual meanings.