Electrochimica Acta 237 (2017) 259–266

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Polycondensation as a Versatile Synthetic Route to Aliphatic Polycarbonates for Solid Polymer Electrolytes

Leire Meabe[a], Nerea Lago[a], Laurent Rubatat[c], Chunmei Li[d], Alejandro J. Müller[a,b], Haritz Sardon[a,b], Michel Armand[d], David Mecerreyes[a,b,*]

[a] POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Centre, Avda. Tolosa 72, 20018 Donostia-San Sebastián, Spain
[b] Ikerbasque, Basque Foundation for Science, E-48011 Bilbao, Spain
[c] CNRS/ UNIV PAU & PAYS ADOUR, INSTITUT DES SCIENCES ANALYTIQUES ET DE PHYSICO-CHIMIE POUR L'ENVIRONNEMENT ET LES MATERIAUX, UMR5254, 64000, PAU, France
[d] CIC Energigune, Alava Technology Park, Albert Einstein 4801510, MIÑANO Álava, Spain

ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form 30 March 2017
Accepted 31 March 2017
Available online 2 April 2017

Keywords:
Aliphatic polycarbonates
solid polymer electrolytes
ionic conductivity

ABSTRACT

Recently, polycarbonates have been proposed as alternative materials to poly(ethylene oxide) as the polymeric matrix for solid polymer electrolytes (SPEs). Aliphatic polycarbonates SPEs have shown excellent ionic conductivity values even at room temperature, good electrochemical stability and high lithium transference number. In most works, the aliphatic carbonates have been synthesized using two main routes, ring-opening polymerization of cyclic carbonates and copolymerization between CO_2 and epoxides. Although these synthetic routes are successful, impose wither 2 or 3 carbon aliphatic chain between the carbonate groups. In this paper we propose conventional polycondensation as a route to aliphatic polycarbonates for solid polymer electrolytes. Thus, we synthesized a series of eight different aliphatic polycarbonates by polycondensation of aliphatic diols and dimethyl carbonate. The reactions were carried out using an organocatalyst under melt-condensation conditions at temperatures ranging between 130 and 180 °C. A series of eight different aliphatic polycarbonates were obtained having between 4 and 12 methylene groups between the carbonate units in each repeating unit and molecular weights between 8,000 and 43,000 g mol^{-1}. All the aliphatic polycarbonates were semicrystalline showing melting temperatures within 45 and 63 °C and glass transition temperatures around −40 °C. The use of those aliphatic polycarbonates as matrix for solid polymer electrolytes was evaluated. First, adding 30 wt% of LiTFSI, the best ionic conductivity measured at ambient temperature $6{\cdot}10^{-6}$ S cm^{-1} was obtained from poly(heptamethylene carbonate). Then, adding different salt weight percent (from 20 to 80 wt%), the highest value was obtained for low molecular weight poly(dodecamethylene carbonate) using 80 wt% of LiTFSI which showed an excellent ionic conductivity value of $1{\cdot}10^{-4}$ S cm^{-1} at room temperature.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

It is well known that the electrolyte has a crucial role in batteries, which acts as the ion transport pathway. The properties of a battery: cell capacity, working temperature range, safety issues and cyclability are affected significantly by the chosen electrolyte [1]. The usage of organic solvents based electrolytes has safety and environmental drawbacks, such as flammability issue and leakage of the liquid [2,3]. Therefore, the research of alternative electrolytes has drawn much attention of researchers during the past four decades trying to enhance properties of the electrolyte, where flammable and volatile organic electrolytes are totally excluded, in order to obtain better and safer batteries [4].

Solid electrolytes have been proposed as alternative to liquid based electrolytes, where inorganic solid electrolytes and solid polymer electrolytes (SPE) are included. Among them, polymer

* Corresponding author at: POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Centre, Avda. Tolosa 72, 20018 Donostia-San Sebastián, Spain. Tel.: 0034943018018.
E-mail address: david.mecerreyes@ehu.es (D. Mecerreyes).

http://dx.doi.org/10.1016/j.electacta.2017.03.217
0013-4686/© 2017 Elsevier Ltd. All rights reserved.

electrolytes have attracted interest in devices because of its easier processability, mechanical properties and thermal stability [5,6]. The gold standard polymer studied as SPE is poly(ethylene oxide) (PEO) [7,8]. Preferred SPEs are based on high molecular weight PEO copolymers with reduced crystallinity and good mechanical properties due to their favorable properties for salt solvation and ion conduction [9,10]. At the end of the day, PEO based solid polymer electrolytes have shown great performance in lithium batteries at 70 °C, but its performance at room temperature is limited due to the relatively low ionic conductivity value. Over the years, several approaches have been performed to further improve properties of the polymer electrolytes such as ionic conductivity, the Li^+ transference number and the poor interfacial contact of the electrolyte at room temperature. Those approaches included adding solvent or a plastizers (gel polymer electrolytes) [11], ionic liquids (iongel polymer electrolytes) [12,13] or inorganic nanoparticles (nanocomposites polymer electrolytes) [14–17]. In the last years, the interest is shifting to improving the lithium transference number of the polymer electrolyte by synthesizing new polymeric single-ion conductors [18–25].

Therefore, there is still a continuous search on solid polymer electrolytes which show high ionic conductivity values at room temperature. In the last years, polycarbonates have been proposed as alternative materials to poly(ethylene oxide) as the polymeric matrix for solid polymer electrolytes (SPEs). Aliphatic polycarbonates' SPEs have shown excellent ionic conductivity values even at room temperature, good electrochemical stability and high lithium transference number [26]. In those works, the aliphatic carbonates have been synthesized using two main routes, ring-opening polymerization of cyclic carbonates [26,27] and copolymerization between CO_2 and epoxides [28–30]. Although these synthetic routes are successful, they show some limitations and synthetic difficulties for the chemical modification of the aliphatic polycarbonate chain. For instance, the chemical structure of the aliphatic polycarbonates obtained is limited to the availability of cyclic monomer undergoing ring-opening polymerization, usually trimethylene carbonate or in the case of epoxides, to two-carbon spacer.

Very recently, polycarbonates having ethylene oxide links have been synthesized through polycondensation showing promising properties [31]. In this article, we present the synthesis of a series of aliphatic polycarbonates by simple melt polycondensation employing organocatalysis [32]. The synthetic reaction involves the melt condensation of dimethyl carbonate with a diol at high temperatures and under high vacuum conditions in the presence of an organocatalyst. This synthetic method offers the possibility of designing great variety of aliphatic polycarbonates by just changing the chemical structure of the commercially available aliphatic diol used in the reaction. Using this method a series of eight different aliphatic polycarbonates are obtained having between 4 and 12 methylene groups between the carbonate units. The different aliphatic polycarbonates are characterized and evaluated as matrix for solid polymer electrolytes.

2. Experimental

2.1. Materials

Dry dimethyl carbonate (99+ %) and 4-dimethilaminopyridine (DMAP) (99%) were purchased from Across Organics. 1,4-butanediol (99 +%), 1,5-pentanediol (98%), 1,7-heptanediol (95%), 1,8-octanediol (99 +%), 1,9-nonanediol (99%), 1,10-decanediol (99%) and 1,12-dodecandeiol (98%) were supplied by Across Organics and 1,6-hexanediol (99%) by Sigma-Aldrich. All diols and DMAP were dried for 5 h prior to use. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) (99.9%) was supplied from Solvionic. Tetrahydrofurane (GPC grade) was obtained from Scharlab, dry acetonitrile (ACN) (99.9%) from Across Organics, dichloromethane (DCM) (Cerfified AR for Analysis) and methanol (MeOH) (Certified AR for Analysis) from Fisher Scientific, toluene (HPLC grace) from Sigma-Aldrich and deuterated chloroform (99.8%) from Deutero GmbH.

2.2. General synthetic route of aliphatic polycarbonate by polycondensation

The chemical route used in this work was similar to the one previously reported [32]. Essentially, DMC, diol and the organocatalyst, DMAP, were added into a schlenk flask, where the flask was connected to the vacuum. A 2:1:0.01 molar ratio of DMC:diol:DMAP was used. The temperature was raised and kept isothermally at 130 °C for 4 h. Then again, the temperature was increased until 180 °C and high vacuum was applied. The reaction was left overnight. The high vacuum was necessary in the second step to remove the MeOH produced during the first step and to evaporate the excess DMC added to the flask. All the polymers were dissolved in dichloromethane and purified by precipitation in cold methanol.

2.3. Preparation of solid polymer electrolytes based on aliphatic polycarbonates and LiTFSI

Solid polymer electrolytes were prepared by solvent casting method from solution in anhydrous ACN (0.3 g of polymer/salt in 0.5 mL dry ACN). The solutions were directly casted onto the stainless steel spacers. First, ACN was removed under vacuum at room temperature during 24 h, and then after, the evaporation was completed inside of an argon filled glovebox, increasing the temperature up to 60 °C and applying vacuum for another 24 h. The samples were sandwiched between two stainless steel (SS) electrodes (average surface area = 2.01 cm^2) in a coin cell CR2016 assembled in an argon-filled glove box (M-Braun).

To perform the electrochemical stability window study the polymer electrolyte, P12C 80 wt% LiTFSI, was prepared directly casting on stainless steel or copper disk, the solvent was removed as it has been explained before. The polymer electrolyte was sandwiched between a metal lithium foil, which served as a reference and counter electrolyte, and a working electrode. Stainless steel disks were used as working electrodes during anodic stability study, whereas copper disks for cathodic measurements. The samples were sealed in a coin cell CR2032.

2.4. Characterization methods

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker spectrometers at 500 MHz at room temperature, using deuterated chloroform.

The absolute molar masses of polycarbonates were analyzed by SEC/MALS/RI. The equipment was composed of a LC20 pump (Shimadzu) coupled to a DAWN Heleos multiangle (18 angles) light scattering laser photometer equipped with an He–Ne laser (λ = 658 nm) and an Optilab Rex differential refractometer (λ = 658 nm), (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Styragel HR2, HR4, and HR6; with pore sizes from 10 2 to 10 6 Å). Filtered toluene was used for the calibration of the 90° scattering intensity. The detectors at angles other than 90° in the MALS instrument were normalized to the 90° detector using a standard (PS 28 770 g mol^{-1}; Polymer Labs), which is small enough to produce isotropic scattering, at a flow rate of THF through the detectors of 1 mL min^{-1}. In addition, the same standard and conditions were used to perform the alignment (interdetector delay volume) between concentration and light-scattering detectors and the

Download English Version:

https://daneshyari.com/en/article/4767151

Download Persian Version:

https://daneshyari.com/article/4767151

Daneshyari.com