

Sol–gel preparation of a di-ureasil electrolyte doped with lithium perchlorate

M.M. Silva^{a,*}, S.C. Nunes^b, P.C. Barbosa^a, A. Evans^a,
V. de Zea Bermudez^b, M.J. Smith^a, D. Ostrovskii^c

^a Departamento de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal

^b Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal

^c Department of Applied Physics, Chalmers University of Technology, 41296 Goteborg, Sweden

Received 25 October 2005; received in revised form 3 February 2006; accepted 24 February 2006

Available online 12 June 2006

Abstract

Solid polymer electrolytes (SPEs) synthesized by the sol–gel process and designated as di-ureasils have been prepared through the incorporation of lithium perchlorate, LiClO₄, into the d-U(2000) organic–inorganic hybrid network. Electrolytes with lithium salt compositions of n (where n indicates the number of oxyethylene units per Li⁺ ion) between ∞ and 0.5 were characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode, thermal analysis and Fourier transform Raman (FT-Raman) spectroscopy. The conductivity results obtained suggest that this system offers a quite significant improvement over previously characterized analogues doped with lithium triflate [S.C. Nunes, V. de Zea Bermudez, D. Ostrovskii, M.M. Silva, S. Barros, M.J. Smith, R.A. Sá Ferreira, L.D. Carlos, J. Rocha, E. Morales, J. Electrochem. Soc. 152 (2) (2005), A429]. “Free” perchlorate ions, detected in all the samples examined, are identified as the main charge carriers in the sample that yields the highest room temperature conductivity ($n = 20$). In the di-ureasils with $n \leq 10$ ionic association is favoured and the ionic conductivity drops.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Solid polymer electrolytes; Lithium perchlorate; Sol–gel process; Organic–inorganic hybrid networks

1. Introduction

The genesis of solvent-free SPEs is generally considered to have taken place in 1973 with the publication of the study of a poly(ethylene oxide)(PEO)-based system by Fenton and co-workers [2]. Recognition of the potential application of these semi-crystalline solids in advanced batteries [3,4] naturally led to a rapid increase of interest and the production of a large number of publications that have formed the foundation of this sub-domain of the solid electrolyte class of materials [5–9]. Although applications have been proposed in sensors, displays, intelligent windows and reactive labels, the main impetus of research continues to be directed toward advanced batteries.

First-generation SPEs were based on commercial PEO, but it was soon realized that the performance limitation imposed by the crystalline component of this macromolecule could be atten-

uated by using amorphous PEO-derived synthetic networks. Many examples can be found of new electrolytes based on co-polymers [10] and blends [11], materials doped with nano-dimensioned fillers [12] or plasticized formulations [13]. In the search for novel host networks a promising strategy is provided by the application of the sol–gel process [14,15] to produce organic–inorganic hybrid networks. This synthetic approach allows networks with tailored physical and chemical properties to be produced without recourse to complex experimental procedures.

In this study we report the thermal and electrochemical properties of PEO/siloxane ormolytes (organically modified silicate electrolytes) synthesized through the addition of controlled quantities of LiClO₄ to a di-ureasil [1,16–18] hybrid host matrix prepared by the sol–gel method. The oxyethylene segments of a commercial diamine were bonded to a silica matrix through urea (–NH(C=O)NH–) bridges to yield a semi-crystalline macromolecular structure [1] with high optical transparency, good thermal stability and encouraging chemical and mechanical properties. An FT-Raman spectroscopic analysis was carried out

* Corresponding author.

E-mail address: nini@quimica.uminho.pt (M.M. Silva).

on representative samples with the objective of gaining insight into the nature of the charge carriers.

2. Experimental details

2.1. Materials

Lithium perchlorate (Aldrich, 99.99%) and α,β -diaminepoly (oxyethylene-co-oxypropylene (commercially available as Jeffamine ED-2001[®], Fluka, average molecular weight 2001 gmol^{-1}) were dried under vacuum at 25 °C for several days prior to use. The bridging agent, 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich 95%), was used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 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.

In agreement with the terminology adopted in previous publications [1,16–18], the ormolytes were identified using the notation $\text{d-U}(2000)_n\text{LiClO}_4$. In this representation the $\text{d-U}(2000)$ denotes the presence of the host di-ureasil framework with average molecular weight of 2000 and n expresses the salt content in terms of the number of ether oxygen atoms per Li^+ cation.

2.2. Synthesis

The LiClO_4 -based di-ureasils were prepared according to an optimized two-step method described in detail elsewhere [1]. The synthetic procedure involved grafting a diamine containing approximately 40.5 oxyethylene repeat units to 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 the synthesis to induce the growth of the siloxane framework.

2.2.1. Step 1: synthesis of the di-ureasil precursor, $\text{d-UPTES}(2000)$

Two grams of Jeffamine ED-2001[®] were dissolved in 10 ml of THF with stirring. A volume of 494 μl of ICPTES was added to this solution in a fume cupboard (molar proportion 1 Jeffamine ED-2001[®]: 2 ICPTES). The flask was then sealed and the solution stirred for about 12 h at moderate temperature (≈ 40 °C). A urea cross-linked organic-inorganic material, designated as di-ureapropyltriethoxysilane ($\text{d-UPTES}(2000)$), was obtained under these conditions. The grafting process was followed by infrared monitoring. During this reaction the intensity of the isocyanate vibrational band situated at approximately 2273 cm^{-1} progressively decreased, finally disappearing when the reaction was complete. These spectral changes were accompanied by the growth of a series of bands due to the presence of urea groups in the region between 1800 and 1500 cm^{-1} .

2.2.2. Step 2: synthesis of the di-ureasil xerogels, $\text{d-U}(2000)_n\text{LiClO}_4$

A volume of 466 μl of $\text{CH}_3\text{CH}_2\text{OH}$, an appropriate mass of LiClO_4 (see Table 1) and 54 μl of water were added to the $\text{d-UPTES}(2000)$ solution prepared in the previous step (molar proportion 1 ICPTES: 4 $\text{CH}_3\text{CH}_2\text{OH}$: 1.5 H_2O). The mixture

Table 1

Relevant details of the synthetic procedure of the $\text{d-U}(2000)_n\text{LiClO}_4$ di-ureasils

		Step 1	Step 2
$\text{d-U}(2000)_n\text{LiClO}_4$			
V (Jeffamine)/g		2.0	
V(ICPTES)/ μl		494	
V(THF)/ml		10	
V($\text{CH}_3\text{CH}_2\text{OH}$)/ μl		–	466
V(H_2O)/ μl		–	54
$n = \text{O}/\text{Li}^+$ (mol mol^{-1})	$m(\text{LiClO}_4)$ (g)	Si/Li^+ (mol mol^{-1})	Si/Li^+ (gg^{-1})
∞	–	–	–
200	0.0215	9.8765	22.9642
80	0.0539	3.9506	9.1857
60	0.0718	2.9630	6.8893
40	0.1077	1.9753	4.5928
35	0.1231	1.7284	4.0187
30	0.1436	1.4815	3.4446
25	0.1724	1.2346	2.8705
20	0.2154	0.9876	2.2964
15	0.2872	0.7407	1.7223
10	0.4309	0.4938	1.1482
8	0.5386	0.3951	0.9185
5	0.8617	0.2469	0.5741
1	4.3088	0.0494	0.1148
0.5	8.6176	0.0247	0.0574

was stirred in a sealed flask for approximately 30 min and then cast into a Teflon mould, covered with Parafilm and stored 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.

The xerogels with n greater than five were obtained as flexible transparent, monolithic films with a yellowish hue, whereas the compounds with $n = 1$ and 0.5 were rather brittle, powdery agglomerates. The content of LiClO_4 in selected samples and other relevant information are included in Table 1.

2.3. Experimental techniques

2.3.1. Ionic conductivity

The total ionic conductivity of the ormolyte was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.95%) to form a symmetrical cell. The electrode/ormolyte/electrode assembly was secured in a suitable constant volume support [19] and installed in a Buchi TO51 tube oven. A type K thermocouple was placed close to electrolyte disk to measure the sample temperature. Bulk conductivities of electrolyte samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyzer and 1286 electrochemical interface) between 25 and 100 °C and at approximately 7 °C intervals.

2.3.2. Thermal analysis

Ormolyte sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between 40 and 350 °C and at a heating rate of 5 °C min^{-1}

Download English Version:

<https://daneshyari.com/en/article/194798>

Download Persian Version:

<https://daneshyari.com/article/194798>

[Daneshyari.com](https://daneshyari.com)