



Preliminary characterisation of LiAsF₆ hybrid polymer electrolytes for electrochromic devices

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ABSTRACT

In this exploratory study the results of characterisation of a poly(oxyethylene) (PEO)/siloxane hybrid network electrolyte doped with lithium hexafluoroarsenate (LiAsF₆) are described. In accordance with convention, the lithium salt concentration is expressed in terms of the number of oxyethylene units in the organic component of the host network per Li⁺ ion guest species.

Samples of solvent-free electrolytes were prepared with a range of guest salt concentration using the sol–gel process. Hybrid materials based on LiAsF₆, were obtained as mechanically robust, flexible, transparent and completely amorphous films and characterised by conductivity measurements, thermal analysis and electrochemical stability.

Preliminary characterisation of electrochromic devices (ECDs) incorporating optimised LiAsF₆-doped di-ureasil compositions has confirmed that these electrolytes perform satisfactorily as multifunctional component layers in this application.

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1. Introduction

According to Judeinstein and Sanchez's classification [1], hybrid materials in which the organic and inorganic components are linked by strong chemical bonds are designated as Class II hybrids. Several new classes of materials with novel physical and chemical properties have been synthesised by different routes using a combination of organic and inorganic segments [2]. These materials are of increasing interest because of potential applications in technologically demanding areas including optical coatings, contact lenses and electrochromic displays [3–6]. Owing to its high versatility, the sol–gel method offers important advantages for the preparation of this class of materials [7]. There is a wide choice of metal alkoxide precursors that allow the preparation of matrices with different physical and chemical properties.

The development of electrochromic (EC) materials is an exciting and rapidly expanding field of research [8]. Electrochromism may be defined as a persistent and reversible switch of colour (typically from a transparent or “bleached” state to a coloured or “written” state) in response to an electrochemical change.

A conventional electrochromic device (ECD) is composed of three elements arranged in a layered, “sandwich”-type config-

uration in which an EC electrode and a counter-electrode (CE) are physically separated, but ionically connected, by a liquid or solid (e.g., polymer) electrolyte. Colour changes occur by charging/discharging this electrochemical cell through the application of an electrical potential. A common feature of ECDs is that once they are coloured, the activating voltage can be switched off and the colour retained (memory effect), making them more energy efficient.

In recognition of their potential application in ECDs, we have prepared d-U(2000)-based hybrid electrolytes with a wide range of LiAsF₆ concentrations and characterised their ionic conductivity, electrochemical stability and thermal behaviour.

2. Experimental

2.1. Materials

Lithium hexafluoroarsenate (LiAsF₆, Aldrich, 99.998%) was used without further purification and stored prior to use in a high integrity, dry argon-filled glovebox.

The O,O'-diamine poly(oxyethylene-co-oxypropylene) (commercially available from Fluka as Jeffamine ED-2001[®], average molecular weight 2001 g mol⁻¹) was dried under vacuum at 25 °C for several days prior to use. The bridging agent, 3-isocyanatopropyltriethoxysilane (ICPTES, Aldrich 95%), was used as received. Ethanol (CH₃CH₂OH, Merck, 99.8%) and tetrahydrofuran

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(THF, Merck, 99.9%) were dried over molecular sieves. High purity distilled water was used in all experiments.

2.1.1. Preparation of the di-ureasil ormolytes

The synthetic procedure used to prepare the LiAsF_6 -based diureasils was based on an optimised two-step method previously described in detail elsewhere [9]. The experimental procedure involves grafting a PEO-based diamine onto the ICPTES substrate to yield the di-urea-bridged hybrid precursor. This grafting process was monitored by IR spectroscopy. As the reaction proceeds the very strong, narrow absorption band located at ca. 2274 cm^{-1} , assigned to the vibration of the isocyanate group of the ICPTES molecule, becomes progressively less intense, while the bands due to the presence of urea cross-links absorb more strongly. This intermediate material was subsequently hydrolysed and condensed in the sol-gel stage to induce growth of the siloxane network.

Step 1. Synthesis of the di-ureasil precursor, d-UPTES(2000)

2.0 g of Jeffamine ED-2001 was dissolved in 10 ml of THF with stirring. A volume of 0.494 ml of ICPTES was added to this solution in a fume cupboard. The reaction flask was sealed and the solution stirred for about 12 h at a moderate reaction temperature of approximately 40°C . A urea bridged organic/inorganic hybrid material, designated as di-ureapropyltriethoxysilane (d-UPTES(2000)), was obtained under these conditions.

Step 2. Synthesis of the di-ureasil xerogels, d-U(2000) $_n$ LiAsF₆

A volume of 0.467 ml of ethanol, an appropriate mass of LiAsF_6 and 0.054 ml of water were added to the d-UPTES(2000) solution prepared in the previous step (molar proportion 1 d-UPTES(2000): $4\text{CH}_3\text{CH}_2\text{OH}$: $1.5\text{H}_2\text{O}$). The mixture was stirred in a sealed flask for approximately 30 min, cast into a Teflon mould, covered with Parafilm and left in a fume cupboard for 24 h. The mould was transferred to an oven at 50°C and the sample was aged for a period of 4 weeks. These films were subsequently transferred to a Buchi TO51 oven, where residual solvent was removed over a period of 3 days. During this period the temperature of the tube oven was raised from 30 to 90°C and the oven was periodically evacuated and purged with dry argon. The ormolytes were identified using the notation d-U(2000) $_n$ LiAsF₆, where d-U(2000) represents the host di-ureasil framework (d stands for di, U denotes the urea group and 2000 corresponds to the average molecular weight of the organic precursor) and n (salt composition) indicates the number of ether oxygen atoms per Li^+ cation.

2.2. Measurements

2.2.1. DSC and TGA measurements

Hybrid electrolyte sections were removed from cast films and subjected to DSC analysis under a flowing argon atmosphere between 25 and 300°C at a heating rate of 5°C min^{-1} using a Mettler DSC 821e. All samples were presented for analysis in $40\ \mu\text{L}$ aluminium cans with perforated lids to permit the release and removal of the decomposition products. Samples for thermogravimetric studies were prepared in a similar manner, transferred to open platinum crucibles and analysed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of $10^\circ\text{C min}^{-1}$ was used to analyse all the hybrid samples.

2.2.2. Impedance spectroscopy

Total ionic conductivities of hybrid samples were determined using a constant volume support equipped with gold blocking electrodes and located within a Buchi TO50 oven. The sample temperature was evaluated by means of a type K thermocouple placed

close to the electrolyte film and impedance measurements were carried out at frequencies between 65 kHz and 500 mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range from 20 to 90°C . Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating-cooling-heating cycles. The excellent reproducibility of the results obtained using this procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

2.2.3. Electrochemical stability

Evaluation of the electrochemical stability window of hybrid compositions was carried out within a dry argon-filled glovebox using a two-electrode cell configuration. The preparation of a $25\ \mu\text{m}$ diameter gold microelectrode surface by the conventional polishing routine was completed outside the glove box. The microelectrode was then washed with THF, dried with a hot-air blower and transferred to the interior of the glove box. Cell assembly was initiated by locating a freshly cleaned lithium disk counter electrode (10 mm diameter, 1 mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of d-U(2000) $_n$ LiAsF₆ was centered over the counter electrode and the cell assembly completed by locating and supporting the microelectrode in the centre of the electrolyte disk. The assembly was held together firmly with a clamp and electrical contacts were made to the Autolab PGSTAT-12 potentiostat used to record voltammograms at a scan rate of 100 mV s^{-1} . All measurements were conducted at room temperature within a Faraday cage located inside the dry argon-filled glovebox.

2.2.4. Assembly and characterisation of the ECDs

Indium zinc oxide (IZO) films were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ceramic oxide target $\text{In}_2\text{O}_3:\text{ZnO}$ ($92:8\text{ wt}\%$; 5 cm diameter, Super Conductor Materials, Suffern, NY, USA, purity of 99.99%). Sputtering was carried out at room temperature, with an argon flow of $20\text{ cm}^3/\text{min}$ and an oxygen flow of $0.4\text{ cm}^3/\text{min}$. During sputtering the total deposition pressure (argon and oxygen) was held constant at 0.15 Pa . The distance between the substrate and the target was 10 cm and the r.f. power was maintained at 100 W . WO_3 (Super Conductor Materials, purity of 99.99%) films with thickness of about 300 nm were deposited on the transparent conductive oxide IZO-coated glass substrates by r.f. magnetron sputtering (Pfeiffer Classic 500). Sputtering was carried out at room temperature, under an argon and oxygen atmosphere with a constant deposition pressure of 2.6 Pa . The distance between the substrate and the target was 10 cm and the r.f. power was maintained at 200 W . The thicknesses of the WO_3 and IZO layers on the WO_3 /IZO-coated glass plate were 400 nm and 170 nm , respectively.

All-solid-state ECDs were constructed using the four-layer sandwich configuration glass/IZO/ WO_3 /d-U(2000) $_n$ LiAsF₆/IZO/glass. Device assembly with the EC layer was carried out by direct application of a small volume of the ormolyte sol to the surface of the WO_3 /IZO-coated glass plate. After a period of about 24 h the IZO-coated glass plate was placed on top of the resulting ormolyte gel and the two plates were pressed together so that the two coated faces bonded together inside the assembled system. In this manner a thin electrolyte layer with a surface area of approximately 2 cm^2 was formed. A strip of contact area was left uncoated on each side of the glass slide in order to make electrical contacts to the external circuit. The entire assembly procedure described in this section was carried out under atmospheric conditions.

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