

Polymer electrolyte membranes and process for the production thereof

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(54) Title: POLYMER ELECTROLYTE MEMBRANES AND PROCESS FOR THE PRODUCTION THEREOF

(57) Abstract: The process for the production of a polymer electrolyte membrane, comprises the successive steps of: preparing a mixed solution of a Room Temperature Ionic Liquid (RTIL), at least one alkaline metal salt and a photosensitive hydrogen abstracting component at a temperature in the range 20 to 70 °C, wherein the RTIL is a compound consisting of at least one organic cation and at least one organic or inorganic anion; adding to the solution a polymeric material at a temperature in the range of 20-70 °C; blending the solution added with the polymeric material at a temperature in the range of 70-140 °C to get a uniform mixture; pressing the mixture between two sheets at a temperature in the range of 60 - 150 °C and a pressure in the range of 20 - 80 bar, so that a film is formed; and exposing the film to UV light, so that the polymeric material of the film is cross-linked and the polymer electrolyte membrane is obtained.



WO 2015/104727 A1

Polymer electrolyte membranes and process for the production thereof

Wide interest is mounting on polymer electrolytes for application in energy efficient devices such as rechargeable batteries, supercapacitors, electrochromics and photovoltaics. In this context, solid polymer electrolytes exhibit unique advantages: mechanical integrity, variety of fabrication methods and intimate electrode/electrolyte interfacial properties. They also improve safety along with more compact and lightweight packaging. Since the discovery of ionic conductivity in alkali metal salt complexes of poly(ethylene oxide), PEO, a lot of research has been devoted to systems containing alkaline metal salts to be used as electrolytes, particularly in Li-based batteries.

The object of the present invention is thus to provide polymer electrolyte membranes and process for the production thereof which are improved with respect to the ones of the prior art.

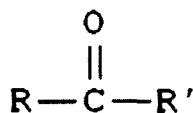
Such object is attained by a process for the production of a polymer electrolyte membrane as disclosed in claim 1 which follows. Preferred features of the process of the invention are disclosed in dependent claims 2 to 12.

In the process of the invention, all polymers having a chain/moiety/repeating unit in which at least an acidic proton is attached to a carbon atom and able to be cross-linked using a suitable diluent and suitable photosensitive hydrogen abstracting component, can be used either alone or in different ratios or in different blending thereof: e.g., poly (propylene oxide) - PPO, poly (methyl methacrylate) – PMMA, poly (acrylonitrile) - PAN, poly (vinylidene fluoride) – PVdF, poly(propylene sulphide) – PPS, etc.

Polymers such as single, di-, or multi- co-polymers (e.g., alternating, statistical, periodic, block co-polymers both linear and/or branched) in which at least one polymerized monomer comprising at least an acidic proton attached to a carbon atom and able to be cross-linked using a suitable diluent and suitable photosensitive hydrogen abstracting component can be also used either alone or in different ratios or in different blending thereof or blending with the above reported polymers (e.g., PEO-PPO, PEO-PMMA, PEO-PAN, PEO-

PVdF copolymers, etc.).

As photosensitive hydrogen abstracting component, it is typically used a compound having a photo-excitabile carbonyl group attached to an aromatic or aliphatic electronic withdraw-  
5 ing group prone to photo-induce hydrogen abstraction of general formula



wherein R is substituted or unsubstituted aryl, preferably phenyl, and R' is hydrogen, substituted or unsubstituted aryl, preferably phenyl, or substituted or unsubstituted C<sub>1</sub>-C<sub>18</sub>-alkyl. The preferred compounds are benzophenone, 2-chlorobenzophenone and methyl-  
10 phenyl-ketone.

The presence of the photo-reactive group either in the main or in the side chain will yield similar effect on the reaction as well as the network structure as long as a hydrogen donor is available in adjacent polymer chains. Photo-irradiation will excite the photo-reactive  
15 group which will thereafter abstract a hydrogen from a donor, yielding two radicals which can subsequently recombine and form a cross-link.

The Room Temperature Ionic Liquid (RTIL) compound used consists of at least one organic cation and at least one organic or inorganic anion, wherein the organic cation is preferably selected in the group consisting of imidazolium, ammonium, pyridinium, pyrrolid-  
20 ium, piperidinium, phosphonium, and sulfonium and is associated with an inorganic or organic anion.

The production process of the invention appears highly advantageous compared to the  
25 conventional ones due to its ease and rapidity, reduction of the manufacturing costs, simplification of the fabrication techniques and compatibility with IC fabrication. It does not necessarily require the use of any solvent at any stage, and, moreover, the materials used can be eventually recycled, thus making the whole process environmentally benign.

30 A polymer electrolyte membrane obtainable from the above-disclosed process constitutes a

further subject of the present invention.

The membrane of the invention has a thickness in the range of 10 to 200  $\mu\text{m}$ , preferably 50 to 120  $\mu\text{m}$ , and may be used in energy production or storage devices, such as a battery  
5 (e.g., lithium and/or sodium-based), a supercapacitor, an electrochromic device or a dye-sensitized solar cell (DSSC).

The characterization and obtained results demonstrated a high ionic conductivity approaching  $10^{-3} \text{ S cm}^{-1}$  at 20 °C, a wide electrochemical stability window (up to 5.5 V vs.  $\text{Li}^+/\text{Li}$   
10 depending on the RTIL used), an outstanding elongation at break, along with a superior flexibility and an enhanced adhesion of the polymer electrolyte membrane to the active electrode materials of a lithium polymer cell assembly of a battery, with an improved cycle performance of the latter. Due to the intimate contact between the electrode material grains and the polymer electrolyte matrix, the interface does not create any problem due to insufficient  
15 adhesion (in fact, the polymeric electrolyte can be also directly prepared by hot-pressing onto the surface of one of the electrodes, then cross-linking by UV exposure). Hence, the cell assembly showed stable charge/discharge characteristics (even when cycled at ambient temperature) without any capacity fading at 1C current regime. In sum, such cell assembly holds a great potential for use in high-performance, versatile and cost-  
20 effective lithium-based polymer batteries.

Examples of preparation processes of a polymer electrolyte membrane according to the invention and comparative, respectively, are now provided by way of illustrative, non-limiting examples.

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### Materials

Poly(ethylene oxide) - PEO (average  $M_v = 1,000,000$ ) was obtained from Aldrich. Bis(trifluoromethane)sulfonimide lithium salt ( $\text{LiTFSI}$ ,  $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{CF}_3$ , battery grade)  
30 was obtained from Solvionic (France). Room Temperature Ionic Liquids (RTILs) were provided by Aldrich. The photosensitive component 2-chlorobenzophenone (Cl-BP) was provided by Aldrich.

The  $\text{LiFePO}_4$  cathode material used for electrochemical testing in lithium cells was synthesized through the mild hydrothermal procedure disclosed in the international patent application WO 2011/057646 A1. The  $\text{LiFePO}_4$  electrode film was prepared in the form of a thin film (average thickness 50  $\mu\text{m}$ ) as reported in [G. Meligrana et al. Journal of Power Sources 160 (2006) 516–522]. Lithium metal foils with a thickness of about 150  $\mu\text{m}$  were obtained from Chemetall.

Unless differently specified, all the starting materials and reagents were purchased from commercial suppliers and used without any further purification. Before their use all chemicals, were kept open in the inert atmosphere of Ar-filled dry glove box for several days and also treated with molecular sieves (Molecular sieves, beads 4 Å, 8-12 mesh, Aldrich) to ensure the complete removal of traces of water/moisture, as they may create problems in long-term properties when these membranes are considered for application as electrolytes in rechargeable Li-based batteries.

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#### Example 1 (standard polymer electrolyte membrane)

This example illustrates the preparation of a cross-linked poly (ethylene oxide) – PEO polymer electrolyte membrane encompassing room temperature ionic liquids (RTIL) and lithium salt (Li) according to the invention.

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Initially, a mixture of 0.10 g of LiTFSI and 0.01 g of Cl-BP was dissolved in 0.45 g of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (RTIL). These ingredients were respectively added in a beaker and stirred at 50 °C for 15 min thus obtaining a viscous liquid solution. Then, 0.45 g of PEO were added to the liquid solution and the resulting mixture was hand-mixed in a mortar. The mixture was kept at 120 °C for 2 hour to melt PEO, in 2 steps: 1 hour at 120 °C followed by 5 min hand-mixing in a mortar and, then, again 1 hour at 120 °C, thus avoiding complications due to the high viscosity at ambient temperature of the polymer and assuring the homogeneous distribution therein of the solution. Successively, the mixture was sandwiched between two Mylar sheets and a film was formed by hot-pressing at 90 °C at 50 bar for 15 min. Finally, the obtained film was exposed to UV light for 3 minutes on each side using a medium vapor pressure Hg UV

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lamp (Helios Italquartz, Milan, Italy), with a radiation intensity on the surface of the samples of about  $30 \text{ mW cm}^{-2}$ , in order to bring about the cross-linking of the PEO polymer matrix. A polymer electrolyte membrane with a thickness of  $100 \pm 5 \text{ }\mu\text{m}$  was thus obtained, which is ready to be used in energy storage and/or production devices.

5

Example 2 (polymer electrolyte membrane using different RTIL)

Initially, a mixture of 0.10 g of LiTFSI and 0.01 g of Cl-BP was dissolved in 0.45 g of 1-Butyl-3-methylimidazolium tris(pentafluoroethyl)tri-fluorophosphate RTIL (Merck Millipore). These ingredients were respectively added in a beaker and stirred at  $50 \text{ }^\circ\text{C}$  for 15 min obtaining a viscous liquid solution. Then, 0.45 g of PEO were added to the liquid solution and the resulting mixture was hand-mixed in a mortar.

Then, the subsequent steps were performed according to the procedure of example 1.

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A polymer electrolyte membrane with a thickness of  $100 \pm 5 \text{ }\mu\text{m}$  was thus obtained, which is ready to be used in energy storage and/or production devices.

Example 3 (composite polymer electrolyte membrane)

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Initially, a mixture of 0.10 g of LiTFSI and 0.01 g of Cl-BP was dissolved in 0.45 g of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (RTIL). These ingredients were respectively added in a beaker and stirred at  $50 \text{ }^\circ\text{C}$  for 15 min obtaining a viscous liquid solution. Then, 0.45 g of PEO were added to the liquid solution along with 0.05 g of cellulose filler (colloidal, microcrystalline, Aldrich) and the resulting mixture was hand-mixed in a mortar.

Then, the subsequent steps were performed according to the procedure of example 1.

30 A polymer membrane with a thickness of  $110 \pm 5 \text{ }\mu\text{m}$  was thus obtained, which is ready to be used in energy storage and/or production devices.

Example 4 (swelled composite polymer electrolyte membrane)

Initially, a mixture of 0.10 g of LiTFSI and 0.01 g of Cl-BP was dissolved in 0.45 g of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (RTIL). These ingredients were respectively added in a beaker and stirred at 50 °C for 15 min obtaining a viscous liquid solution. Then, 0.45 g of PEO were added to the liquid solution along with 0.05 g of cellulose filler (colloidal, microcrystalline, Aldrich) and the resulting mixture was hand-mixed in a mortar.

Then, the following steps were performed according to the procedure of example 1.

A polymer membrane with a thickness of  $110 \pm 5$   $\mu\text{m}$  was thus obtained. The polymer membrane was then soaked into a liquid electrolyte solution for 5 to 30 min (wherein 15 min leads to the highest performance) thus obtaining a pseudo-gellified polymer electrolyte membrane to be used in DSSC. The liquid solution containing 0.5 M NaI (Aldrich) and 0.05 M  $\text{I}_2$  (Aldrich) dissolved in acetonitrile (Aldrich). Same performances were obtained using commercial iodide based redox electrolyte (AN-50 Iodolyte from Solaronix and EL-HPE High Performance Electrolyte from Dyesol). Due to the cross-linking of the PEO matrix, the swelled polymer electrolyte retained most of the physical properties of the parental polymer electrolyte membrane, thus demonstrating remarkably stable mechanical properties, easily hand-ability and efficient liquid electrolyte retainability.

The following examples 5-8 relate to the measurement of physico-chemical properties of intermediate products and final membranes of the previous examples 1-4.

Example 5 (standard polymer electrolyte membrane)

The UV treatment is fundamental for the resulting polymer electrolyte membranes, which would otherwise be in the fluid state, as it gives a remarkable consistency, elasticity and resistance. Tensile tests carried on the polymer electrolyte membrane showed a remarkable elasticity in terms of elongation (up to 250 mm from the starting length of 25 mm) and a low stress resistance. These properties clearly result from figure 1 showing photos of the



same membrane before (left) and after (right) UV treatment.

Thermal properties of the electrolyte membranes are important to battery safety.

- 5 Figure 2 is a diagram showing the Thermogravimetric analysis (TGA) of the PEO-RTIL-Li-UV polymer electrolyte membrane under nitrogen atmosphere. As it is apparent there-  
from, the prepared polymer electrolyte membranes were found to be highly thermally sta-  
ble: high  $T_5$  and  $T_{10}$  (temperatures at which the 5 or 10 wt. % of sample is decomposed, re-  
spectively) values of about 250 and about 360 °C, respectively; after  $T_{10}$  the decomposition  
10 of PEO begins.

Differential scanning calorimetry (DSC) results of the PEO-RTIL-Li-UV polymer electro-  
lyte demonstrated a  $T_g$  of about -56 °C.

- 15 Figure 3 shows the XRD patterns of the PEO-RTIL-Li-UV compared with the one for  
PEO-Li and PEO-RTIL-Li not UV treated. For the PEO-Li, intense characteristic peaks are  
observed due to the crystalline characteristics of the polymer matrix. The addition of  
RTIL greatly reduces the intensity of the peaks and, after the UV induced photopolymeri-  
sation step, reflections are almost negligible (peaks at 29 37 and 44 are due to the alumini-  
20 um support), thus indicating an almost completely amorphous polymer electrolyte.

Figure 4 illustrates the results of FESEM analysis of a PEO-RTIL-Li polymer electrolyte  
membrane not UV treated (left) and PEO-RTIL-Li-UV polymer electrolyte membrane  
(right).

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- Such Figure further demonstrates the effect of UV photopolymerisation on the morphology  
of the polymer electrolytes. In fact, the addition of 45 % of RTIL, without UV photopoly-  
merisation (left-side image), generates a membrane having very low homogeneity, where  
the RTIL creates micro bubbles thus being a separate phase with respect to the polymer  
matrix. When testing this membrane at higher temperatures, leakage of the RTIL was also  
30 observed. The UV-induced cross-linking effect produced by photopolymerisation allows  
the incorporation of more liquid and generates a membrane with dramatically different

morphological characteristics (right-side image): proper morphology, homogeneous and resistant with improved mechanical and electrochemical properties. Moreover, the UV cured PEO membrane can efficiently hold the RTIL without any leakage even after prolonged testing at high temperatures.

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Figure 5 is a plot of data of ionic conductivity vs. temperature, obtained by impedance spectroscopy.

Such figure shows the temperature dependence of the ionic conductivity of the UV-cured PEO-RTIL-Li-UV polymer electrolyte membrane. The ionic conductivity at 20 °C ( $3.6 \times 10^{-4}$  S cm<sup>-1</sup>) is highly sufficient for practical use and can be increased to almost  $4 \times 10^{-3}$  S cm<sup>-1</sup> at 90 °C, which are values almost comparable with the ones of commonly used Li-ion liquid electrolytes. The ionic conductivity shows a linear increase with the temperature due to the amorphous structure of the membrane (the changes/inflections corresponding to the melting of the PEO crystallites are not evident).

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Figure 6 illustrates the current–potential curves resulting from cyclic voltammetry test on the PEO-RTIL-Li-UV polymer electrolyte membrane. The electrochemical stability window was evaluated at 20 °C. Very good electrochemical response was found. The onset of the current increase, which is representative of the decomposition of the electrolyte, indicates an anodic break-down voltage at above 4.5 V vs. Li<sup>+</sup>/Li reference electrode, largely sufficient for practical use.

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#### Example 6 (polymer electrolyte membrane using different RTIL)

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Figure 7 shows the temperature dependence of the ionic conductivity of the UV-cured PEO-RTIL-Li-UV polymer electrolyte membrane, where the RTIL used was 1-Butyl-3-methylimidazolium tris(pentafluoro-ethyl)trifluorophosphate. The data were obtained by impedance spectroscopy. The ionic conductivity at 20 °C was found to be close to  $10^{-3}$  S cm<sup>-1</sup> and higher than the previous example and it can be increased to almost  $6 \times 10^{-3}$  S cm<sup>-1</sup> at 90 °C, which are very high values for a fully solid polymer electrolyte.

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Figure 8 illustrates the current–potential curves resulting from cyclic voltammetry test on the PEO-RTIL-Li-UV polymer electrolyte membrane encompassing 1-Butyl-3-methylimidazolium tris(pentafluoro-ethyl)trifluorophosphate. The electrochemical stability window was evaluated at 20 °C. Very good electrochemical response was found, higher than in the previous example. The onset of the current increase, which is representative of the decomposition of the electrolyte, indicates an anodic break-down voltage at above 5.5 V vs. Li<sup>+</sup>/Li, highly sufficient for practical use even with high voltage cathodes.

The impedance spectra carried out on a Li/PEO-RTIL-Li-UV/Li cell stored for long time period under open circuit voltage (O.C.V.) conditions at 20 °C were also evaluated and the electrolytes demonstrated stable interfacial properties versus the lithium metal electrode. The stability versus storage time was also evaluated by running impedance measurements of a stainless-steel/PEO-RTIL-Li-UV/stainless-steel cell kept for long time period under open circuit conditions at 20 °C. In general, the polymer electrolyte membranes maintained optimum mechanical stability (i.e., they are flexible, yet robust) and integrity after prolonged time of storage and testing. The polymer electrolyte membranes were able to retain remarkable ionic conductivity and, thus, their integrity upon the entire storage time exceeding 2 months were satisfactory. Only minor fluctuations in the resistance value (correspondingly, in the ionic conductivity) with time and no deviation from linearity were found, which indicate the capability of the polymer matrix to retain the liquid and the salt. This indirectly means that no structural or physical changes occurred in the matrix. Such good storage stability, in combination with the enhanced electrochemical and ionic conductivity characteristics discussed above, good mechanical and thermal properties are key factors in view of the practical application of the optimised composition under study in advanced energy storage and production devices characterised by a long operational life.

In view of their possible practical application, the polymer electrolyte membranes were assembled in all-solid-state lithium polymer cell laboratory prototypes, and their electrochemical behaviour investigated by means of galvanostatic charge/discharge cycling.

Figure 9 illustrates the galvanostatic cycling behaviour of a lithium polymer cell, assembled contacting in sequence a LiFePO<sub>4</sub> cathode, the PEO-RTIL-Li-UV polymer electrolyte

membrane and a Li metal anode at 20 °C: diagram a) illustrate typical charge/discharge potential vs. time profiles and diagram b) relates to specific capacity vs. cycle number at 1C current rate.

5 Overall, although the specific capacity obtained is slightly lower than that the one obtained for the same  $\text{LiFePO}_4$  cathode material at the same current in liquid electrolyte (1.0 M  $\text{LiPF}_6$  in 1:1 w/w EC/DEC solution, Ferro Corp., battery grade, G. Meligrana et al. Journal of Power Sources 160 (2006) 516–522), the polymer cell showed good capacity retention. This is a convincing indication of the good interfacial contact between the electrodes and  
10 the polymer electrolyte separator. The rate capability of the lithium metal polymer cell was also good. Good performance at high current rate may be ascribed to the efficient ionic conduction in the polymer-coated separator and the favourable interfacial charge transport between electrodes and electrolyte in the cell.

#### 15 Example 7 (composite polymer electrolyte membrane)

This example relates to the testing of the membrane prepared according to example 3.

Figure 10 illustrates the thermogravimetric analysis (TGA) of the PEO-RTIL-Li-UV polymer electrolyte membrane, which shows both  $T_5$  and  $T_{10}$  values higher than those obtained in Figure 2, thanks to the use of the cellulosic filler.  
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Figure 11 is a plot comparing the ionic conductivity data vs. temperature of the PEO-RTIL-Li-UV standard polymer electrolyte membrane with those for the composite polymer electrolyte membrane (data obtained by impedance spectroscopy).  
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Figure 12 illustrates the current–potential curves resulting from cyclic voltammetry test on the composite polymer electrolyte membrane, indicating the electrochemical stability window (anodic branch) at 20 °C, with a scan rate of 0.100 mV s<sup>-1</sup>.  
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#### Example 8 (swelled gel polymer electrolyte membrane)

Such example refers to the testing of the composite pseudo-gellified polymer electrolyte of example 4.

The polymer electrolyte was also tested for its performances in electrochromic devices and, particularly, in dye-sensitized solar cells – DSSC. In both cases it demonstrated very good performances. Particularly, it demonstrated an efficiency of above 6 % and high durability in DSSC cells.

Figure 13 is a photo showing the appearance of the sealed Lab-scale quasi-solid DSSC used for performing the testing, comprising the pseudo-gellified polymer electrolyte membrane.

Figure 14 illustrates the J–V curves of the quasi-solid DSSC at 20 °C and different light intensities: 1000 W m<sup>-2</sup> (or 1 sun) upper line and 400 W m<sup>-2</sup> (or 0.4 sun) lower line.

Table 1, which follows, summarizes the photovoltaic parameters of the quasi-solid DSSC described before. It can be seen that under a light intensity of 1 sun, the efficiency of the DSSC with the quasi-solid electrolyte is higher than 6%. Thus, in the presence of such an electrolyte, obtained by a unique rapid, economic, easily up-scalable and environmentally friendly process of photo-curing, the laboratory-scale cells showed remarkable performances.

Table 1. Photovoltaic parameters of the quasi-solid DSSC at 20 °C and different light intensities.

	1000 W m <sup>-2</sup>	400 W m <sup>-2</sup>
<b>Area (cm<sup>2</sup>)</b>	0.16	0.16
<b>Voc (V)</b>	0.688	0.63
<b>FF</b>	0.64	0.64
<b>Jsc (mA cm<sup>-2</sup>)</b>	14.0	6.71
<b>Efficiency (%)</b>	6.21	6.76

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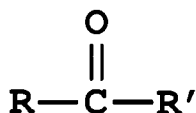
Contextualizing, the efficiency obtained for the DSSC containing this quasi-solid polymer

electrolyte is one of the highest reported in the literature so far among other DSSCs assembled with other well-functioning quasi-solid photo-polymerized polymer electrolytes. In fact, it must be noticed that the highest light-to-electricity conversion efficiency hitherto reported for a DSSC containing a photo-crosslinked polymer electrolyte is close to 6.10 %, in the presence of an aliphatic urethane acrylate.

It shall be apparent that, applying the principles of the invention, the implementation details and the embodiment may be widely varied relative to what has been described by way of example only within the scope defined by the present claims. E.g., the process of the invention may provide for one or more additional steps, such as a final step wherein the polymer membrane is soaked in a liquid electrolyte solution.

CLAIMS

1. Process for the production of a polymer electrolyte membrane, comprising the successive steps of:
- 5 preparing a mixed solution of a Room Temperature Ionic Liquid (RTIL), at least one alkaline metal salt and a photosensitive hydrogen abstracting component at a temperature in the range 20 to 70 °C, wherein said RTIL is a compound consisting of at least one organic cation and at least one organic or inorganic anion;
- adding to the solution a polymeric material at a temperature in the range of 20-70 °C;
- 10 blending the solution added with the polymeric material at a temperature in the range of 70-140 °C to get a uniform mixture;
- pressing said mixture between two sheets at a temperature in the range of 60 – 150 °C and a pressure in the range of 20 - 80 bar, so that a film is formed; and
- exposing said film to UV light, so that the polymeric material of the film is cross-linked
- 15 and said polymer electrolyte membrane is obtained.
2. Process according to claim 1, wherein said at least one alkaline metal salt is chosen in the group consisting of  $M^{n+}X_n^-$ , wherein  $M^{n+}$  is an inorganic, organic, or organometallic cation of charge n, wherein n is 1 or 2, preferably 1, and  $X^-$  is a monovalent anion, and
- 20 wherein two anions  $X^-$  can be linked together with covalent chains or chains belonging to a polymer chain.
3. Process according to claim 1 or 2, wherein said photosensitive hydrogen abstracting component is a compound having a photo-excitable carbonyl group attached to an aromatic
- 25 or aliphatic electronic withdrawing group prone to photo-induce hydrogen abstraction of general formula



- wherein R is substituted or unsubstituted aryl, and R' is hydrogen, substituted or unsubstituted aryl, substituted or unsubstituted C<sub>1</sub>-C<sub>18</sub>-alkyl, and is preferably benzophenone, 2-
- 30 chlorobenzophenone or methyl-phenyl-ketone.

4. Process according to any one of the previous claims, wherein said at least one anion of the alkaline metal salt is an halogen ion, a phosphate ion, a sulfate ion,  $\text{AlCl}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{NTf}_2^-$ ,  $\text{DCA}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{B}(\text{C}_2\text{O}_4)_2^-$ , or  $\text{CH}_3\text{SO}_3^-$ .
5. Process according to any one of the previous claims, wherein said at least one anion of the RTIL is an halogen ion, fluorophosphate ( $\text{PF}_6^-$ ), fluoro alkyl phosphate (FAP), fluoroborates ( $\text{BF}_4^-$ ), oxalato borates  $\text{B}(\text{C}_2\text{O}_4)_2^-$ , bis(trifluoro methylsulfonyl)imide ( $\text{NTf}_2^-$ ), or triflate ( $\text{Tf}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) and is associated with an organic cation.
6. Process according to any one of the previous claims, wherein said alkaline metal salt is a Li, Na or K salt, preferably a Li or Na salt.
7. Process according to any one of the previous claims, wherein said polymeric material is poly(ethylene oxide) (PEO) having viscosity average molecular weight ( $M_v$ ) in the range of 500 – 8,000,000, end-capped poly (ethylene glycols) having  $M_v$  in the range of 500 – 8,000,000, or a blend thereof.
8. Process according to any one of the previous claims, wherein said film is exposed to UV light with a radiation intensity in the range of 5 to 500  $\text{mW cm}^{-2}$ , and preferably in the range 30 to 50  $\text{mW cm}^{-2}$ .
9. Process according to any one of the previous claims, wherein said mixed solution comprises Room Temperature Ionic Liquid (RTIL) in an amount in the range 5-70 % by weight, alkaline metal salt in an amount in the range 1-30 % by weight, and photosensitive hydrogen abstracting component in an amount in the range 0.01-5 % by weight.
10. Process according to any one of the previous claims, wherein said at least one organic cation of the RTIL is selected in the group consisting of imidazolium, ammonium, pyridinium, pyrrolidinium, piperidinium, phosphonium, and sulfonium and is associated with an inorganic or organic anion.
11. Process according to any one of the previous claims, wherein said polymeric mate-



rial is added to said mixed solution in a ratio by weight in the range of 10-80 %.

12. Process according to any one of the previous claims, wherein said polymeric material is added with micro-fillers and/or nano-fillers, which are inorganic, such as  $\text{Al}_2\text{O}_3$ ,  
5  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{SiO}_6$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ , or  $\text{TiO}_2$ , and/or organic and/or bioresourced, such as cellulose, chitin, chitosan, keratin or caffeine, in order to improve specific properties of the resulting membrane.
13. Polymer electrolyte membrane obtainable from a process according to any one of  
10 the previous claims.
14. Polymer electrolyte membrane according to claim 13, having a thickness in the range 10 to 200  $\mu\text{m}$ , preferably 50 to 120  $\mu\text{m}$ .
- 15 15. Energy production or storage device, such as lithium and/or sodium-based battery, supercapacitor, electrochromic device or dye-sensitized solar cell (DSSC), comprising at least one membrane according to claim 13 or 14.

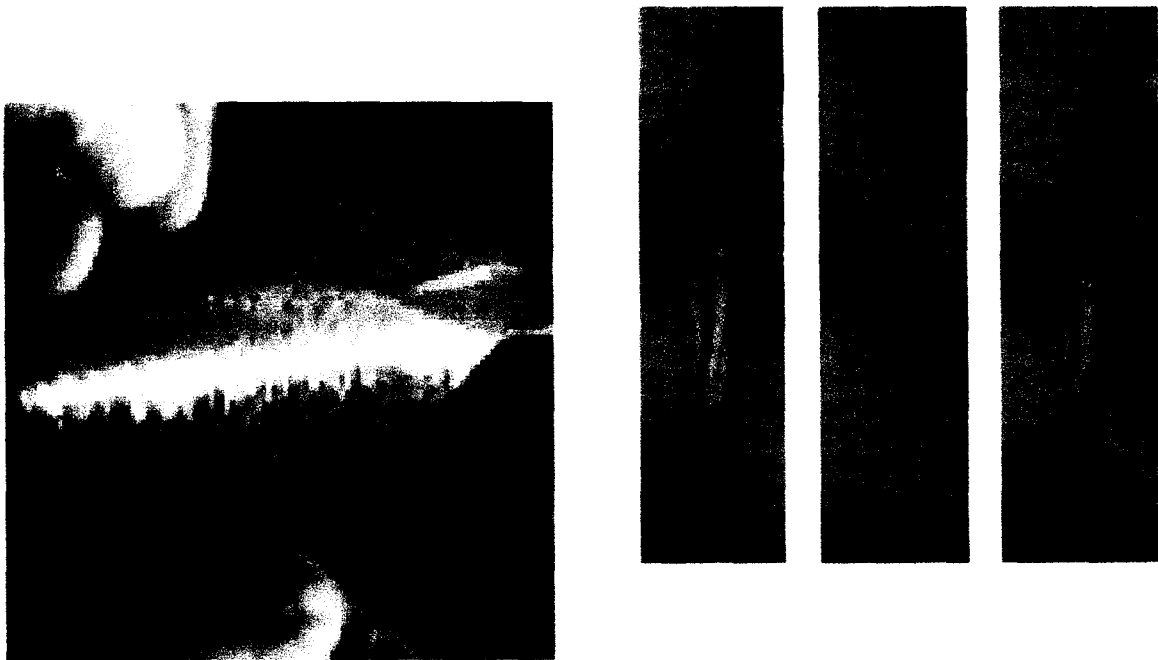


FIG.1

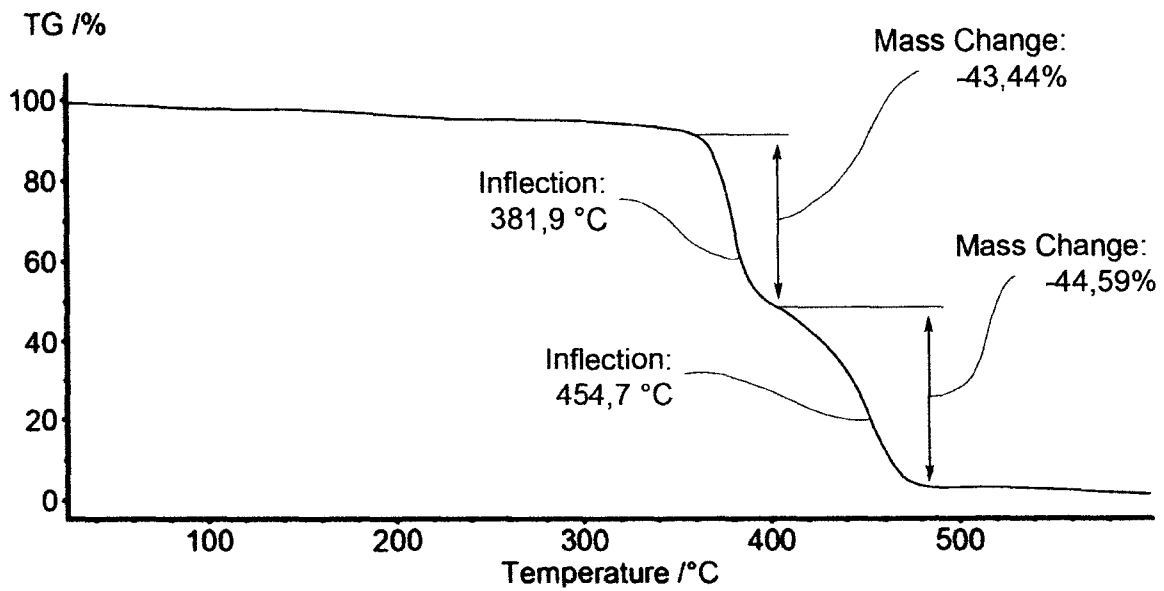


FIG.2

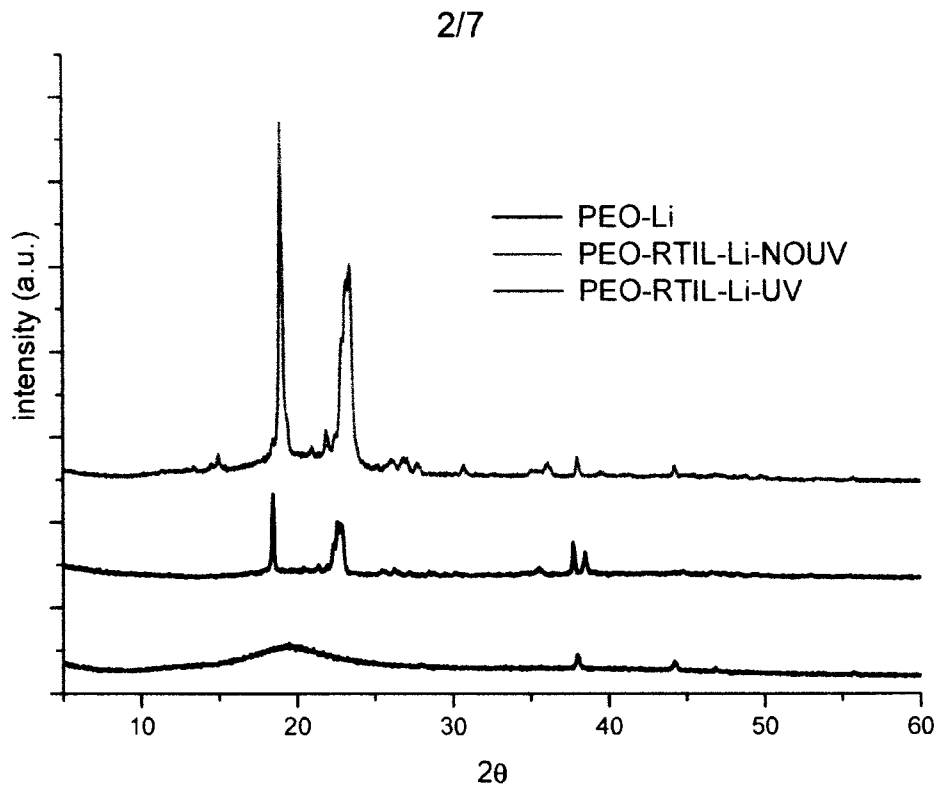


FIG.3

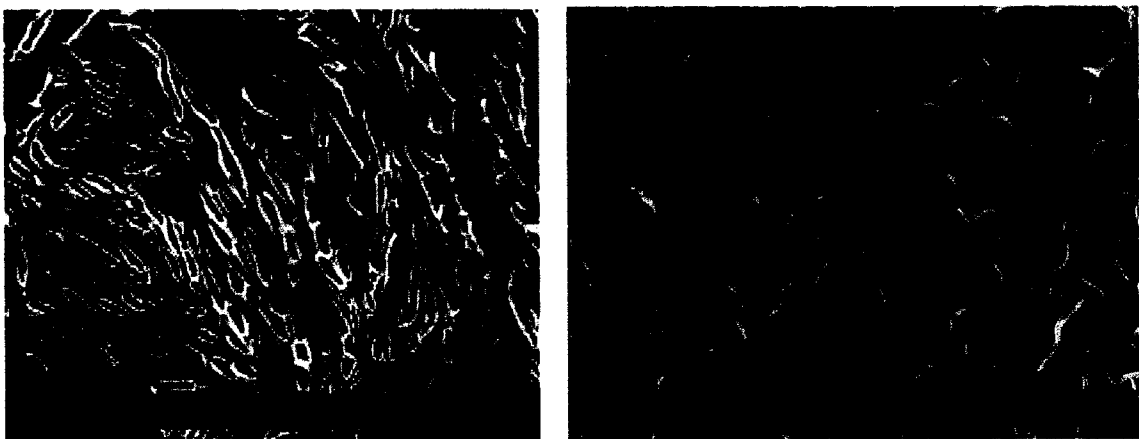


FIG.4

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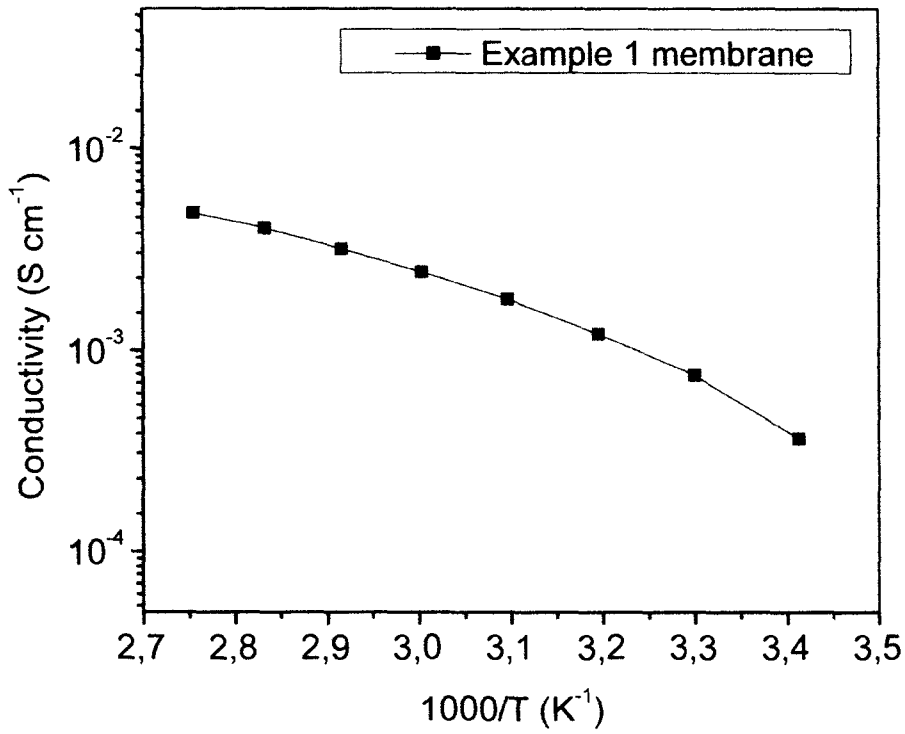


FIG.5

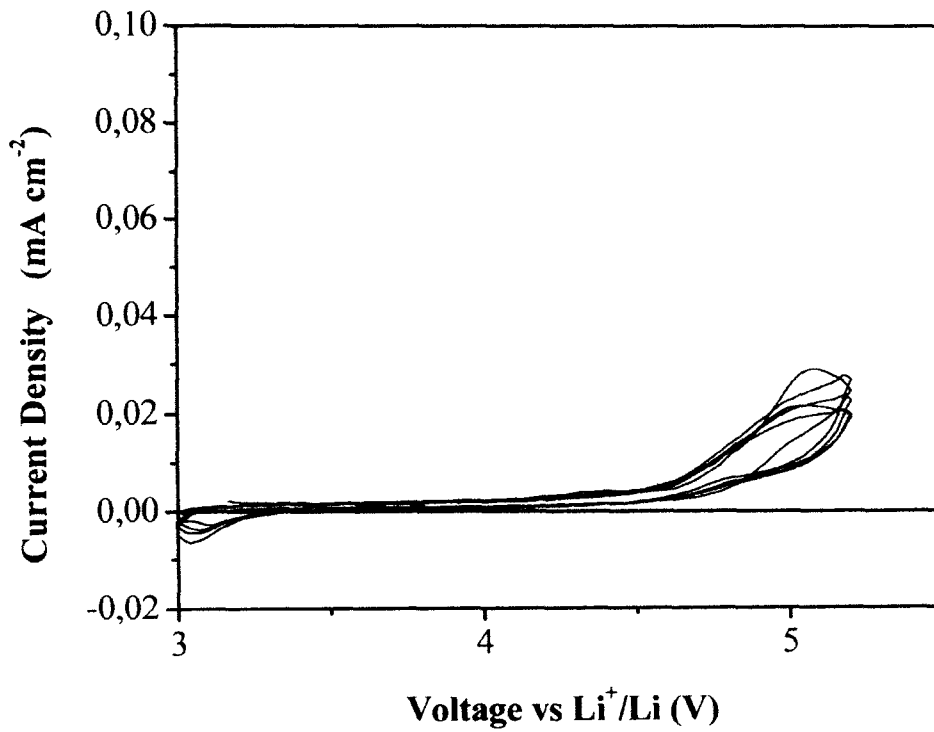


FIG.6

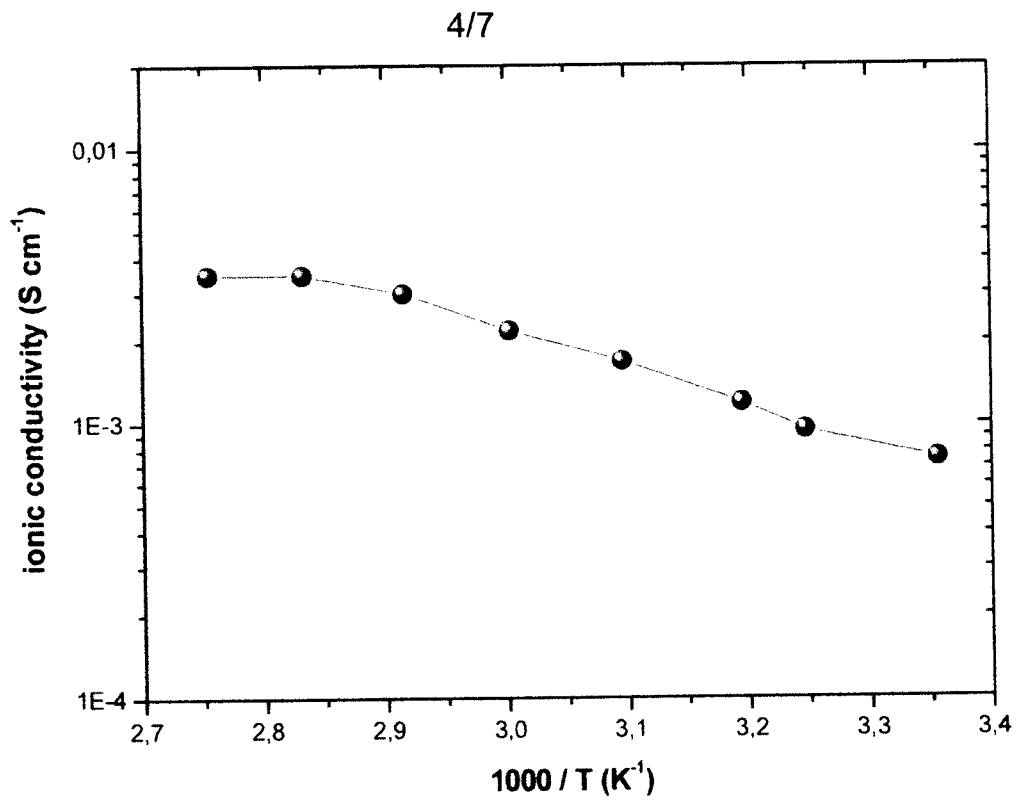


FIG.7

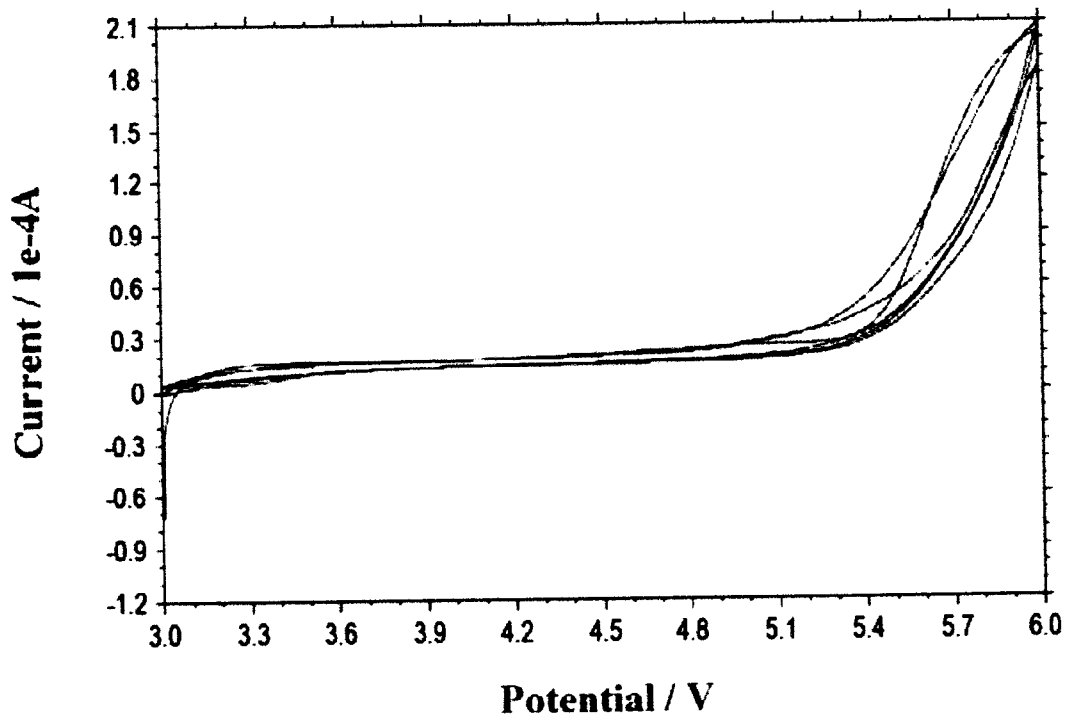


FIG.8

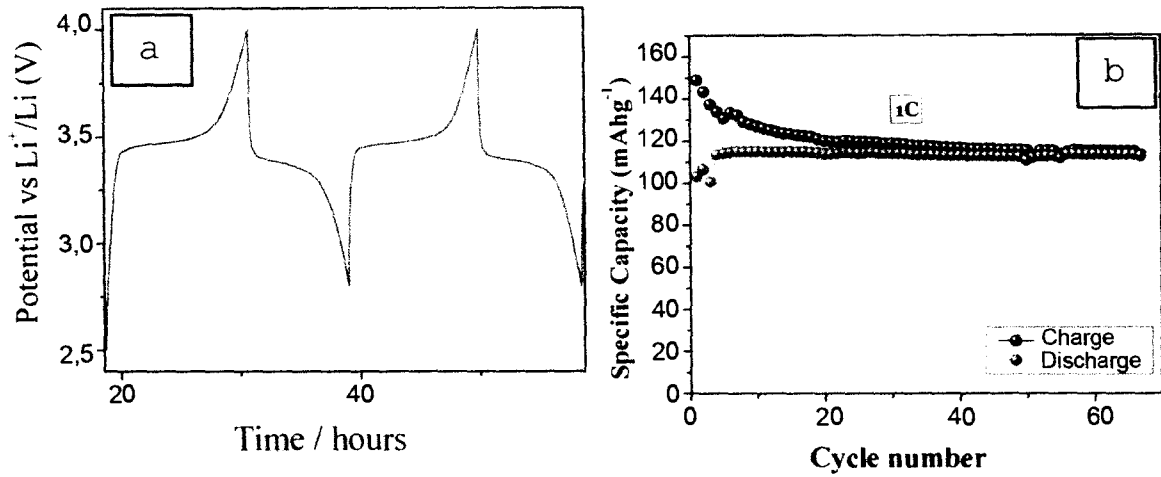


FIG.9

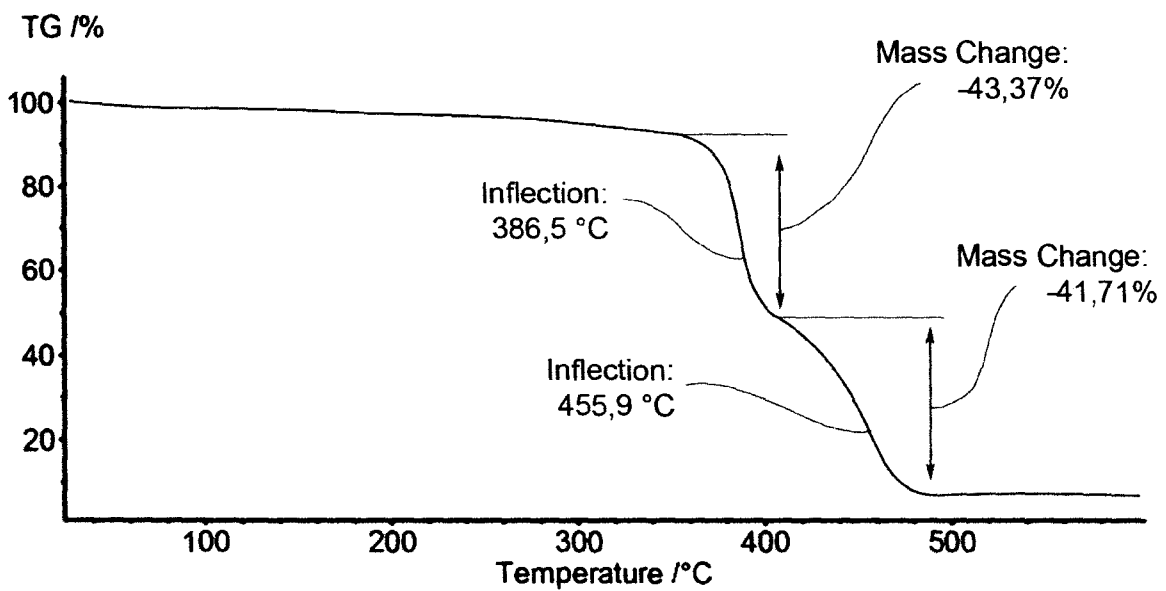


FIG.10

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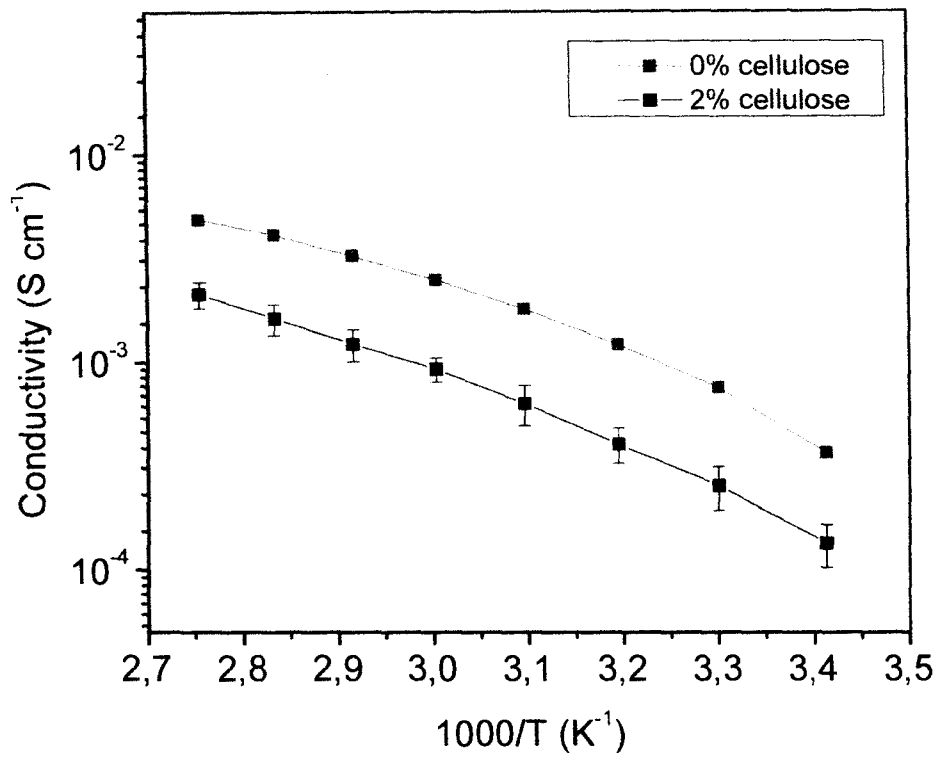


FIG.11

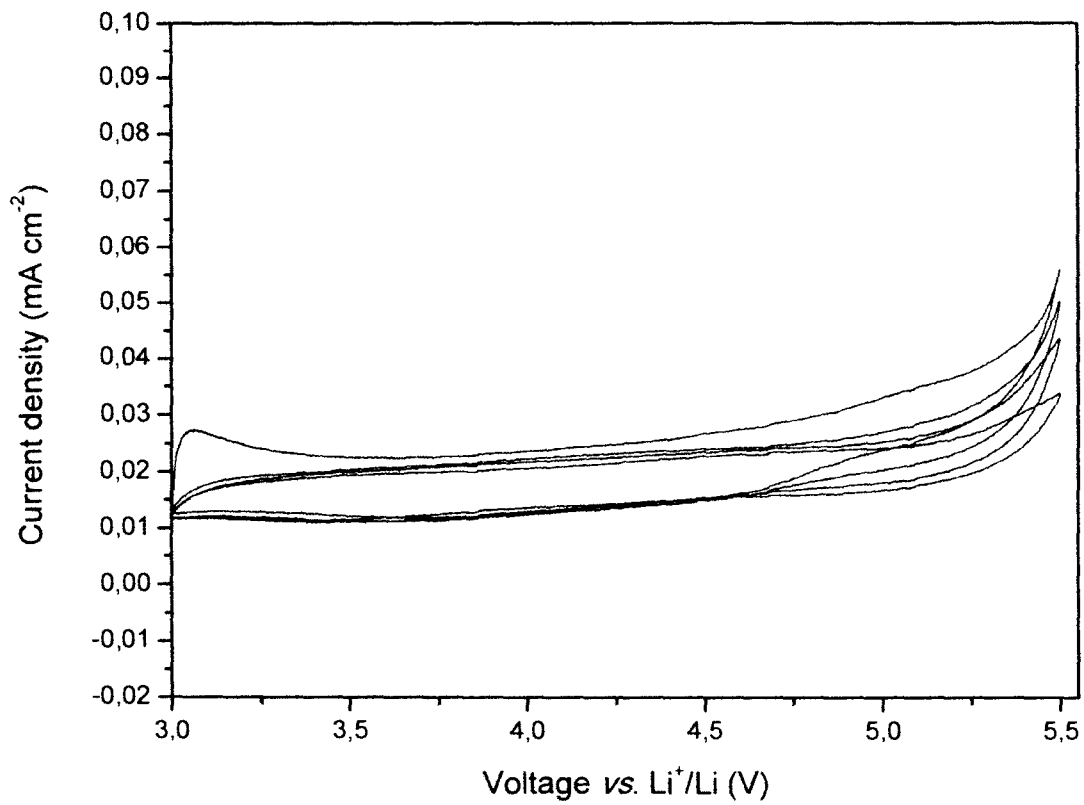


FIG.12

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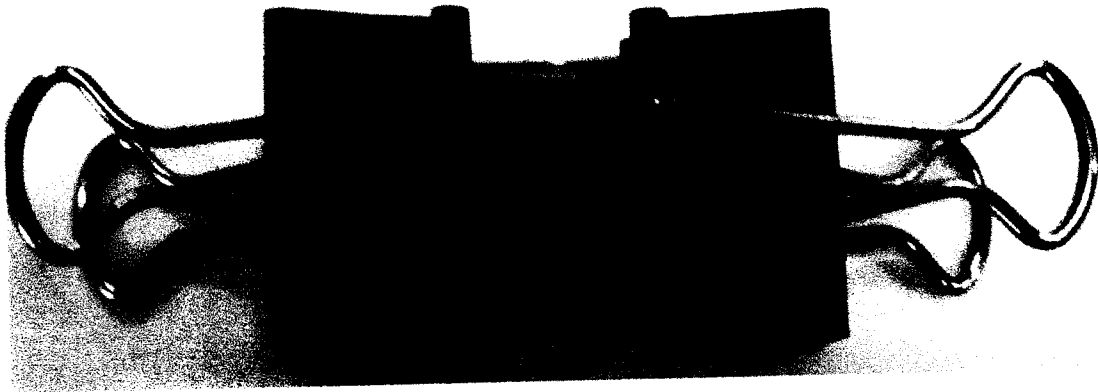


FIG.13

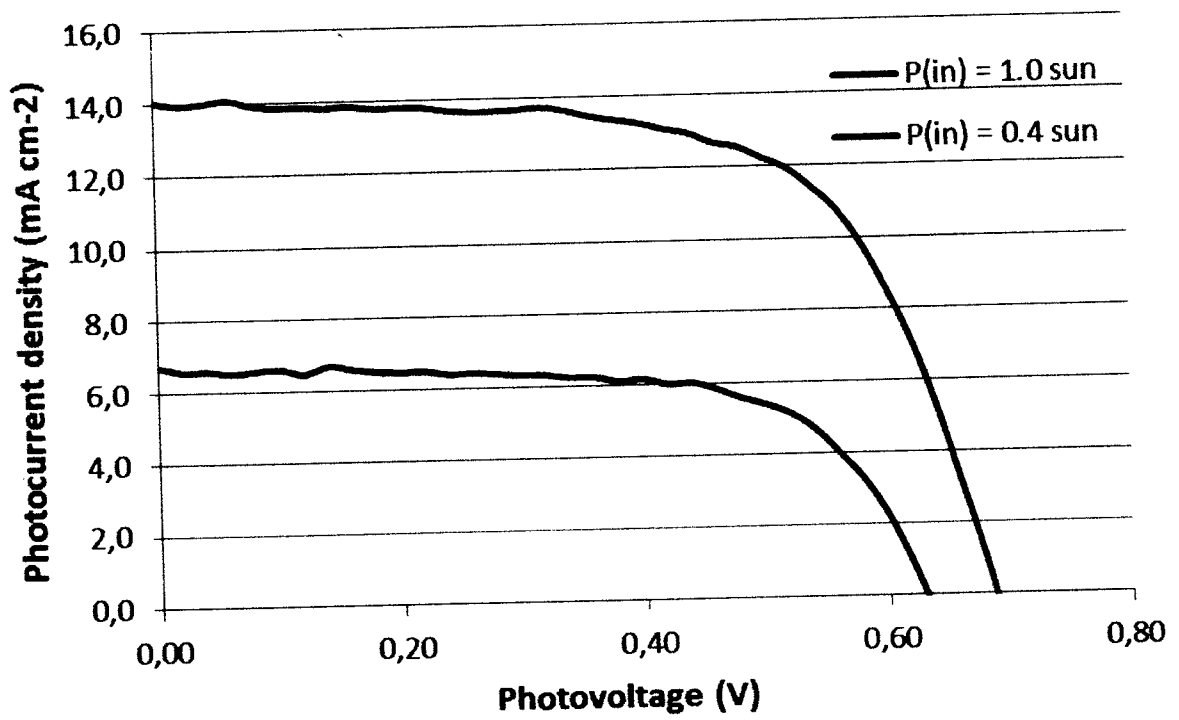


FIG.14



INTERNATIONAL SEARCH REPORT

International application No  
PCT/IT2014/000008

A. CLASSIFICATION OF SUBJECT MATTER  
INV. H01M10/052 H01M10/0565 H01M10/0569  
ADD.  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/035137 A1 (MARUO TATSUYA [JP] ET AL) 16 February 2006 (2006-02-16) paragraphs [0001], [0010], [0034] - [0051], [0061], [0106] - [0118]; claim 11	1-15
X	WO 2014/006333 A1 (FED STATE BUDGETARY INSTITUTION FOR SCIENCE A N NESMEYANOV INST OF ORG) 9 January 2014 (2014-01-09) claims 1,2; examples 1-3	1-15
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Further documents are listed in the continuation of Box C.

See patent family annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search  2 September 2014	Date of mailing of the international search report  10/09/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Götz, Heide

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IT2014/000008

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>RUPP B ET AL: "Polymer electrolyte for lithium batteries based on photochemically crosslinked poly(ethylene oxide) and ionic liquid", EUROPEAN POLYMER JOURNAL, PERGAMON PRESS LTD. OXFORD, GB, vol. 44, no. 9, 1 September 2008 (2008-09-01), pages 2986-2990, XP025398857, ISSN: 0014-3057, DOI: 10.1016/J.EURPOLYMJ.2008.06.022 [retrieved on 2008-06-25] the whole document -----</p>	1-15

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Information on patent family members

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			KR	20050056994 A	16-06-2005
			US	2006035137 A1	16-02-2006
			WO	2004021500 A1	11-03-2004
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WO 2014006333	A1	09-01-2014	NONE		
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