Short communication

Lithiated short side chain perfluorinated sulfonic ionomeric membranes: Water content and conductivity

Walter Navarrini [a,*], Bruno Scrosati [b], Stefania Panero [b], Alessandro Ghielmi [c], Aldo Sanguineti [c], Giuliana Geniram [c]

[a] *Politecnico di Milano, Dipartimento di Chimica, via Mancinelli 7, Milano, Italy*
[b] *Università "La Sapienza", Via Aldo Moro 5, Roma, Italy*
[c] *C.R.S. Solvay-Solexis,Viale lombardia 20, Bollate, Milano, Italy*

Abstract

In view of possible applications as single-ion electrolyte for lithium batteries, some aspects of the lithium form of Hyflon Ion ionomer, a sulfonic short side chain (SSC) electrolyte, have been investigated. The synthesis of the ionomer and the successive membrane preparation is reported. An appropriate methodology for the direct salification of the ionomeric membrane from the SO_2F form to lithium salt, using lithium hydroxide in absence of organic solvent has been found. Utilizing these SSC lithium ionomer membranes and though a particular methodology for the dehydration of the lithium ion membrane in non-aqueous media, it has been possible to achieve an ionic conductivity of 10^{-3} S cm^{-1} at room temperature [W. Navarrini, S. Panero, B. Scrosati, A. Sanguineti, European Patent 1,403,958 A1 (2003)]. Surprisingly it was observed that the membrane ionic conductivity depends on the dehydration methodologies adopted.

1. Introduction

Since the late 1960s perfluorinated sulfonic ionomer membranes such as solid polymer electrolytes (SPEs) have been studied as ion-conducting polymer separators in electrochemical applications [2]. More recently, an innovative industrial route to produce SSC ionomeric polymers has been intensively studied and is being exploited. Specifically, an appropriate sulfonic monomer synthesis [3] and micro-emulsion polymerization reaction technology has been developed [4]. These highly innovative synergic processes have allowed the industrial development of the perfluorinated short side chain (SSC) sulfonic ionomers Hyflon Ion®, (Solvay Solexis) [5]. These SSC ion-conducting polymers have revealed a better electrochemical behavior compared to the long side chain (LSC) Nafion-like

polymer as membranes in the important polymer electrolyte membrane fuel cell (PEMFC) application [6]. The lithium polymer batteries have many potential advantages such as low manufacture cost, diversity of size and shape, high voltage and large capacity. In addition, in the LPBs family, the ionomeric single-ion lithium polymer batteries should be characterized by high transport number, since the anionic species are bonded to the polymeric backbone and lithium cations are the only mobile ions able to conduct electricity [7]. Nevertheless these ionomeric electrolytes are affected by low conductivity [8] and low cyclability [9], probably due to segregation phenomena and surface instability [10].

2. Experimental

The analytical determinations mentioned hereinafter were carried out by using a dry-box under nitrogen atmosphere because of the sensitivity of the membrane properties to water content.

* Corresponding author. Tel.: +39 0223993029; fax: +39 0223993080.
E-mail address: walter.navarrini@polimi.it (W. Navarrini).

2.1. Specific conductivity determination

The ionic conductivity determination was carried out by the electrochemical impedance spectroscopy technique, using a Solartron.RTM. 1250 instrument, in the frequency range 65 kHz–100 mHz.

The ionic conductivity was calculated from bulk sample impedance value on the real axis R_e, the specific conductivity σ is determined by the relation:

$$\sigma = \frac{l}{R_e A}$$

where l is the distance between the electrodes, R_e the value of the real component of the complex impedance (Ω) and A is the area of the electrodes. $1/A$ represents the geometric constant of the measurement cell. The conductivity determination is carried out by using two SS310 blocking electrodes (surface area about 0.78 cm^2). All conductivity measurements were performed after equilibrating the membrane with pure solvent or a solution of different solvents.

2.2. Membrane swelling

Membrane swelling is determined by the difference in weight with respect to the initial weight of the unswollen membrane. Thickness measurements were made using a micrometer with accuracy of 2–3.0 μm. Non-aqueous solvents were purchased as high purity battery grade (0.1% water). All solvents were additionally dried under 4 A activated molecular sieves and stored in a dry-box atmosphere.

2.3. Water content determination

Membrane water content and solvent water content were determined by Karl Fischer coulometric titration with a Mitsubishi apparatus analysis.

The Karl Fischer apparatus was directly introduced in the dry-box under nitrogen atmosphere during the water analysis. The water content of the lithium ionomeric membrane specimen was made by introducing the membrane sample directly in the Karl Fischer titration chamber. After few minutes from the introduction of the membrane sample the coulometric titration went to stable equilibrium. It has been found that without these practical expedients the membrane water content determinations were erratic and inconsistent.

In fact, the remaining amount of water in the dehydrated membrane prepared under vacuum as low as 10^{-3} mbar at 110 °C for 64 h was still significant. The amount of water remaining in the membrane after the above treatment could be determined only by introducing the ionomeric membrane directly in the Karl Fischer titration chamber. The dehydration process based on diffusion through the swollen identical ionomeric membrane described in examples 4 and 5 of the experimental part gives very low water content. Therefore lithium ions and sulfonate anionic species do not interfere with this quantitative analysis. The direct Karl Fischer analysis was possible due

to the high affinity of methanol shown by the ionomeric membrane, that allowed rapid diffusion of the water molecules in the titration.

2.4. TFE copolymerization with CF$_2$=CFOCF$_2$CF$_2$SO$_2$F perfluoro(3-oxa-4-pentene-1-sulphonylfluoride)

The following reactants were introduced into a 5 l autoclave.

1. 124.7 g of a microemulsion of perfluoro polyoxyalkylenes previously obtained by mixing: 49.9 g. of a perfluoropolyoxyalkylene ammonium carboxylate of formula CF$_2$ClO(CF$_2$CF(CF$_3$)O)$_n$(CF$_2$O)$_m$CF$_2$COONH$_4$ where $n/m = 10$ and average molecular weight of 527 g m^{-1}, 24.9 g of a perfluoropolyether oil Galden® D02 of formula CF$_3$O(CF$_2$CF(CF$_3$)O)$_n$(CF$_2$O)$_m$CF$_3$ $n/m = 20$ and average molecular of 450 and 49.9 g of water.
2. Three thousand milliliters of demineralised water.
3. A hundred and thirty-seven milliliters of sulphonic monomer of formula CF$_2$=CF–O–CF$_2$CF$_2$–SO$_2$F.

Under stirring at 630 rpm, the mixture in the autoclave was heated to 75 °C; 40 ml of an aqueous solution at a concentration 15 g l^{-1} of ammonium persulphate (APS) was then introduced in the autoclave.

The pressure was brought to 12 atm by introducing TFE monomer of formula CF$_2$=CF$_2$. The polymerization reaction started after 1 min. The pressure was maintained at 12 atm by feeding TFE monomer. During the polymerization an amount equal to 22.8 ml of sulphonic monomer of formula CF$_2$=CF–O–CF$_2$CF$_2$–SO$_2$F was added every 6.5 g of fed TFE. The total amount of TFE introduced into the reactor was 1000 g. The reaction was stopped after 70 min from the start, by decreasing the stirring, cooling the reactor and venting the unreacted TFE. The produced latex had a solid content of 32% by weight. The latex was coagulated by freezing and the obtained coagulum washed with demineralised water until reaching the neutrality of the washing waters. The polymer was then dried at 150 °C for 2 h. The copolymer composition, determined by NMR, was the following: 82% by moles of TFE and 18% by moles of sulphonic monomer CF$_2$=CF–O–CF$_2$CF$_2$–SO$_2$F, corresponding to an equivalent weight of 750 g equiv^{-1}.

2.5. Membrane preparation in the –SO$_2$F form and subsequent salification in the –SO$_3$Li form

2.5.1. Membrane preparation by pressure moulding

About 11 g of the copolymer obtained in Section 2.4, with equivalent weight of 750 g equiv^{-1}, were placed in a PTFE template (20 cm × 20 cm) having a thickness ranging from 0.2 to 0.3 mm, between two PTFE films put on two sample-holder steel plates. The template was placed in a press equipped with a water circulation cooling system at the temperature of 250 °C. Then a first step lasting 10 min was carried out, including a preheating step (9 min, 30 s) followed by degassing operations (30 s). In the second step the pressure was increased up to 9.8 MPa

$(100 \, \text{kg cm}^{-2})$ for 1 min and the temperature was kept constant at 250 °C. Successively, the temperature was decreased to 150 °C for 10 min maintaining constant the pressure at 9.8 MPa. Lastly the specimen was cooled to room temperature by water flowing.

2.5.2. Salification and washing

A membrane prepared in Section 2.5.1, was salified by dipping for 6 h at the temperature of 80 °C in 500 ml of aqueous lithium hydroxide, obtained by dissolving 40 g of LiOH·H$_2$O in 500 ml of deionised water. The so obtained membrane was washed several times with deionised water at room temperature until neutrality of the washing waters was obtained. Finally the membrane was kept in a closed vessel in deionised water ready to use. The water content, as per cent weight increase of the membrane, compared to the membrane dried under vacuum at 10^{-3} mbar for 8 h at 130 °C, was 60%. The infrared analysis showed the disappearance of the band at 1470 cm^{-1} due to the –SO$_2$F groups, indicating the completed conversion of the –SO$_2$F functional group into –SO$_3$Li.

2.6. Solvent uptake and water content of "one pot" swollen and dehydrated membrane prepared in Section 2.5.2

From the membrane prepared in Section 2.5.2 a disk having a diameter of 1 cm was cut, dripped and wiped with filter paper, was transferred into a 100 ml flask containing 40 ml of anhydrous propylene carbonate (PC) (battery grade), and about 5 g of molecular sieves (3 A 4–8 mesh, Aldrich) previously activated under vacuum at 250 °C for 3 h. The flask was sealed and introduced in the dry-box. The membrane was left in contact with the anhydrous PC in the presence of the molecular sieves for 3 h at room temperature. Lastly the membrane was recovered and the water content was 260 ppm. The solvent uptake compared to the hydrated membrane prepared in Section 2.5.2, as per cent weight increase of the membrane, was 120%.

2.7. Specific conductivity determination of "one pot" swollen and dehydrated membrane prepared in Section 2.5.2

From the membrane prepared in Section 2.5.2 a disk having a diameter of 1 cm was cut. The process described in Section 2.6 was repeated. The membrane was left in contact with the anhydrous PC in the presence of the molecular sieves for 24 h at room temperature. The solvent uptake, compared to the membrane dried under vacuum, 10^{-2} mbar for 16 h at 80 °C, was 125%. The obtained swollen membrane was malleable and could be easily bent without cracks. The specific conductivities measured at room temperature at various conditioning times are reported in Fig. 5, the conductivity remained constant in the order of $6 \times 10^{-4} \, \text{S cm}^{-1}$.

2.8. Specific conductivity of a swollen membrane in anhydrous PC in absence of molecular sieves after dehydration at 80 °C under vacuum for 16 h

From the membrane prepared in Section 2.5.2 a disk having a diameter of 1 cm was vacuum treated at 80 °C for 16 h. The residual water content was 1.1%. The dried specimen was swollen in anhydrous PC in absence of molecular sieves, by dipping the specimen in the anhydrous PC for 24 h. The solvent uptake, as per cent weight increase of the membrane compared to the dried membrane under vacuum at 80 °C, was 10%. The specific conductivity determined at room temperature on a disk of the swollen membrane having a diameter of 1 cm was $1.6 \times 10^{-6} \, \text{S cm}^{-1}$.

3. Results and discussion

The methodology scheme adopted for the preparation of the inactive Hyflon Ion SSC ionomeric membrane is illustrated in Fig. 1.

The emulsion polymerization, polymer coagulation and membrane preparation steps are described in examples 1 and 2A,
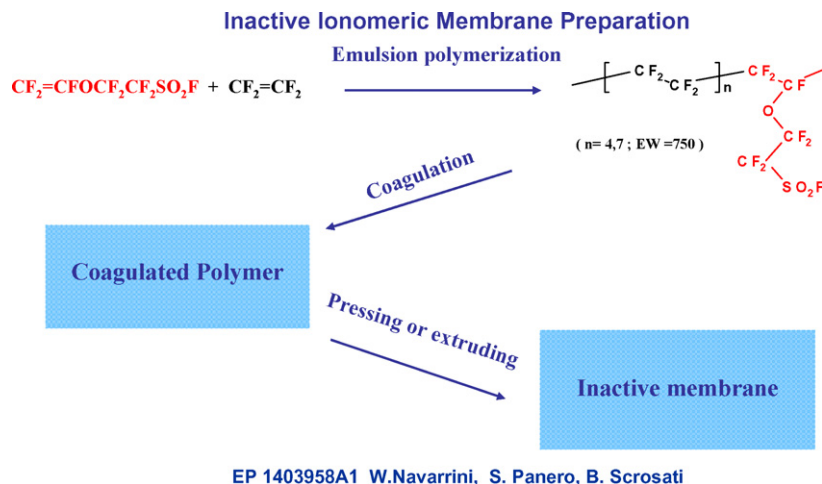

Fig. 1. Scheme for the preparation of the inactive Hyflon Ion SSC ionomeric membrane [1].

Ionomeric Lithiated Membrane Preparation

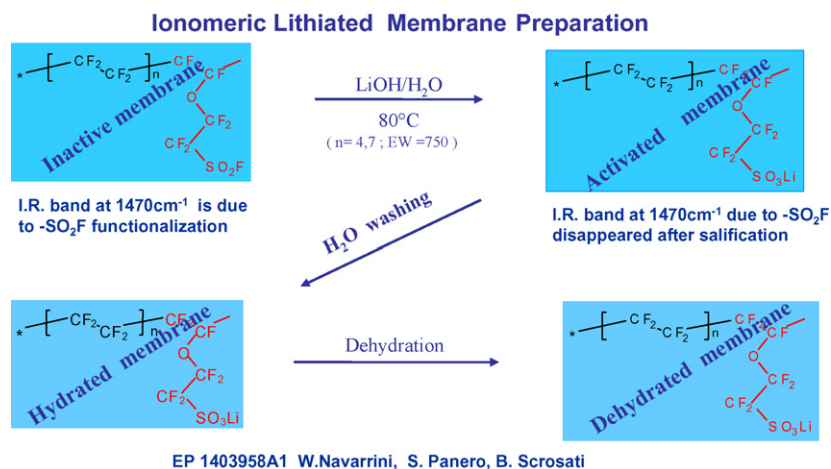EP 1403958A1 W.Navarrini, S. Panero, B. Scrosati

Fig. 2. Scheme for the salification, water washing and dehydration of the Hyflon Ion SSC ionomeric lithiated membrane [1].

respectively, of Section 2. The direct salification with lithium hydroxide, consequential washing and dehydration steps are illustrated in Fig. 2 and are specifically described in example 2B of Section 2. The direct salification of the SO_2F pendant groups with lithium hydroxide is performed straightaway without the necessity of co-solvents [1] like dimethylsulfoxide as reported in the literature [11,12]. This may be due to the lower equivalent weight or to the shorter side chain of this material compared to the similar Nafion based ionomeric material. The complete conversion of the membrane from the $–SO_2F$ form in the $–SO_3Li$ can be conveniently followed by the disappearance of the I.R. absorption peak at $1470\,cm^{-1}$ as described in Section 2. For comparison IR spectra of the membrane in the $–SO_2F$ (Spectra (A), red) and membrane in the $–SO_3Li$ (Spectra (B), blue) are reported in Fig. 3.

The dehydration process reported in Fig. 2 can be performed following different procedures and the membrane obtained is characterized by completely different specific conductivity and mechanical properties depending on the dehydration process adopted as shown in Figs. 4 and 5. If the dehydration process is conducted by heating at $80\,°C$ under vacuum, the specific conductivity of the membrane swollen in propylene carbonate
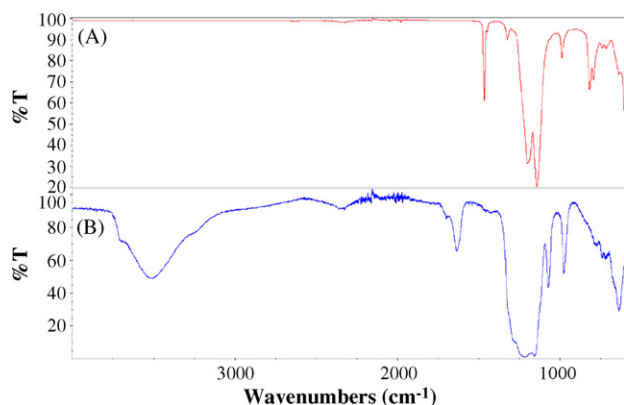
during time is reported in Fig. 4. It can be seen that the conductivity is very low ($9 \times 10^{-9}\,S\,cm^{-1}$) in the first hours of swelling and it increases very slowly up to $1 \times 10^{-6}\,S\,cm^{-1}$ after 160 h as shown in Fig. 4. In addition, the treated membrane remains fragile and the swelling procedure is very slow and after 9 days of swelling in PC at room temperature the solvent uptake is only 23%.

If the dehydration process is conducted by following the new water diffusion dehydration process illustrated in Fig. 5, a better conductivity and membrane flexibility are achieved in comparison to the heating dehydration process previously shown in Fig. 4.

The dehydration/swelling process can be explained as a diffusion of water molecules from the hydrated membrane through the carbonate solvent to the dehydration material, contemporarily the solvent penetrates the membrane that swells. The dehydration materials adopted are molecular sieves located in the same vessel together with the hydrated membrane. The water diffusion equilibrium is reached after few hours, lower water content can be obtained by a second diffusion process utilizing freshly activated molecular sieves.

From these SSC lithium ionomer membranes and utilizing this particular methodology for the dehydration of membranes, it has been possible to achieve an ionic conductivity of $1 \times 10^{-3}\,S\,cm^{-1}$ at room temperature in PC as solvent.

Surprisingly it was observed that the membrane ionic conductivity depends on the dehydration methodologies adopted at identical equivalent weight of the ionomer, solvent type and solvent uptake.

In Table 1 different drying processes are compared and analyzed in terms of PC uptake, conductivity, aspect and mechanical properties of the swollen 754EW membrane. It can be seen that identical ionomeric membranes, equally swollen, have different conductivity, water content, aspect and mechanical properties. Specifically by adopting the water diffusion dehydration methodology higher conductivity, lower water content and better mechanical properties are obtained. It should be noticed that the highest conductivity is obtained at lower water content; this is also unexpected since the conductivity of a lithiated perfluo-

Fig. 3. IR spectra of the membrane in the $–SO_2F$ (Spectra (A), red) and membrane in the SO_3Li (Spectra (B), blue).
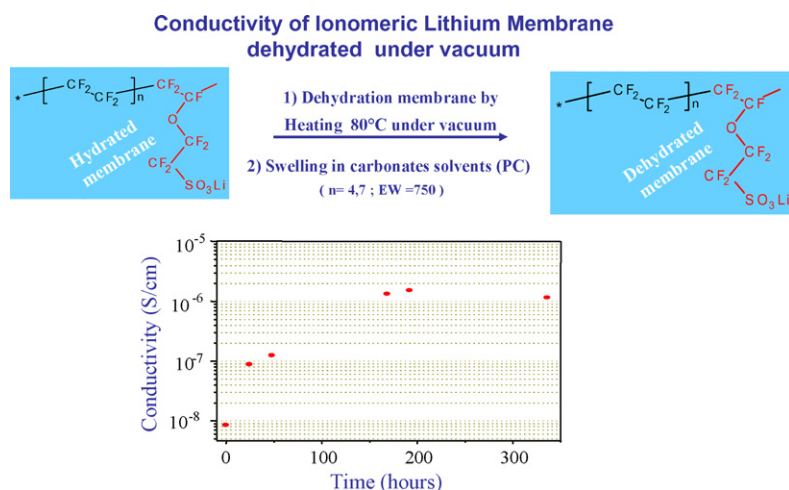
Fig. 4. shows the specific conductivity during time of a 750EW SSC lithiated membrane, dehydrated by heating at 80 °C under vacuum and swollen in PC at room temperature.
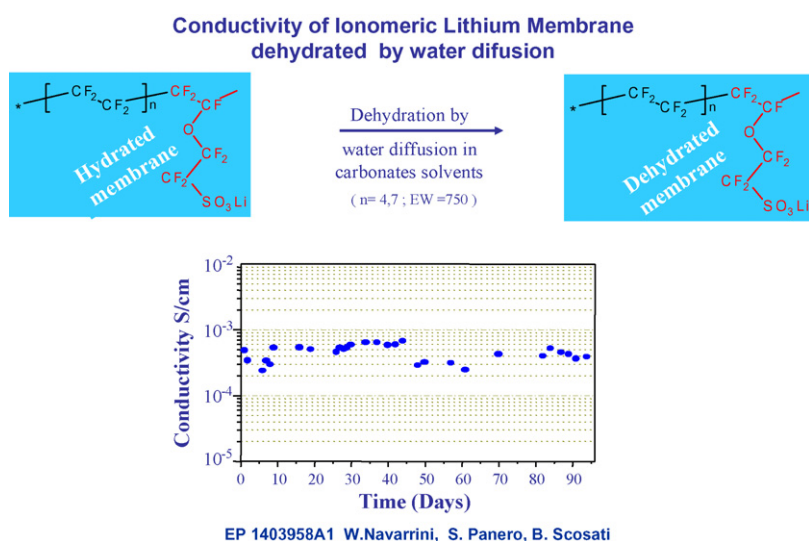

Fig. 5. Specific conductivity during time of a 750EW SSC lithiated membrane and dehydrated by diffusion in PC at room temperature [1].

Table 1
Propylene carbonate uptake (24 h treatment), specific conductivity, water content, aspect and mechanical properties of 754EW membrane after different dehydration processes

Membrane	ΔW (%) water evaporation	ΔW (%) solvent uptake (24 h treatment)	σ (S cm^{-1})	Water content (%)	Aspect after swelling
EW 754 wet after washing	–	125 (molecular sieves)	2×10^{-4}	<0.1	flexible, tough, transparent
EW 754 8 h at 80 °C vacuum (0.2 mmbar)	11	127	7×10^{-5}	>2	Stiff, opaque
EW 754 16 h at 80 °C vacuum (0.2 mmbar)	13	10	1.6×10^{-6}	>1	Opaque, brittle

rinated ionomer membrane is known to increase by increasing the water content in the membrane [11].

In Table 1 the membrane heated at 80 °C for 16 h under vacuum, prepared following the procedure illustrated in Section 2.8, was opaque and fragile. This can be due to more pronounced segregation phenomena of the heated membrane compared to the membrane dehydrated by water diffusion, these experimental evidences are also in agreement with the higher

transparency and conductivity observed for the membrane prepared by water diffusion following the procedure described in Section 2.7.

4. Conclusion

A straightforward methodology for the preparation and dehydration of perfluorinated SSC lithiated ionomeric membranes

by water diffusion in carbonate media has been found and described. Through this methodology it was possible to achieve good membrane ionic conductivity at room temperature in carbonate solvents.

References

[1] W. Navarrini, S. Panero, B. Scrosati, A. Sanguineti, European Patent 1,403,958 A1 (2003).

[2] D.J. Connolly, W.F. Gresham, US Patent 3,282,875 (1966).

[3] W. Navarrini, V. Tortelli, A. Russo, S. Corti, J. Fluorine Chem. 95 (1999) 27–39.

[4] V. Arcella, A. Ghielmi, G. Tommasi, US Patent 6,767,977 (2004) .

[5] V. Arcella, A. Ghielmi, G. Tommasi, Ann. N.Y. Acad. Sci. 984 (2003) 226–244.

[6] A. Ghielmi, P. Vaccarono, C. Troglia, V. Arcella, J. Power Sources 145 (2005) 108–115.

[7] W.H. Mayer, Adv. Mater. 10 (1998) 439–447.

[8] K.E. Thomas, S.E. Sloop, J.B. Kerr, J. Newman, J. Power Sources 89 (2000) 132.

[9] H.Y. Liang, X.P. Qiu, S.C. Zhang, W.T. Zhu, L.Q. Chien, J. Appl. Elec. 34 (2004) 1211.

[10] T.C. Wen, W.C. Chen, J. Power Sources 92 (2001) 139.

[11] M. Doyle, M.E. Lewittes, M.G. Roelofs, S.A. Perusich, R.E. Lowrey, J. Membr. Sci. 184 (2001) 257–273.

[12] C.M. Doyle, M.E. Lewittes, S.A. Perusich, European Patent 0,938,755 B1 (2004).