A STUDY ON THE ELECTRO-OPTICAL PROPERTIES OF HV AND TMPD WITH THEIR APPLICATION IN ELECTOCHROMIC DEVICES

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This study is about the systematic exploration on the electro-optical properties of viologen and its application to the solution-type [1] complementary electrochromic device (ECD). Heptyl viologen (HV) [2] is chosen as a cathodic electrochrome and N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD) is incorporated as a complementary anodic electrochrome. Conducting ITO glass is used as a substrate. Cyclic voltammetry (as shown in Fig. 1 and Fig. 2), potentiometry, gavanostatic method, and UV-VIS spectrometer were combined to study the spectroelectrochemical properties of these two materials. The obtained properties were used to find the proper assembling and operating conditions for the ECD.

Side reactions, such as the comproportionation and dimerization reactions of viologen, can be observed in aqueous solution. Besides, the darkened $HVBr_2$ film deposited on the cathode is not easily oxidized so the reversibility is not good. From these points of view, viologen in aqueous system is not suitable for electrochromic applications. But when the solvent is replaced by propylene carbonate (PC) with $TBABF_4$, side reactions are not present and the reversibility gets better. In terms of electrochemistry, an applied cathodic potential of –1.3V (as shown in Fig. 3) is the best for darkening.

A darkening potential of –0.3V (as shown in Fig. 4) is the best for TMPD oxidation. But the oxidized $TMPD^{\bullet+}$ tends to segregate because of gravity, leaving the whole solution inhomogeneously colored. Electron transfer takes place between darkening species $HV^{\bullet+}$ and $TMPD^{\bullet+}$ without applying any voltage. The cell gap must be kept thin enough or the cell will not bleach completely because of iR drop.

Reference:
[1]. H.J. Byker, U. S. Patent, 5,294,376 (1994).
[2]. P. M. S. Monk, The viologen, p. 5, John Wiley & Sons, Chichester, UK (1998).

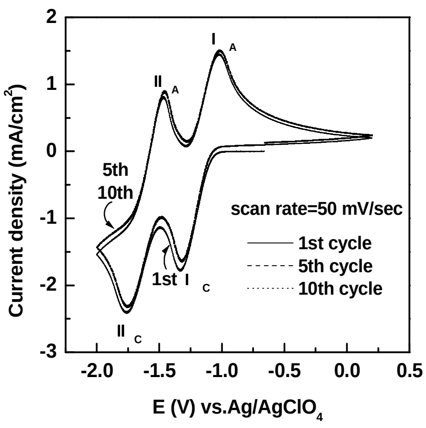

Fig. 1 Cyclic voltammograms of 0.05M $HV(BF_4)_2$ in PC with 0.5M $TBABF_4$. Both redox reactions are taking place.

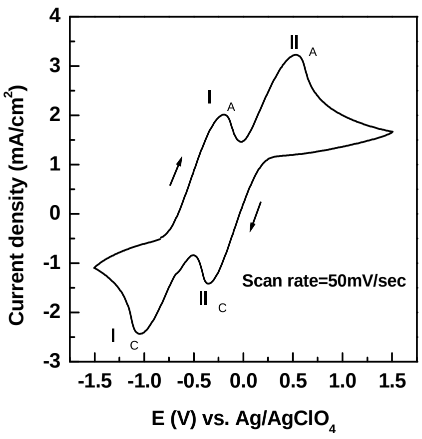

Fig. 2 A cyclic voltammogram of 0.05M TMPD in a 0.5M $TBABF_4$ electrolyte.

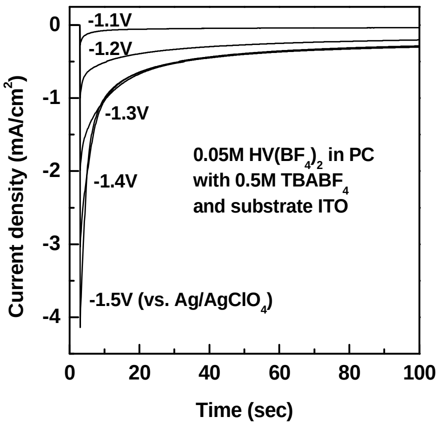

Fig. 3 Current density responses of $HV(BF_4)_2$ for the reduced potential stepping from -0.9V to -1.1 ~ -1.5V.

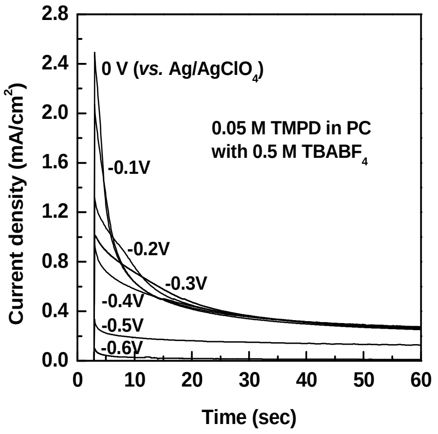

Fig. 4. Current-time responses of TMPD under various oxidized potentials, ranging from -0.6V~0V.