IN-SITU RESONANCE RAMAN SPECTROSCOPIC STUDIES OF UREASIL NANOCOMPOSITE REDOX ELECTROLYTES IN HYBRID ELECTROCHROMIC DEVICES

A. Surca Vuk[1], B. Orel[1], Ph. Colomban[2]
[1] National Institute of Chemistry
[1] Hajdrihova 19, SI – 1000 Ljubljana, Slovenia
[2] LADIR UMR 7075 CNRS & Paris VI University
[2] 2 Rue Henry Dunant, 94320 Thiais, France

Solid or semi-solid (gel) redox electrolytes with incorporated I_3^-/I^- species gain importance due to the recent advances in dye sensitized photo electrochemical cells (DSPEC)[1]. These type of redox electrolytes represent a better option because of the long- and short-term sealing problems usually encountered with DSPEC employing liquid electrolytes. Recently, a new nanocomposite organic/inorganic gel redox conductor made using acetic acid solvolysis was made in our laboratory and used as a semi–solid (gel) electrolyte in DSPEC[1]. It consists of bis end-capped triethoxysilane chemically bonded via urea groups to the polypropylene glycol (PPG) chain (n= 3 and 68) while the KI and I_2 served as a source of I_3^-/I^- redox pair. Since the electrolyte contained also mobile K^+ ions we decided to test if it could be used as gel electrolyte in hybrid electrochromic devices (ECD)[1,2].

The ECD was assembled from electrochromically active WO_3 film facing a thin Pt (sputtered) counter-electrode while the space between them was filled with the electrolyte, which after gelling laminated both halves of the cell together. ECD exhibited fast (< 10 s) coloring /bleaching changes up to 60 %. Cyclovoltammetric curves of the ECDs were recorded at different scan rates and observed current waves correlated to the transmittance changes obtained in *in-situ* UV-visible spectra. At slow scan speeds (5 $mV\ s^{-1}$) in the potential range between –2 and 0 V bleaching took place before the corresponding potential in the CV was reached indicating the presence of a side reaction ($I_3^- \leftrightarrow 3I^- + e^-$) at the WO_3|electrolyte interface. This reaction took place simultaneously with the electrode reaction at the Pt counter-electrode, i.e. $3I^- \leftrightarrow I_3^- + 2e^-$.

Because of high stability (> 2000 cycles), ease of preparation and absence of the counter-electrode with intercalation properties, the ECD seemed a suitable system for *in- situ* resonance micro Raman spectroscopic studies of redox electrolytes during the ECD's operation. The reasons for using resonance Raman spectroscopy lies in the fact that the vibrations of the I_3^- ions, which in great extent determine the suitability of the redox electrolyte for ECDs, give in Raman spectra distinct and well defined symmetric $\nu(I_3^-)$ and asymmetric $\nu(I_3^-)$ stretching bands at 111 and 141 cm^{-1}, respectively.

The resonance Raman spectra were measured by focusing the laser radiation on the redox electrolyte encapsulated in the ECD. During the potential cycling between +2 and –2 V (scan rate 5$mV\ s^{-1}$) the spectra were recorded for 120 s every 400 s (Fig. 1) so that for every potential cycle four Raman spectra were obtained. Figure 2 showed that the relative intensity of the 111 cm^{-1} ($\nu_s(I_3^-)$) band increased during the cathodic cycle and then decreased at positive potentials. That explained the functioning of ECD: the insertion of K^+ ions in the WO_3 film created excess of I^- ions in the electrolyte which transformed at the Pt electrode to the I_3^- while bleaching requires that some of I_3^- ions turned back to I^-.

Instead of electrolyte with ethanol as a solvent other redox electrolytes containing aprotic polar solvents (propylene carbonate and sulpholane) with high boiling point (> 200 °C) will be synthesized and used in ECDs. The corresponding resonance Raman spectra will be presented and results discussed in view of obtaining information how the presence of the co-solvents with strong Lewis base centers influenced redox reactions during the coloring /bleaching changes of ECD.

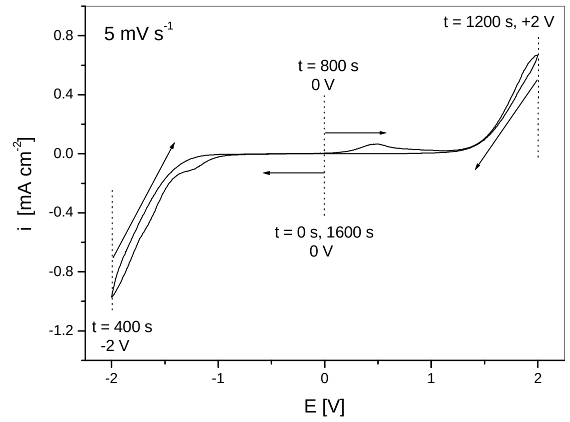

Fig. 1 Cyclovoltammetric response of a hybrid EC device (FTO // WO_3 // ICS-PPG4000 / KI / I_2 / EtOH / AcOH // Pt // FTO) during in-situ resonance Raman measurements. The dotted lines represent the potentials at which the Raman spectra recording started.

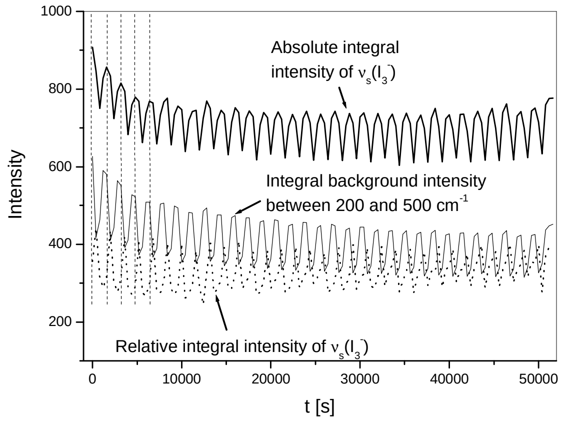

Fig. 2 In-situ resonance Raman measurements of a hybrid EC device (FTO // WO_3 // ICS-PPG4000 / KI / I_2 / EtOH / AcOH // Pt // FTO) during CV at a scan rate of 5 $mV\ s^{-1}$. Dotted lines indicate separate cycles. The absolute integral intensity of the $\nu_s(I_3^-)$ band at 111 cm^{-1}, the absolute background intensity at 200 cm^{-1} and the relative integral intensity of the $\nu_s(I_3^-)$ band at 111 cm^{-1} are shown. The laser excitation line was 647.089 nm and the power below 5 mW.

[1] B. Orel, U. Lavrencic Stangar, A. Surca Vuk, P. Lianos, Ph. Colomban, Mat. Res. Soc. Proc. 725, P7.3 (P7.3.1-P7.3.6) (2002).
[2] R. D. Rauh, *Electrochim. Acta* 44, 3165 (1999).