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A Maceiras

University of the Basque Country

A Goren

University of Minho

Vitor Sencadas

University of Wollongong, University of Minho, victors@uow.edu.au

Carlos M. Costa

University of Minho

J L. Vilas

University of the Basque Country, Basque Center for Materials

See next page for additional authors

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Abstract

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Keywords

polyimide, electrospun, battery, ion, lithium, membranes, performance, electrolyte, groups, dipolar, cyano, effect, gel

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Authors

A Maceiras, A Goren, Vitor Sencadas, Carlos M. Costa, J L. Vilas, Senentxu Lanceros-Méndez, and L M. Leon

Effect of cyano dipolar groups on the performance of lithium-ion battery electrospun polyimide gel electrolyte membranes

A. Maceiras¹, A. Gören^{2,3}, V. Sencadas^{2,4}, C.M. Costa^{2,3*}, J.L. Vilas^{1,5}, S. Lanceros-Méndez^{2,5,6}, L.M. León^{1,5}

¹Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco/EHU, Apdo. 644, Bilbao E-48080, Spain.

²Centro/Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal

³Centro/Departamento de Química, Universidade do Minho, 4710-057 Braga, Portugal

⁴School of Mechanical, Materials and Mechatronics Engineering, Faculty of Engineering and Information Science, University of Wollongong, Wollongong, NSW 2522, Australia

⁵Basque Center for Materials, Applications and Nanostructures (BCMaterials), Parque Tecnológico de Bizkaia, Ed. 500, Derio 48160, Spain.

⁶IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

*corresponding author: victors@uow.edu.au

Abstract:

Three polyimide membranes (polymer 0CN, copolymers 0CN/2CN (50/50) and polymer 2CN), with and without –CN dipolar groups, have been prepared by electrospinning and evaluated as lithium-ion battery separators. The prepared membranes show average fiber diameters between 0.5 and 1.09 μm and a degree of porosity of ~80%. The thermal stability, uptake, tortuosity and ionic conductivity values are influenced by the presence of the –CN dipolar groups in the polyimide polymer chain.

The best battery performance in LFP/Li system is obtained for the 0CN sample, which shows discharge capacity values of 149.7 mAh.g^{-1} , 146.5 mAh.g^{-1} and 124.6 mAh.g^{-1} at C/20, C/10 and C/5, respectively. The obtained high solution uptake, ionic conductivity values and rate capability show that these materials are promising candidates for battery separators for rechargeable lithium-ion batteries, when compared to glass microfibre separators.

Keywords: polyimide, battery separator, gel electrolyte, lithium-ion battery

1. Introduction

Aromatic polyimides show outstanding thermal and thermo-oxidative stability, excellent solvent resistance, good electrical and mechanical properties and chemical resistance [1]. Nonetheless, polyimides have just found applications in a limited number of technologies, due to their typical infusible and insoluble nature. Nowadays, thanks to advances in polymer research and structural modifications of the polymer backbone, these drawbacks can be overcome, opening the way to a wider range of applications areas.

Polyimides have rigid molecular chains, resulting in poor solubility in common organic solvents which affects their synthesis, processing and application [2]. Therefore, significant efforts have been performed to chemically modify the structure in order to improve their processability without affecting other relevant properties, such as thermal stability or mechanical properties. These modifications often rely on the introduction of flexible groups, such as $-O-$, $-CO-$, $-SO_2-$, $-S-$ and $-C(CF_3)_2-$, into the backbone of the polyimides, inclusion of bulky side groups or incorporation of a kink in the backbone through *ortho* or *meta* catenation instead of *para* catenation [3].

Traditionally, polyimide processing was carried out with poly(amic acid) intermediate which is then converted to polyimide by thermal treatment, i.e. the so called two-step process [4]. This method involves reacting a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent such as N-methylpyrrolidinone (NMP) or N,N-dimethylacetamide (DMAc) to yield an intermediary product (polyimide precursor) called poly(amic acid) (PAA), which is cyclized into the final polyimide, by thermal treatment. However, this process has several problems such as emission of volatile byproducts and the storage instability of the poly(amic acid) intermediate [5]. Therefore, alternative synthetic methods have been developed in order to obtain polyimide directly in a unique step. The so-called one-step polycondensation method is employed for the synthesis of polyimides soluble in organic solvents at polymerization temperatures [6]. It involves heating at 180-220°C a stoichiometric mixture of monomers in a high boiling solvent or in a mixture of solvents. The imidization proceeds rapidly at these temperatures and the water generated is distilled off continuously as an azeotrope mixture along with the solvent (normally nitrobenzene, m-

cresol, or other dipolar aprotic amide solvents) in the presence of a catalyst. An acidic catalyst such as benzoic acid is added to promote the formation of trans-isoimide and later a basic catalyst such as isoquinoline to convert it into a polyimide.

The possibility of obtaining directly soluble polyimides has widened the range of applications. Apart from the typical applications as films or varnishes for electronic/energy applications that take advantage of their thermal and mechanical stabilities, aromatic polyimides are being used in advanced technologies such as composites [7], nanomaterials [8], electrochromic [9], photomechanical [10], thermo-optical [11], fuel cells [12], or gas separation membranes [13]. In addition, there is a relatively new use of certain amorphous aromatic polyimides as piezoelectric polymers [14] or magnetoelectric materials [15].

With respect to the area of energy and taking into account their properties, polyimides can be used as battery separator membranes for lithium-ion batteries where it is necessary to improve both, performance and safety [16].

Battery separators consists on a porous membrane soaked with an electrolyte solution (salts dissolved in organic solvent) that allows controlling the movement of the ions between anode and cathode during charge and discharge of the battery [17].

The main parameters affecting the performance of a battery separator are permeability, porosity/pore size, electrolyte absorption and retention, chemical, mechanical and thermal stability [17, 18].

Different types of polymers are being investigated, the most used being poly(ethylene) (PE) [19], poly(propylene) (PP) [20], poly(ethylene oxide) (PEO) [21], poly(acrylonitrile) (PAN) [21], polyimide (PI) [22], poly(vinylidene fluoride) and its copolymers (PVDF-TrFE and PVDF-co-hexafluoropropene, PVDF-HFP) [23, 24].

The advantages of polyimide in comparison with the aforementioned polymers is that it exhibits higher thermal stability and chemical resistance [25].

Different works show that polyimide membranes have higher capacity when compared to Celgard membranes and that it improves the safety of the battery [22, 25-27] and thus, several approaches and materials have been used in order to obtain electrospun polyimide membranes [22, 26], different from the one presented in this work.

New amorphous copolyimides containing nitrile groups obtained from a mixture of two aromatic diamines, 1,3-Bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene (diamine 2CN) and 1,3-Bis(3-aminophenoxy)benzene (diamine 0CN) have been synthesized in that the conduction process and electric behavior is dependent on the CN group content

present in the polyimides [14]. The aim of this work is to evaluate the suitability of electrospun membranes from these materials for battery separators and the determination of the influence of cyano dipolar groups in their electrochemical properties. The battery separator performance is thus evaluated for membranes without CN groups (poly0CN) and with two CN groups (poly2CN), as well as for a copolymer of both polymers (0CN/2CN (50/50)).

2. Experimental details for materials and methods

2.1. Reagents

The commercial products used for the synthesis of monomers and polymers were used as received: 4,4'-oxydiphtalic anhydride (ODPA), 2,6-dichlorobenzonitrile, N,N-Dimethylacetamide (DMAc), meta-Cresol (m-cresol) and isoquinoline supplied by Sigma-Aldrich. 1,3-bis(3-aminophenoxy)benzene, N,N-dimethylformamide (DMF) and Toluene were purchase from Tokyo Chemical Industry, TCI, Merck and Fluka, respectively.

2.2. Synthesis and electrospun membranes fabrication

2.2.1. Synthesis of the polyimides

Two homopolymers and one copolymer have been prepared by the one step polycondensation method: a homopolyimide with zero cyano lateral groups in its backbone (polymer 0CN); a polyimide with two cyano groups (polymer 2CN); and a random copolyimide which is a equimolar mixture of the two previous ones, i.e, a 50 mole percentage of repetitive unit with zero cyano groups (0CN) and another 50 mole percentage of the two cyanos unit (2CN) (copolymer 0CN-2CN (50/50)).

Polycondensation polymerizations start with a reaction between a dianhydride (4,4'-oxydiphtalic anhydride) and a diamine, the 1,3-bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene (Diamine 2CN) [4] or the 1,3-Bis(3-aminophenoxy)benzene (Diamine 0CN), in the case of the homopolymers, but with both diamines when a copolymer is developed.

Polyimides were synthesized via one-step polycondensation with m-cresol as solvent as illustrated in figure 1, with a few milliliters of toluene in order to generate a new lower-boiling azeotrope than the pure one. Stoichiometric quantities of dianhydride and diamine were placed in a two-necked flask fitted with a mechanical stirrer and a condenser. The reaction flask was purged with dry N₂ and the solution was progressively heated to 185°C and maintained at that temperature for 8h. During heating, the water produced by the imidization reaction was removed continuously by azeotropic distillation and a stream of nitrogen [14]. The reaction mixture was then cooled to room temperature and poured into excess methanol. The fibrous polymer obtained was washed thoroughly with boiling ethanol using a soxhlet extractor and dried at 80°C under vacuum overnight.

Figure 1 - Reactive structures and scheme of the one-step method for the copolyimide 0CN-2CN

2.2.2. Electrospinning conditions

The three different polymers (polymer 0CN, copolymer 0CN-2CN (50/50) and polymer 2CN with $M_n = 2.9, 2.5$ and $3.4 \text{ (g.mol}^{-1}\text{).10}^{-4}$, respectively (see supporting information)) were dissolved in a mixed solvent of N,N-dimethylformamide and N,N-dimethylacetamide (1/1 volume ratio) to achieve a polymer concentration of 50% (w/v) in the solution. The dissolution was performed at room temperature under magnetic stirring. Then, the solution was transferred to a glass syringe fitted with a metallic needle with an inner diameter of 0.5 mm. Electrospinning was conducted at 1.5 kV cm^{-1} with a high voltage power supply from Glassman (model PS/FC30P04). A syringe pump (from Syringe pump) was used to feed the polymer solutions into the needle tip at 0.2 mL h^{-1} (Q, flux). A schematic representation of the experimental setup is shown in Figure 2. Polymer 0CN, copolymers 0CN/2CN (50/50) and polymer 2CN were prepared and will be called hereafter 0CN, 0CN/2CN(50/50) and 2CN, in the following.

Figure 2 - Schematic representation of the electrospinning setup and the corresponding optimized processing conditions.

2.3. Membrane characterization

2.3.1. Electrolyte solution and uptake

Electrospun membranes were immersed during 1h in a liquid electrolyte (1 M of LiPF₆ in EC:DMC (LP30, Merck)) and the uptake was evaluated by equation 1:

$$Uptake = \left(\frac{M - M_0}{M_0} \right) \times 100\% \quad (1)$$

where M_0 is the mass of the membrane and M is the mass of the membrane after immersion in the electrolyte solution.

2.3.2. Porosity

The porosity of the membranes was determined by the method of dry-wet weight [28]. The wet weight of the membranes was measured after wiping the excess water. The dry weight of membranes was measured after a freeze drying process. The porosity of the membranes was calculated after equation 2:

$$\varepsilon = \frac{W_w - W_d}{\rho_w A \delta} \times 100\% \quad (2)$$

where ε is the porosity of membrane, W_w (g) is the mass of the wet membrane, W_d (g) is the mass of the dry membrane, ρ_w (g/cm³) is the density of water, A (cm²) is the area and δ (cm) is the thickness of the membrane.

2.3.3. Characterization techniques

Electrospun membranes were coated with a thin gold-layer using a sputter coating (Polaron, model SC502 sputter coater), and their morphology and average fiber size were analyzed using a scanning electron microscopy, SEM (NanoSEM – FEI Nova 200) with an accelerating voltage of 10 kV. The size of the fibers was measured in 10,000x magnified SEM images using the Image-Pro Plus software.

Infrared measurements (FTIR) were performed in the fiber mats at room temperature with a Jasco FTIR 4100 apparatus in ATR mode from 4000 to 600 cm^{-1} after 32 scans and a resolution of 4 cm^{-1} .

The thermal behavior was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurements were performed using a Mettler DSC 822 equipment from 30 to 250 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C min}^{-1}$, under nitrogen atmosphere in aluminum pans. Thermogravimetric analysis was performed in a Mettler TGA/SDTA 851 thermobalance. Samples (about 10 mg) were heated from room temperature up to 900 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. The initial degradation temperature was determined from the intersection between the tangent to the baseline and the inflection point in the thermogram.

2.4. Cell preparation and electrochemical measurements

Electrochemical impedance spectroscopy of the electrospun polyimide samples was evaluated with a Biologic VMP3 instrument in a frequency range from 1 MHz to 10 mHz with an amplitude of 10 mV at room temperature. The ionic conductivity (σ) was determined according to:

$$\sigma = \frac{t}{A \times R_b} \quad (3)$$

where t is the thickness, A is the area of the samples and R_b is the bulk resistance obtained from the intercept of the imaginary impedance (minimum value of Z'') with the slanted line in the real impedance (Z') through the Randles circuit [29].

Lithium metallic/Separator/C-LiFePO₄ half-cells were assembled in an argon-filled homemade glove box using Swagelok-type cells with C-LiFePO₄ electrode (8 mm diameter) as cathode material, electrospun polyimide membranes and glass microfibre separators soaked in electrolyte solution as separator (10 mm diameter) and 0.75 mm thick Li metal foil (8 mm diameter) as anode material. The C-LiFePO₄ based cathode preparation was described in [30].

Galvanostatic cycling was carried out at room temperature at different C rates (C/20, C/10 and C/5) between a minimum and a maximum limit of 2.5 and 4.0 V, respectively, using a Landt CT2001A Instrument.

3. Results and discussion

3.1. Morphology and physico-chemical characteristics of the membranes

Different electrospinning processing parameters can affect sample morphology, such as applied electric field, solution temperature, viscosity and collection procedure, among others.

In order to obtain uniform electrospun fiber membranes, a stable Taylor cone is required, so preliminary electrospinning experiments were conducted in order to evaluate the best conditions while maintain its stability (data not shown). As a result, it was found that a distance between the needle tip and the ground collector of 20 cm, a polymer feed rate of 0.2 mL h^{-1} and a needle with an inner diameter of 0.5 mm, represent the optimum conditions for the different modified polyimides, and therefore they were kept constant in the experiments.

The microstructure of the obtained polyimide electrospun samples is presented in Figure 3. Independently of the type of polyimide, smooth and beadless individual fibres were obtained with random alignment and open overall microstructure. The average fibre diameter decreases with the incorporation of dipolar –CN groups in the polymer chain: while neat polyimide presents an average diameter of $1.09 \pm 0.24 \text{ }\mu\text{m}$, the modified polymer shows average diameters of $0.50 \pm 0.13 \text{ }\mu\text{m}$ for the 0CN/2CN and $0.59 \pm 0.13 \text{ }\mu\text{m}$ for the 2CN sample (table 1).

Figure 3 –

The average porosity of the polymer membranes was determined according to equation 2 and ranges around 80% for all samples, showing that the modification of the polyimides by incorporation of CN-dipolar groups and even the reduction of the average fiber diameter does not play any role in the membrane porosity. Table 1 summarizes the average fiber diameter and degree of porosity for the different samples.

Table 1 – Average fiber diameter and degree of porosity for the different electrospun membranes.

Sample	Average fiber diameter / μm	Porosity ± 5 / %
0CN	1.09 ± 0.24	82
0CN/2CN (50/50)	0.5 ± 0.13	79
2CN	0.59 ± 0.13	83

Infrared spectroscopy was used for the determination the influence of the incorporation of the –CN dipolar groups in the vibrational modes of the polyimide electrospun membranes. As shown in Figure 4, independently of the samples, the vibrational modes characteristics of polyimide are detected at 720 cm^{-1} (deformation of the imide ring or the imide IV carbonyl group), 1028 cm^{-1} (symmetric C-O-C tension), 1117 cm^{-1} (imide III band), 1244 cm^{-1} (asymmetric C-O-C tension) and $1437\text{--}1641\text{ cm}^{-1}$ (C-C tension) [31, 32]. Further, with the incorporation of the –CN dipolar groups, no vibrational modes are totally suppressed and no new modes appear in the spectra (figure 4).

Figure 4 – FTIR spectra of the electrospun membranes

The thermal stability of the electrospun polyimide membranes was evaluated by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) and the results are shown in figure 5. It is observed that the 0CN and 2CN polyimides show a glass transition temperature (T_g) at 176 and 174 °C, respectively, while the copolymer 0CN/2CN (50/50 w/w) shows the lowest T_g , at around 157 °C (table 2), which is lower than the one reported in [33] for polymer films. It was reported that the high electric field used to obtain electrospun fibers can lead to polymer chain alignment along the longitudinal direction of the polymer fiber [34], which in turn can influence the glass

transition temperature of the polymer, as demonstrated for poly(vinyl alcohol) (PVA) [35].

In the present work, it was expected that the alignment of the polymer chains along the polymer fiber would increase T_g , as observed in macroscopic polymer systems [36]. Nevertheless, just a slight change from 178 °C in 0CN and 176 °C in 2CN from bulk polymer [33] down to 176 °C and 174 °C (table 2) in 0CN and 2CN electrospun fibers, respectively, was observed. On the other hand, a strong decrease of T_g is observed in the 0CN/2CN (50/50 w/w) copolymer sample, which can be related to polymer chain [35] and amorphous regions confinement [37] in the copolymer due to the different nature of the polymer phases with and without CN-dipolar groups.

It was observed the absence of cold-crystallization or melting processes, which indicates a complete amorphous polymer with a good thermal stability up to 250 °C (figure 5a).

TGA results show that the 0CN and 2CN samples exhibit a single step thermal degradation process that starts at ~500 and 403 °C, respectively, while the copolymer 0CN/2CN presents two main degradation steps, the one at lower temperature corresponding to the degradation of the 2CN fraction of the material, and the one at higher temperature corresponding to the 0CN polyimide fraction (figure 5b). The thermal stability of the polyimides and the copolymer are thus dependent on the amount of CN units present in the main chain: increasing the amount of cyano groups (CN) in the polymer chain leads to a decrease of the thermal degradation temperature (table 2).

Figure 4 – a) DSC and b) TGA characteristic curves of the electrospun membranes

Finally, the amount of residue measured at 800 °C is between 57% for the 0CN and 64% for the 2CN sample (table 2), being therefore the same for all samples, within experimental error.

Table 2 – Glass transition temperature (T_g), onset temperature of degradation (T_d) and residue at 800 °C for the different samples.

Sample	$T_g \pm 2 / ^\circ\text{C}$	$T_d \pm 5 / ^\circ\text{C}$	Residue at 800 °C
0CN	176	500	57

0CN/2CN (50/50)	157	390	60
2CN	174	403	64

Thus, it is confirmed the relationship between the initial degradation temperature (T_d) and the presence in the structure of the CN groups, the presence of the two cyano groups (2CN) in the polyimide decreasing the thermal stability of the electrospun membranes.

3.2. Electrical properties

Impedance spectroscopy was used for the determination of the ionic conductivity of the electrospun membranes. The room temperature Nyquist plots of the electrospun membranes after soaked with electrolyte solution are represented in Figure 6a). Generally, in the Nyquist plot it is possible to detect two main regions: a semicircle located at the high-frequency range that corresponds to the charge transfer process and a straight line at lower frequencies that is related to the diffusion process [29].

For the 0CN and 0CN/2CN (50/50) samples, it was not detected the semi-circle at high frequency, the ionic conductivity value (Figure 6d) being determined by the intersection of the linear relation between the imaginary part axis with the real axis. For the 2CN sample the semi-circle is observed, its width representing the bulk resistance of the electrospun membrane. Thus, the inclusion of –CN dipolar groups strongly affects the ionic conductivity of these membranes (Figure 6d and Table 3).

Figure 6b shows the impedance modulus as a function of frequency for the electrospun membranes at room temperature. The impedance modulus increases with decreasing frequency, in particular for frequencies below 5 kHz due to the restricted dynamics of ion mobility within the porous membranes

The phase angle as a function of frequency for the electrospun membranes is illustrated in Figure 6c). Independently of the sample, it is observed that the maximum phase angle occurs above -60° , with the existence of multi peaks for the 0CN and 0CN/2CN samples. This behavior can be represented by a constant phase element, which can be modeled as a capacitor with a distribution of relaxation times [38]. Finally, the ionic conductivity value determined through the Nyquist plot (Figure 5a) is represented in Figure 6d.

Figure 6 – a) Nyquist plot, b) impedance modulus, c) phase angle and d) ionic conductivity for the electrospun membranes at room temperature.

Thus, the presence of –CN dipolar groups in the polyimide polymer affects the ionic conductivity and the uptake value (Table 3).

Uptake, tortuosity and ionic conductivity values of the samples are summarized in Table 3.

The tortuosity (τ) represented in Table 3 is the ratio between the effective capillarity to thickness of the sample and was determined through equation 4 [39]:

$$\sigma_{eff} = \sigma_0 \frac{\phi}{\tau^2} \quad (4)$$

where σ_0 is the electrical conductivity of the liquid electrolyte ($\sigma_0=11.6 \text{ mS.cm}^{-1}$), σ_{eff} is the conductivity of the membrane and the electrolyte set and ϕ is the porosity of the membrane. The values of the tortuosity range from 4 for the 0CN/2CN copolymer up to 11 for the 2CN sample (table 3). Ideally the tortuosity should be 1 and describes an ideal porous membrane, nevertheless these results confirm the good porous interconnectivity, in agreement with the results shown in figure 3, which enhances the ionic transport through the membrane and consequently to high battery cycling performance [40].

Table 3 – Uptake, tortuosity and ionic conductivity values for the different samples.

Sample	Uptake / %	τ	$\sigma_{eff} / \text{mS.cm}^{-1}$
0CN	1153	5	0.44
0CN/2CN (50/50)	509	4	0.70
2CN	564	11	0.08

Table 4 compares the physicochemical properties of the polyimide electrospun membranes developed in this work with related ones in the literature.

Table 4 – Ionic conductivity value and degree of porosity for the polyimide electrospun membranes produced in this work and comparison with other polyimide separator membranes reported in the literature. The electrolyte solution is also indicated.

Type of membrane	Electrolyte solution	Porosity	σ_i / mS.cm ⁻¹ at 25°C	Ref
Composite	1 M LiPF ₆ in EC-DMC-EMC	65	0.897	[25]
Nanofiber	0.5M LiBOB/PC	73%-87%	0.89	[22]
Nanofiber	-----	-----	-----	[26]
Composite	1M LiPF ₆ in EC-PC-DMC-EA	-----	0.65	[27]
Nanofiber	1M LiPF ₆ in EC-DMC	82	0.44	This work

The ionic conductivity and degree of porosity values determined for the polyimide electrospun membranes are analogous to the values observed for other polyimide separator membranes reported in the literature (Table 4). The differences can be related to the microstructure and the electrolyte uptake values, as different electrolyte solutions have been used (Table 4).

The electrochemical stability window of polyimides for lithium-ion battery separators has been determined [22, 27], the different polyimides showing excellent electrochemical stability at voltages above 4.0 versus Li/Li⁺, *i.e.*, showing compatibility with different cathodes.

3.3. Battery performance

In order to determinate the battery performance of the electrospun membranes as battery separators in rechargeable lithium-ion batteries, half-swagelok cells were fabricated with C-LiFePO₄ as cathode material and lithium metal as anode material, the results being shown in figure 7.

Taking into account the uptake and ionic conductivity values presented in Table 3, the battery performance is just evaluated for the 0CN and 2CN samples. The polyimide samples with –CN dipolar groups do not show stable mechanical properties after 2hours in contact with the electrolyte solution.

Figure 7 shows the voltage *versus* capacity value at different scan rates from C/20 to C/5 for the 0CN (Figure 6a) and 2CN samples (Figure 6b) where the scan rates are shown at C/20 and C/10 (4° cycle for 0CN and 3° cycle for 2CN). The differences

observed in battery performance (Figure 7) is related to the ionic conductivity and uptake of the samples. The electrolyte uptake occurs in the amorphous region which undergo swelling to accommodate the electrolyte, the ion migration in this region being also supported by large-scale segmental motions of the polymer chains [41].

Independently of the samples, figure 7 shows the typical flat plateau of the C-LiFePO₄ cathodes that reflects the reversible charge (lithium removal)-discharge (lithium insertion) behavior.

This flat plateau corresponds to the Fe²⁺/Fe³⁺ redox reaction and depends on the scan rate [42].

Figure 7 – Voltage *versus* capacity value for the a) 0CN and b) 2CN samples at different scan rates

Figure 7 also shows that the discharge capacity value decreases progressively as the scan rates increases, which is a result of ohmic drop polarization within the electrode material. For the 0CN sample, the discharge capacity value at C/20, C/10 and C/5 is 149.7 mAh.g⁻¹, 146.5 mAh.g⁻¹ and 124.6 mAh.g⁻¹, respectively, and for the 2CN sample, the discharge capacity values at C/20 and C/10 are 98.7 mAh.g⁻¹ and 4 mAh.g⁻¹, respectively

The cyclability of the electrospun membranes (Figure 8) is compared in relation to a commercial glass fiber separator. Thus, Figure 8 shows a summary of the rate performance of the polyimide electrospun membranes and a glass microfibre separator.

Figure 8 – Discharge capacity as a function of cycle number for different scan rates.

Independently of the scan rate, significant differences are observed in the discharge capacity behavior of the polyimide electrospun membranes. The higher discharge capacity of the lithium-ion battery of the 0CN sample is attributed to the higher ionic conductivity which is favorable for the fast transportation of lithium ions between the electrodes. Comparing this sample with the ones with the glass microfiber separators, the discharge value of the polyimide membrane is similar up to a discharge current rate of C/10.

Figure 9 – Cycling performance at C/5 of C-LiFePO₄ cathodic half cells containing 0CN based separator membranes.

The cycling performance of the 0CN sample at C/5 is shown in figure 9. The discharge capacity value after 15 cycles is 125 mAh.g⁻¹ and corresponds to a capacity retention of 74%. This high value is attributed to the ionic conductivity and electrolyte uptake values that facilitates the repeated lithium ion insertion/de-insertion. The capacity retention was calculated based on the theoretical capacity of C-LiFePO₄ (170 mAh.g⁻¹). Further, the Coulombic efficiency at C/5 for the 0CN sample is 100% for all cycles, which indicates excellent reversibility and stability upon charge–discharge cycling. In summary, the 0CN sample shows good cyclability and rate capability in comparison to glass microfibre separators. Considering also its thermal stability, high wettability and ionic conductivity value, the 0CN membrane is an excellent battery separator for high power density lithium-ion batteries.

Conclusions

Three types of polyimide membranes (polymer 0CN, copolymers 0CN/2CN (50/50) and polymer 2CN) with different –CN dipolar groups were fabricated by electrospinning. For all samples, the electrospun membranes showed a homogeneous morphology based on uniform fibers. The thermal stability, uptake, tortuosity and ionic conductivity values depend on the presence of –CN dipolar groups in the polyimide. These novel polyimide separators show good wettability, high ionic conductivity and cycling performance for lithium-ion battery applications, the cycling performance being dependent on the cyano groups.

The cathodic half-cell containing the 0CN based separator shows stable cycling performance independently of the scan rate, the 0CN membrane being therefore a promising separator for high power lithium-ion battery application.

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Figure 3: Representative SEM images and fiber size distribution of polyimide membranes for (a-b) 0CN, (c-d) 0CN/2CN(50/50) and (e-f) 2CN.

Figure 4 – FTIR spectra of the electrospun membranes

Figure 4 – a) DSC and b) TGA characteristic curves of the electrospun membranes

Figure 6 – a) Nyquist plot, b) impedance modulus, c) phase angle and d) ionic conductivity for the electrospun membranes at room temperature.

Figure 7 – Voltage *versus* capacity value for the a) 0CN and b) 2CN samples at different scan rates

Figure 8 – Discharge capacity as a function of cycle number for different scan rates.

Figure 9 – Cycling performance at C/5 of C-LiFePO₄ cathodic half cells containing 0CN based separator membranes.