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Electrochimica Acta 52 (2007) 2938–2943

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Studies of solid-state electrochromic devices based on PEO/siliceous hybrids doped with lithium perchlorate

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Received 19 May 2006; received in revised form 26 October 2006; accepted 30 October 2006

Abstract

Sol–gel hybrid organic-inorganic networks, doped with a lithium salt, have been used as electrolytes in prototype smart windows. The work described in this presentation is focused on the application of these networks as dual-function electrolyte/adhesive components in solid-state electrochromic devices. The performance of multi-layer electrochromic devices was characterized as a function of the choice of precursor used to prepare the polymer electrolyte component and the guest salt concentration. The prototype devices exhibited good open-circuit memory, coloration efficiency, optical contrast and stability.

Keywords: Solid polymer electrolytes; Sol–gel; Electrochromic materials; Tungsten oxide

1. Introduction

During the last two decades a remarkable international research effort has been dedicated to the development of solvent-free solid polymer electrolytes based on poly(ethylene oxide) [1–8]. The most probable applications of these materials are in primary and secondary lithium batteries [7] or electrochromic windows [9]. Thin films of electrochromic materials deposited onto transparent conductive surfaces provide the basis of variable light transmission through controlled electrochemical oxidation or reduction. Applications in windows with adjustable light transmission for use in automotive and aeronautic vehicles and houses have already been proposed [10,11].

In recent years, the sol–gel method has been successfully used for the production of various novel organic–inorganic frameworks with tunable characteristics [12–15]. The intense activity in this sub-domain of solid-state research is motivated by advantages of tailoring advanced multifunctional compounds by mixing organic and inorganic components at the nano-dimension level in a single material [14–17]. The synergy of this combination and the specific role of the internal organic–inorganic interfaces enhances the range of application of nanohybrid materials in areas such as electrochemistry, biology, mechanics, ceramics, electronics and optics [14,15]. The hybrid concept is well-adapted to the production of advanced solid-state materials presenting ion-conducting properties, with the advantage of replacing viscous liquid systems by solid or rubbery materials [16–19].

Electrochromic materials are able to change their optical properties in a reversible manner over a large number of coloration/bleaching cycles as a result of the application of a voltage pulse. These materials are of interest as components of displays, rear-view mirrors, smart windows and time-elapse labels. Many polymers are soluble in common organic solvents and can be deposited as thin films, permitting the construction of low-cost devices with large display surfaces. In this presentation the use of sol–gel tecniques to prepare thin electrolyte films containing $LiClO_4$ dissolved in diureasil matrices is described.

2. Experimental details

2.1. Sample preparation

Host networks of organically modified silicates (ormosils), prepared from oxyethylene chains of controlled lengths grafted onto siloxane groups through urea bridges (di-ureasils), have

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doi:10.1016/j.electacta.2006.10.067

been designated as d-U(2000) and d-U(900). In agreement with traditional terminology [20,21], electrolytes were identified using the d-U(2000)$_n$LiClO$_4$ notation. In this system d-U(2000) indicates the average molecular weight of the host framework and n expresses the salt content as the number of ether oxygen atoms per Li$^+$ cation. Known amounts of lithium perchlorate were incorporated into host matrices, forming di-ureasils with compositions of $200 \geq n \geq 0.5$.

Lithium perchlorate (LiClO$_4$, Aldrich, 99.99%), α,β-diamine poly(oxyethylene-co-oxypropylene) (Jeffamine ED-2001®, Fluka, average molecular weight 2001 g mol^{-1}) and O,O'-bis(2-aminopropyl) polyethylene glycol (Jeffamine ED-900®, Fluka, average molecular weight 900 g mol^{-1}) were dried under vacuum at 25 °C for several days. The bridging agent, 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich 95%), was used as received. Ethanol (CH$_3$CH$_2$OH, Merck, 99.8%) and tetrahydrofuran (THF, Merck, 99.9%) were dried over molecular sieves prior to use. High purity distilled water was used in all experiments.

Transparent conductive oxide:gallium doped zinc oxide films (ZnO:Ga) were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ceramic oxide target (ZnO:Ga$_2$O$_3$ (95:5 wt%), SCM, Suffern, NY, USA). Sputtering was carried out at room temperature, with an argon flow of 20 sccm and a deposition pressure of 0.11 Pa. The substrate/target separation was 10 cm and the r.f. power was held constant at 175 W [22]. Electrochromic films of tungsten oxide (WO$_3$) were prepared by thermal evaporation using WO$_3$ pellets (SCM, 99.99% purity) at 1.2×10^{-3} Pa and at a rate of 1.03 nm/seg.

The synthesis of LiClO$_4$-doped di-ureasils has been described in detail elsewhere [20,21]. The procedure used for d-U(900)$_n$LiClO$_4$ involved grafting a diamine containing approximately 15.5 oxyethylene repeat units onto the ICPTES precursor, to yield the di-urea cross-linked hybrid precursor. This material was subsequently hydrolyzed and condensed in the sol–gel stage of synthesis to induce the growth of the siloxane framework. Xerogels with n greater than 5 were obtained as flexible transparent, monolithic films with a yellowish hue, whereas compounds with $n = 1$ and 0.5 were rather brittle, powdery agglomerates.

2.2. Sample characterization

2.2.1. Impedance spectroscopy

Total ionic conductivities of ormolytes were determined by impedance measurements carried out at frequencies between 96 kHz and 500 mHz with a Solartron 1250 FRA and 1286 ECI. Electrolyte samples were located between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.95%) to form a symmetrical cell which was secured in a constant-volume support [23] installed in a Buchi TO51 tube oven. Measurements of conductivity were effected during heating cycles between 20 and 90 °C. A calibrated type K thermocouple was used to measure the sample temperature with a precision of about ±0.2 °C. Repeated conductivity measurements confirmed that reproducibility was better than 5%. A typical impedance spectra is illustrated in Fig. 1.

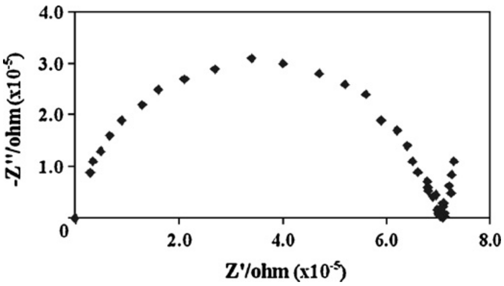

Fig. 1. AC impedance spectra of a d-U(900)$_8$LiClO$_4$ electrolyte sample at 41.7 °C.

2.2.2. Thermal analysis

Samples cut from dry films were transferred to 40 μL aluminium cans within a dry argon-filled glovebox. Analysis was carried out under flowing argon with a Mettler DSC 821e, using a heating rate of 5 °C min^{-1} between 25 and 300 °C. Thermogravimetric studies were effected using a Rheometric Scientific TG1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10 °C min^{-1} was used with all samples.

2.2.3. Electrochemical stability

Electrochemical stability of electrolytes was evaluated within a dry argon-filled glovebox using a two-electrode cell configuration. Surface polishing of a 25 μm diameter gold microelectrode was completed outside the dry-box and the electrode was washed and dried before transfer into the dry-box. Cell assembly was initiated by locating a clean lithium disk counter electrode (Aldrich, 99.9%, 10 mm diameter, 1 mm thick) on a stainless steel current collector. A sample of electrolyte was centered on the counter electrode and cell assembly was completed by supporting the microelectrode in the centre of the electrolyte disk. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at a scan rate of 100 mV s^{-1}. Measurements were conducted at room temperature within a Faraday cage located inside a glovebox.

2.2.4. Device assembly and characterization

Device assembly was carried out by spreading a small sample of electrolyte on the surface of a ZnO:Ga/WO$_3$ coated glass substrate using a spinner rotating at 2000 rpm for 40 s. Typical coating thicknesses were 200 nm (ZnO:Ga) and 300 nm (WO$_3$). A second ZnO:Ga coated plate was placed on top of the electrolyte layer. Optical transmission measurements were obtained using a Shimadzu-3100 UV–Vis–NIR double beam spectrophotometer in the wavelength range from 300 to 900 nm [22]. The choice of coloring and bleaching voltages applied to the assembled devices was based on a series of exploratory experiments. In these experiments the device response was observed as the voltage limits were progressively increased. The objective was to determine the conditions under which a rapid device response was obtained while preserving an acceptable cycle life. The maximum range of potential limits applied was from −4.0 to 4.0 V.