UREASIL IONIC NANOCOMPOSITE ORGANIC-INORGANIC GEL CONDUCTORS AS REDOX ELECTROLYTES FOR HYBRID ELECTROCHROMIC CELLS

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The synthesis of ionic conductors via the sol-gel route represents a growing field of research in the last decade. The discovery that organic-inorganic hybrid materials served as a suitable host for various salts and organic molecules paved the way to a development of organically modified silane electrolytes (ormolytes) with different ionic conductivities: proton (fuel cells), lithium (rechargeable lithium batteries and electrochromic devices (ECDs)) and redox (I_3^-/I^-) (dye sensitized photoelectrochemical cells (DSPEC)[1] and hybrid-type ECDs[2]). Recently, we made redox (gel) electrolyte from organically modified alkoxysilane (Fig. 1) and gelled it with acetic acid (AcOH), while KI and I_2 were used as a source of redox species and EtOH as a solvent. Despite a high overall photovoltaic efficiency of the (semi-solid) DSPEC (4 – 5 %) the long-term stability of the cell did not exceed few months; EtOH evaporated causing the crystallization of KI while the cell lost optical transparency [1].

The first objective of this work was to make a new type of redox electrolyte that resembles in certain aspects gel polymeric electrolytes. Polymeric gel electrolytes consist of the conductive liquid electrolyte contained within polymeric matrix, providing a stable and appropriate microstructure to immobilize and entrap the liquid electrolyte. Various alkoxysilanes with different length of the polypropylene glycol (PPG) chains were combined with various co-solvents (propylene carbonate, sulfolane, butanediol, etc.) having high boiling points (> 200 °C) with dissolved KI and I_2 and catalysed with salicylic acid. Gels did not shrink during ageing because they did not contain volatile components like AcOH and EtOH.

The interactions of KI and I_2 with co-solvents and sol-gel matrix were assessed from the intensities of the absorptions of I^- (225 nm) and I_3^- (290 and 360 nm) ions obtained from the UV-visible spectra and ionic conductivities measured with impedance spectroscopy. The main accent was given to the infrared and Raman spectroscopic investigations of the solvolysis reactions of organic acid catalysts (AcOH, valeric acid and salicylic acid) with the hybrid sol-gel precursor(s). Results of the infrared and Raman spectroscopic studies confirmed that the acetic acid reacted with the ethoxy groups of the hybrid precursor forming acetoxysilane and ethanol as reaction products. In the next step ethanol was consumed due to the reaction with AcOH giving ethylacetate and water. Water then served for the hydrolysis of the ethoxy groups and led to the formation of the silanol groups and finally to the Si-O-Si network. In-situ IR spectroelectrochemical measurements of the electrolyte encapsulated in ECD were done and the degradation mechanism established from the vibrational mode changes observed in reflection/absorption IR spectra of ECD at different potentials.

The synthesized redox electrolytes were tested in the hybrid ECDs. The main advantage of the hybrid ECD with regard to the battery-like ECD lies in the fact that they for their operation do not need the counter-electrodes with intercalation properties. The hybrid ECD consisted of an electrochromically active WO_3 film and a thin Pt-sputtered electrode encapsulating the redox electrolyte. The monochromatic transmittance changes (λ = 634 nm) between the bleached and colored states were up to 60 % depending on the co-solvent and the concentration of the incorporated KI and I_2. The best stability of more then 3000 repetitive potential cycles was obtained for the ECD employing the electrolyte with sulfolane as co-solvent.

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[2] R. D. Rauh, *Electrochim. Acta* 44, 3165 (1999).

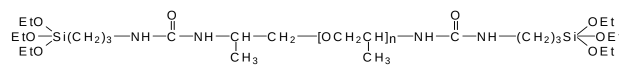

Fig. 1 Chemical structure of an ureasil precursors (ICS-PPG 4000, n~68, ICS-PPG 230, n~3).

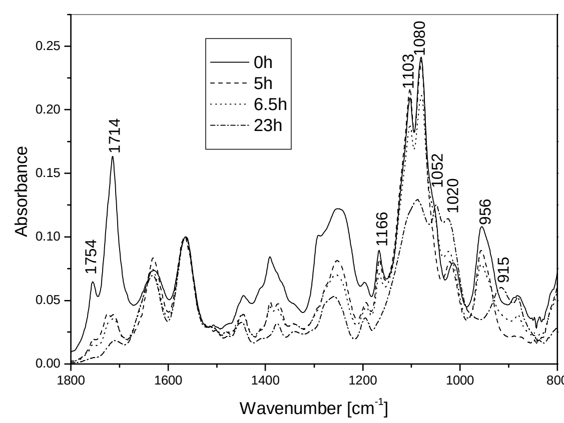

Fig. 2 Temporal IR ATR (Attenuated total reflectance) spectra of ICS-PPG 230 catalysed with AcOH. The spectra were obtained in dry atmosphere (0, 5 and 6.5 h) and after exposure to ambient (23 h).

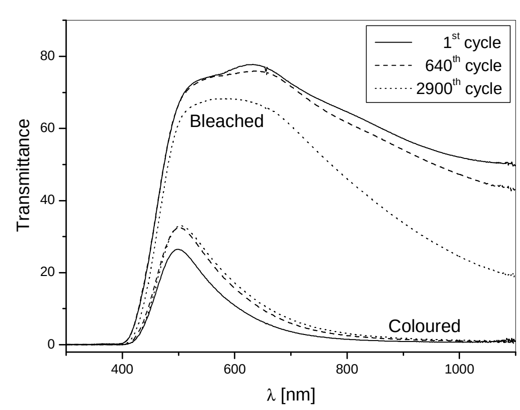

Fig. 3 In-situ UV-visible spectroelectrochemical measurements of a hybrid EC device containing redox gel I_3^-/I^- electrolyte with sulfolane co-solvent encapsulated between WO_3 and thin Pt counter-electrode film.