Morphology, ionic diffusion and applicability of novel polymer gel electrolytes with LiI/I₂


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Novel polymer gel electrolytes have been prepared by incorporating LiI–I₂ solutions into a polyethylene oxide matrix supported by a TiO₂ filler. The gel electrolytes, based on either acetonitrile or propylene carbonate solvents are compared with liquid standard ones and are examined by ⁷Li solid state nuclear magnetic resonance relaxometry and diffusion measurements. In parallel, the triiodide apparent diffusion coefficient has been determined by linear sweep voltammetry. The results are correlated with atomic force microscopic images of the electrolytes and give insight of the dynamic properties of the ions in the constrained polymer medium. Furthermore, the dissociation of the ions is estimated by relating the ionic conductivity to the ionic diffusion. As a prime application, the polymer gel electrolytes were incorporated in dye sensitized solar cells and the measured energy conversion efficiencies were successfully correlated with their morphological, diffusive and conducting properties.

1. Introduction

Polymer-based pure solid-state electrolytes have been synthesized in order to be used as alternative to liquid ones, but their applicability is limited due to the fact that they present rather low ionic conductivity (10⁻⁵–10⁻⁷ S cm⁻¹) at ambient temperature. To overcome the problem, an extensive research was directed towards the development of polymer gel electrolytes. These electrolytes appear to possess, simultaneously, the cohesive properties of solids and the diffusive transport properties of liquids owing to their unique hybrid network structure which allows a significant quantity of mobile compounds to be hosted in the polymer matrix. In this way, sealing and evaporating problems, which are detrimental in the use of liquid electrolytes, are now severely suppressed. Moreover, several other advantages emerge which advance polymer gel electrolytes related applications. In Li batteries, electrode interfacial contact can be maintained during volumetric changes associated with charging and discharge cycles. In dye-sensitized solar cells (DSSCs), non-liquid contact to the dye and the working electrode as well as stable performance under both thermal stress and light soaking are achieved. In order to improve the dye regeneration, improves the cell’s performance and reduces the fabrication cost.

To develop polymer gel electrolytes, several polymeric matrices including poly(acrylonitrile), poly(methyl methacrylate), poly (vinyl chloride) and polyethylene oxide (PEO) have been used. Although PEO often forms solvent free polymer/salt complexes, this polymer may also deploy very interesting gel electrolytes, provided a high molecular weight is used combined with a solvent of high dielectric constant. Thus, it has been established that the introduction of filler particles with large surface area in the polymer gels prevents the recrystallization of the PEO and enhances the mobility of the ions. The structure modification of the polymer electrolyte may be produced by a combination of steric hindrance effects or/and of acid–base interactions between the filler surface groups and the oxygen of the PEO. The Lewis acid character of the inorganic filler favors the formation of complexes with the PEO. In that way the filler may act as a cross-linking center for the PEO reducing the tension of the polymer for self-organization and promoting stiffness. It is believed that this structure provides the conducting pathways for the ions at the surface of the filler improving thus the conductivity of the gel.

Low cost, construction simplicity and high conversion efficiency (~10%) have placed nanocrystalline DSSCs among the most promising candidates of photovoltaic solar energy conversion. The stability of the DSSCs depends strongly on the chemical composition and physical state of the electrolyte. The use of electrolytes based on ionic liquids presenting low vapor pressure and good electrochemical stability led to "semi-solid" DSSCs with overall light to electrical power efficiency of 4%. To improve stability and lifetime, essential emphasis has been recently given to the development of “solid-state” DSSCs, where solvent losses are prevented and device long-term operation is assured thanks to use of hole-transport organic materials, p-type semiconductors and polymer electrolytes.

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Polyethylene oxide (PEO) based electrolytes showing a high energy conversion efficiency up to 4.2% under direct sunlight illumination employing a very simple DSSC architecture were reported by our group. These systems were prepared by the addition to ‘solid plasticizers’ (inorganic oxides like TiO$_2$) in PEO mixed with LiI/I$_2$ in acetonitrile (AN) and the subsequent evaporation of the organic solvent up to the point that the electrolyte had a quasi-solid character. To avoid decay of the material’s efficiency under aging attributed to the complete evaporation of the AN solvent and the subsequent crystallization of the polymer, firm sealing and complete absence of humidity (inert atmosphere) during the whole cell preparation procedure as well as during operation, is necessary. The drawback of the AN facile evaporation can be avoided by using a much less volatile solvent such as the propylene carbonate (PC). PC has been used either exclusively or as a mixture with other solvents, in lithium batteries as well as in DSSCs.

This study combines electrical and electrochemical analysis in conjunction with nuclear magnetic resonance (NMR) characterization of the new developed AN and PC based electrolytes in an attempt to measure the ionic diffusion properties and correlate them to the solvent characteristics, the structure of the PEO and the role of the filler. Thus, interaction between the filler nanoparticles and the polymer network is explored and diffusion of both cations (Li$^+$) and anions (I$^-$/I$_3^-$) is determined. Finally, the efficiency of the polymer gel electrolytes was tested in DSSCs, under atmospheric mass absorption, AM 1.5, simulated solar light, provided that the active electrolytes was tested in DSSCs, under atmospheric mass absorption, AM 1.5, simulated solar light, provided that the active electrolyte has a quasi-solid character. To avoid decay of the material’s efficiency under aging attributed to the complete evaporation of the AN solvent and the subsequent crystallization of the polymer, firm sealing and complete absence of humidity (inert atmosphere) during the whole cell preparation procedure as well as during operation, is necessary. The drawback of the AN facile evaporation can be avoided by using a much less volatile solvent such as the propylene carbonate (PC). PC has been used either exclusively or as a mixture with other solvents, in lithium batteries as well as in DSSCs.

2. Experimental

Polymer electrolytes were prepared by introducing liquid electrolyte (LiI and I$_2$, having 10/1 molar ratio, dissolved in acetonitrile, AN) into a polymer matrix with long organic chains (PEO, MW = 2 $\times$ 10$^6$). To improve the conductive properties of the above electrolyte (sample G1), a quantity of a large BET surface TiO$_2$ powder (commercial Degussa P25) in a relative proportion to PEO 14.5% w/w was added in the later dispersion (G2). Both samples were continuously stirred, sonicated and finally cool-heated in order to evaporate the solvent (AN) up to a point that the final product had a gel character. However, a small portion of the solvent eventually remains even in the solid-like G2 sample since whenever it was left free to vaporization for several hours, it gradually became hard and inhomogeneous. Further details of the preparation can be found in ref. 21.

In an effort to improve the stability of our electrolyte, a small quantity of low volatility solvent (PC) was added in the starting dispersion of the G1/G2 electrolytes. The new samples were prepared without (G3) and with the addition of the TiO$_2$ filler (G4), in the same relative proportion to PEO as for sample G2. After mixing the components of the G3 and G4 PC based electrolytes (polymer, filler redox couple, solvent and plasticizer), the resulting slurry is heated at approximately 85 °C in order to fully evaporate AN (above that temperature iodine I$_2$ steamers may also appear). After about 4 h of treatment, the slurry was placed in a glove box for another 24 h. Then, IR and Raman measurements were performed focusing the laser directly at a “gelly pellet” of the composite electrolyte as prepared. No peaks attributed to acetonitrile modes were detected. In situ micro-Raman spectroscopy was also applied at DSSCs using the above electrolyte. The laser was then focused at the side of the electrolyte. Also, no AN peaks were found. On the other hand, PC is still residual, acting as a plasticizer of the polymer. In fact, Raman peaks of PC were clearly detected. For example, a standard peak at about 774 cm$^{-1}$ was found with intensity almost comparable with a liquid DSSC (PC as a solvent). The nominal concentration of LiI and I$_2$ in PC were 0.34 M and 0.034 M, correspondingly, which is within the range reported in the literature for constructing DSSCs with high efficiencies. The above nominal proportion is retained in the final concentration. This was verified within a 3% error, by testing the solvent at the conditions of the experiment. For comparison of the results, two reference liquid electrolytes were also prepared with salt concentrations similar to those in the corresponding polymer based electrolytes: (a) a dense solution of 1 M LiI, 0.1 M I$_2$ in AN (AN-liq) and (b) a 0.34 M LiI, 0.034 M I$_2$ in PC (PC-liq).

Atomic force microscopy (AFM) images of the polymer gel electrolytes were obtained with an (AFM-Nanoscope III, Digital Instruments), operating in the tapping mode. The ionic conductivity of the various quasi-solid electrolytes was measured by electrochemical impedance spectroscopy. All measurements were conducted with a computer controlled potentiotstat, the AUTOLAB12/FRA2 (Eco Chemie) electrochemical analyzer. Each sample was sandwiched between two conductive TEC8 glasses and masked with an insulating tape, leaving an opening of 0.5 $\times$ 0.5 cm$^2$ and a space of about 50 μm. The film-covered glasses can be represented by an RC-circuit consisting of the total resistance and the double-layer capacitance. The conductivity experiments were carried out at a 30 kHz frequency (the voltage amplitude of the sine waveform is 10 mV), in order to drastically suppress the contribution of the capacitance to the overall impedance. The values of the film resistance were calculated from the total measured resistance corrected for the resistance of the glass. Presented values were recorded at a 0 V potential. The aging of the electrolytes was tested by recording impedance spectra (Nyquist plots) of the various electrolytes over the frequency range 100 kHz–0.1 Hz. The liquid standard electrolytes were electrically characterized by a Hach sension7 conductivity meter. Linear sweep voltammetry was employed for measuring the triiodide apparent diffusion coefficient $D^{*}$I$_3^-$. The experimental setup consists of a simple sandwich device where two platini-zed conducting glass electrodes are held at a distance of about $d = 50 \mu m$, whereas the electrolyte was enclosed in between. The system was polarized at a rate of 10 mV s$^{-1}$ and the voltage was swept from $-0.75$ to $+0.75$ V while $D^{*}$I$_3^-$ was determined by measuring the diffusion-limited current. $^7$Li NMR measurements were performed on the PEO composite electrolytes using a Bruker MSL spectrometer with
a superconducting magnet at 4.7 T. $^7$Li NMR resonance was detected at a Larmor frequency $\omega_0/2\pi = 77.783$ MHz. The electrolytes were put into a polyvinylchloride (PVC) holder and covered with parafilm which prevented them from evaporation. For the lineshape analysis, the sample was covering only the center of the coil in order to obtain high magnetic field homogeneity. The $^7$Li NMR profile of the sample as well as the measurements of the diffusion coefficient were obtained by setting out the NMR probe in the region of a non-uniform magnetic field with a mean value of 2.05 T and an almost linear magnetic field gradient equal to 33 T m$^{-1}$. In these experiments, the signal intensity was measured at the peak of the echo-amplitude. The method is reliable and does not require the advanced instrumentation of the pulsed field gradient methods. $^7$Li spin lattice relaxation times $T_1$ were determined by applying the saturation and inversion recovery pulse sequences. For all other measurements, namely spectra acquisition, spin–spin relaxation time ($T_2$) and diffusion coefficient, the quadrupolar echo pulse sequence was employed.\textsuperscript{25} Also, we have tried to measure the $^{127}$I NMR resonance but we have not detected any signal due to its large quadrupole moment and the non-symmetric iodide electrostatic environment.

Polymer gel electrolyte solar cells of lamellar structure were fabricated by sandwiching the electrolyte between a TiO$_2$ photoelectrode sensitized by the Ru(dcbipy)$_2$(NCS)$_2$ (Ruthenium 535 or N3) dye which contains both bipyridyl ligands and isothiocyanato groups\textsuperscript{26} and a platinized F-doped SnO$_2$ counter electrode. An adhesive tape (approximately 50 $\mu$m thick) was placed between the electrodes to avoid short-circuiting and the two electrodes were firmly pressed. $I$–$V$ measurements were performed by illuminating the cell through the active photoelectrode, under solar simulator from a 300 W Xe lamp operating with an AM 1.5 filter.

The entire characterization \textit{i.e.} NMR, AFM, electrochemistry, impedance and $I$–$V$ of DSSCs, was carried out at room temperature, about 20 $^\circ$C.

### 3. Results and discussion

The properties of the polymer gel electrolytes are expected to depend strongly on the selection of the solvent. A summary of some important AN and PC solvent properties, namely, boiling point, viscosity coefficient and dielectric constant, is given in Table 1. Apparently, PC shows low volatility and evaporates at very high temperature, remaining permanently, as a plasticizer of the polymer and assuring long term stability. On top, it has a high dielectric constant which facilitates ion dissociation. A drawback, though, of the PC use, in comparison to AN, is its high viscosity which constrains the ionic diffusion.

### Table 1

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>MF</th>
<th>bp/°C</th>
<th>$\eta$/cP</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN Acetonitrile</td>
<td>C$_2$H$_3$N</td>
<td>82</td>
<td>0.343</td>
<td>36.6</td>
</tr>
<tr>
<td>PC Propylene carbonate</td>
<td>C$_4$H$_6$O$_3$</td>
<td>241.7</td>
<td>2.530</td>
<td>64.92</td>
</tr>
</tbody>
</table>

3.1. Morphological AFM analysis

The AFM three-dimensional (3-D) image of the binary electrolyte, (Fig. 1), when compared to the non treated PEO,\textsuperscript{22} shows that the introduction of the inorganic filler induces important structural and morphological modifications indicating a physical cross linking of polymer chains in a gel network. Therefore, only G2 and G4 electrolytes are, strictly speaking, polymer gels while the filler free G1 and G3 will be regarded as highly viscous liquids which retain some flow properties. Titanium dioxide nanoparticles in the composite electrolytes possess dimensions of 20–25 nm in diameter and they are represented as bulk spheres on the surface of the polymer chains, clearly identified in high magnification images. The supported polymer is depicted in the form of long and stiff interconnected chains. The titania nanoparticles are positioned along with and between the polymer chains, keeping them apart and thus preventing crystallization of the organic matrix. In this way, a mechanically stable network is created that leaves free space in the form of voids into which the iodide/triiodide anions can easily migrate. The size of the voids revealed in the immobilized (solid) phase of the structure varies with a mean length of a few 2–5 $\mu$m and a mean width which is an order of magnitude smaller (100–200 nm). It is interesting to note that the composite organic–inorganic phase is characterised by a height difference that expands up to 400 nm. Therefore, the electrolyte is structured by a 3-D network extending to its mass. The titanium dioxide nanoparticles support the formation of this network by an electrostatic interaction mechanism between the surface hydroxyl groups of TiO$_2$ and the oxygen atoms of the polymer chain. This interaction stabilizes inorganic nanoparticles on the surface of the polymer and therefore acts as a molecular “fence” against aggregation or crystallization of the polymeric chains. In this way the formed network is stable and resembles a molecular sieve that is permeable from the bulky triiodide anions.
The above structure is not permanent. After a few hours of exposing the electrolyte in ambient conditions, cracks are formed on its polymer matrix. Then the electrolyte presents a dendrite structure which is clearly observed under the optical microscope (inset Fig. 1). This structural transition is detrimental to the conductive properties of the material. On the contrary, PC based gel sample G4 presents stable behaviour without visible cracks after several days in ambient conditions.

### 3.2. $^7$Li NMR linewidth and relaxation analysis

In order to investigate ion–polymer interactions and modifications induced by the introduction of the TiO$_2$ filler nanoparticles, we examine the $^7$Li NMR spectrum for all different electrolytes. In all cases, a single $^7$Li NMR resonance was detected having a Lorenzian lineshape with a linewidth of 60–70 Hz (see, for example, the spectrum of sample G2 in the inset Fig. 2). Under the experimental error of these measurements, the resonance frequency and the linewidth of all samples are essentially the same. This shows that the quasi-solid state electrolyte is accomplished by hosting the solvent into the PEO matrix; otherwise the linewidth would be in the order of several KHz.27 In principle, strong electrostatic interactions between polar polymer oxygen and Li cations could be verified with pure solid character of the electrolyte. This would be revealed by broad NMR signals. Such possibility is though excluded by the non observation of broad peaks underneath the narrow $^7$Li NMR lines. Apparently, the existence of AN or PC which pose a high dielectric constant diminishes the strength of the O$^2−$−Li$^+$ electrostatic interactions and sustains the gel character of the electrolyte.

To get insight into the local structure and the chemical environment of the Li ions, we have performed $^7$Li NMR $T_1$ and $T_2$ relaxation measurements. For measuring $T_1$, magnetization recovery curves for the polymer gel and liquid samples were recorded. Characteristic curves for the liquids and the filled samples (G2 and G4) are shown in Fig. 2. In all cases, the relaxation curves present a single exponential form. The resulting $T_1$ values are presented in Table 2. The inversion recovery pulse sequence was also used to compare the accuracy of our results. The obtained $T_1$ values (Table 2), are in good agreement with the ones we obtained with the saturation recovery method, especially for the gels. However, this is not the case of the liquid samples where we observed slightly higher $T_1$ values (up to 15%).

For the determination of $T_2$, echo decays were recorded as a function of the delay time (Fig. 3). $T_2$ values extracted by fitting the data to single exponential decay functions, are also presented in Table 2. Apparently, $T_1$ and $T_2$ of the liquid electrolytes are 5–6 times higher than those of the polymer based ones. The effect is analyzed in the Discussion section in relation to the Li constrained motion in the host polymer matrix and provides bulk microstructural and morphological characterization of the polymer gel electrolytes and the filler induced modifications.

### 3.3. Ionic conductivities and aging of the electrolytes

Ionic conductivity values ($\sigma$) determined by impedance spectroscopy of the various samples examined within the first 1–3 h of preparation are also presented in Table 2. A statistical deviation of 2–4 $\Omega$ was found which induces a rather big error in the presented values. After one day, the conductivities of sample G1 and G2 AN prepared electrolytes have been reduced by 2 and 3 orders of magnitude, correspondingly.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>$T_1/\mu$s</th>
<th>$T_2/\mu$s</th>
<th>$T_1/T_2$</th>
<th>$\sigma$/mS cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-liq</td>
<td>Liquid standard—1 M LiI, 0.1 M I$_2$ in AN solvent</td>
<td>3370</td>
<td>438</td>
<td>7.7 ± 0.5</td>
<td>41</td>
</tr>
<tr>
<td>G1</td>
<td>Gel without filler and AN solvent</td>
<td>560</td>
<td>75</td>
<td>7.5 ± 0.5</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>G2</td>
<td>Gel with TiO$_2$ filler and AN solvent</td>
<td>546</td>
<td>60</td>
<td>9.1 ± 0.6</td>
<td>2.0 ± 1.0</td>
</tr>
<tr>
<td>PC-liq</td>
<td>Liquid standard—0.34 M LiI, 0.034 M I$_2$ in PC solvent</td>
<td>1055</td>
<td>492</td>
<td>2.2 ± 0.2</td>
<td>3.9</td>
</tr>
<tr>
<td>G3</td>
<td>Gel without filler and PC solvent</td>
<td>211</td>
<td>110</td>
<td>1.9 ± 0.1</td>
<td>0.85 ± 0.1</td>
</tr>
<tr>
<td>G4</td>
<td>Gel with TiO$_2$ filler and PC solvent</td>
<td>234</td>
<td>52</td>
<td>4.5 ± 0.3</td>
<td>1.25 ± 0.4</td>
</tr>
</tbody>
</table>

* Within 5% error. $^b$ From NMR. $^c$ From impedance. $^d$ Inversion recovery experiments.
while those of the PC ones did not show any significant change.

The aging of the electrolytes was tested by performing additional electrochemical impedance spectroscopy measurements. Spectra for samples G2 and G4 recorded 1 h (denoted as (a)) and 24 hours (denoted as (b)) after the assembly of the cells, are illustrated in Fig. 4. Corresponding spectra for samples G1 and G3 are not provided, since their behavior is similar to that of samples G2 and G4, respectively. Spectra of sample G2 (with AN solvent) depend strongly on aging. The Nyquist plot recorded after 24 h (G2-b) presents a broad pattern of the low frequency semi-circle which is in accordance to the high resistance values recorded and mentioned in the previous paragraph. It is important to mention that Bode plot of the aged G2 film (plot is not shown here), revealed an extra time constant at the high frequency region ($4 \times 10^4$ kHz), which is indicative of the high heterogeneity of the aged films.

Nyquist plots (spectra a and b) referring to sample G4 are similar and do not show any remarkable decrease of the film overall conductivity over time.

It is obvious that the conductivity of the polymer gel films is strictly dependent on their morphological characteristics. The violent evaporation of acetonitrile results in the formation of a dendrite structure where a lot of conductive paths are not interconnected, causing, thus, the decrease of the overall film conductivity. Upon replacement of AN with a non volatile solvent, that is, PC, formation of a highly homogeneous film, which is stable over time, is realized.

3.4. Electrochemical measurements of the apparent triiodide diffusion

When a potential is applied to the Pt/electrolyte/Pt electrochemical cell, the total reaction at the Pt/electrolyte interface is described as:

$$3I^- \leftrightarrow I_3^- + 2e^- \quad (1)$$

Characteristic linear sweep voltammetry curves of the electrochemical system are presented in Fig. 5, for electrolytes G2 and G4 and the liquid standards. Above about 300 mV, the current density saturates for both polarities. The anodic and cathodic limiting current plateaus are quite similar indicating steady state conditions (sample G2 deviates from the steady state). For our electrolytes, the excess iodide concentration over triiodide (9 : 1) ensures that triiodides are the limiting current ions. Therefore limiting current densities ($J_{lim}$) can only be used to calculate the triiodide apparent diffusion coefficient $D_{I_3^-}$ according to the following relation:

$$J_{lim} = \frac{2nF C_0 D_{I_3^-}}{d} \quad (2)$$

where $n = 2$ is the electron number required for the reduction of triiodide to iodide, $C_0$ is the initial concentration of the triiodide ions, $d$ the thickness of the cell and $F$ the Faraday constant. The values of $D_{I_3^-}$ are presented in Table 3. The results of $D_{I_3^-}$ for the liquid electrolytes are in accordance to those calculated by Hauch and Georg and based on diffusion limiting current electrochemical measurements. Significant reduction of $D_{I_3^-}$ for the gels relative to the corresponding ones in the liquids is observed due to the restricted motion of triiodides in the solid polymer network. Nevertheless, in the case of ideal gelation in polymers that permit free ionic motion...
Table 3  Diffusion coefficients of I\textsuperscript{-} and Li\textsuperscript{+} measured by linear sweep voltammetry and NMR, correspondingly. About 12% error was estimated for both values. Extracted values of ionic dissociation ratio \( \lambda \) and effective hydrodynamic radius ratio \( \kappa \) are also given (see section 3.7). Results in parentheses are under big experimental error and can only be used for qualitative analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D_{Li}/10^{-6} \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( D_{L}/10^{-6} \times \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( \kappa )</th>
<th>( \lambda % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-liq</td>
<td>12.7</td>
<td>8.1</td>
<td>1.6 ( \pm ) 0.3</td>
<td>51 ( \pm ) 5</td>
</tr>
<tr>
<td>G2</td>
<td>(1.5)</td>
<td>(4.3)</td>
<td>(0.4)</td>
<td>(9)</td>
</tr>
<tr>
<td>PC-liq</td>
<td>2.8</td>
<td>2.0</td>
<td>1.4 ( \pm ) 0.2</td>
<td>62 ( \pm ) 6</td>
</tr>
<tr>
<td>G4</td>
<td>1.1</td>
<td>0.5</td>
<td>2.2 ( \pm ) 0.4</td>
<td>60 ( \pm ) 18</td>
</tr>
</tbody>
</table>

without entrapment of the solution in pores, the apparent diffusion of ions in the polymer gels and corresponding bare liquid electrolytes can be virtually identical.\(^{6,10}\) The results for the AN gel electrolyte can only be considered as qualitative, since the ionic concentration is not known with accuracy. For distinctness, the \( D_{Li}^* \) value of this sample is enclosed in parentheses.

3.5. \(^{7}\)Li NMR profile and diffusivity measurements

In addition to NMR linewidth analysis and relaxometry, \(^{7}\)Li NMR measurements in a magnetic field gradient were carried out in order to record the cation profile and determine the Li diffusion coefficient. In the inset of Fig. 6, the \(^{7}\)Li NMR profile of the sample in the magnetic field gradient is presented. The range of frequencies where the signal is observed corresponds to a sample thickness of about 4 mm which, in fact, equals the inner diameter of the sample holder in the NMR coil. This profile has a multiple utility: firstly it confirms that the resonance is related to the material and not to a parasitic signal and secondly it permits setting the resonance frequency (at \( \approx \) 33 MHz) in order to map the central region of the sample for safely performing diffusion experiments. Furthermore, the method of recording the sample profile has also been used for qualitative analysis.

The echo signal amplitude is proportional to \( M(t) \), hence \( D \) can be measured by fitting the echo decay to eqn (3). The accuracy of the method was tested by measuring \( D \) for \(^{1}H\) in distilled water. The extracted value 2.0 \( \times \) 10\(^{-5} \) cm\(^2\) s\(^{-1}\) for \(^{1}H\) with 1\% error in agreement to the one generally accepted in the literature (2.0 \( \times \) 10\(^{-5} \) cm\(^2\) s\(^{-1}\) at 20 °C).\(^{33}\)

The experimental data of the various liquid and the filled polymer gel electrolytes reported in Fig. 6, have been fitted to eqn (3), using \( T_2 \) values from Table 2, \( \gamma = 10.3975 \times 10^7 \) T\(^{-1}\) s\(^{-1}\) and \( G = 33 \) T m\(^{-1}\). Extracted \(^{7}\)Li diffusion coefficients are presented in Table 3. \( D_{Li} \) of the polymer gel electrolytes are in the 10\(^{-5}\)–10\(^{-6} \) cm\(^2\) s\(^{-1}\) range and match the reported ones in the literature,\(^{34}\) whereas the corresponding values for pure solid electrolytes are much smaller.\(^{25}\) As shown in Table 3, the diffusion coefficients of Li in the polymer gel electrolytes are significantly reduced relative to the self-diffusion coefficients in the corresponding liquid ones, due to the motion of the Li atoms in the constrained polymer medium. Therefore, the values given in Table 3 for the polymer gel samples can only be treated as the effective Li diffusion coefficients since, strictly speaking, the self-diffusion of Li atoms in the solvent does not change when the atoms are enclosed in the polymer matrix.

In the main Fig. 6, we present \(^{7}\)Li NMR diffusion measurements under magnetic field gradient. The technique relies on mapping the random thermal motion of the nuclear spins. In the presence of a field gradient, the spins experience a linear distribution of different magnetic fields. The consequent distribution in their resonance frequencies introduces a phase incoherence which causes a reduction of the spin magnetization \( M \) as long as the mobile spins diffuse outside the slice of the sample which is imaged by the radiofrequency pulse. The decrease of \( M \) as a function of the duration \( \tau \) between the \( \pi/2\)–\( \pi \) pulses in the quadrupolar echo is described by the following equation:\(^{32}\)

\[
M = M_0 \exp \left( -\frac{2\tau}{T_2^*} - \frac{\gamma^2 DG^2\tau^2}{3} \right)
\]

where \( M_0 \) is the initial spin magnetization, \( \gamma \) is the nuclear gyromagnetic ratio, \( G \) the magnetic field gradient, \( T_2 \) the transverse relaxation time and \( D \) the self-diffusion coefficient. The echo signal amplitude is proportional to \( M(t) \), hence \( D \) can be measured by fitting the echo decay to eqn (3). The accuracy of the method was tested by measuring \( D \) for \(^{1}H\) in distilled water. The extracted value 2.0 \( \times \) 10\(^{-5} \) cm\(^2\) s\(^{-1}\) for \(^{1}H\) was within 1\% error in agreement to the one generally accepted in the literature (2.03 \( \times \) 10\(^{-5} \) cm\(^2\) s\(^{-1}\) at 20 °C).\(^{33}\)

The experimental data of the various liquid and the filled polymer gel electrolytes reported in Fig. 6, have been fitted to eqn (3), using \( T_2 \) values from Table 2, \( \gamma = 10.3975 \times 10^7 \) T\(^{-1}\) s\(^{-1}\) and \( G = 33 \) T m\(^{-1}\). Extracted \(^{7}\)Li diffusion coefficients are presented in Table 3. \( D_{Li} \) of the polymer gel electrolytes are in the 10\(^{-5}\)–10\(^{-6} \) cm\(^2\) s\(^{-1}\) range and match the reported ones in the literature,\(^{34}\) whereas the corresponding values for pure solid electrolytes are much smaller.\(^{25}\) As shown in Table 3, the diffusion coefficients of Li in the polymer gel electrolytes are significantly reduced relative to the self-diffusion coefficients in the corresponding liquid ones, due to the motion of the Li atoms in the constrained polymer medium. Therefore, the values given in Table 3 for the polymer gel samples can only be treated as the effective Li diffusion coefficients since, strictly speaking, the self-diffusion of Li atoms in the solvent does not change when the atoms are enclosed in the polymer matrix.

3.6. Hosting and constrained motion of the ionic solutions in the polymer matrix

The AFM images have shown that the addition of the filler causes substantial morphological changes to the host polymer. Analysis of the microscopical images has been performed and the results match those reported in ref. 35 by our group for the G2 type electrolyte, namely, the introduction of the filler increases the roughness by almost three times while the structure is significantly expanded following a reduction of the fractal dimension (a measure of the material’s surface complexity) from about 2.3 to 2.2. This means that the self-similararity and self-character of the polymer electrolyte decreases upon the addition of the TiO2 filler. In excellent agreement with the AFM results, differential scanning calorimetry (DSC) data have shown that the introduction of the inorganic filler significantly decreases the crystallization of the polymer gel electrolyte.\(^{21,35}\)

Fig. 6  Measurements of the \(^{7}\)Li NMR echo amplitude decay vs. delay time in a magnetic field gradient of 33 T m\(^{-1}\). In the inset figure, the \(^{7}\)Li NMR profile of sample (G2) in the region of the magnetic field gradient is shown superimposed upon the cross section image of the sample holder.

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NMR relaxation results are in accordance with the AFM analysis. In particular, the shorter $T_1$ and $T_2$ values for the polymer based relative to the liquid ones are attributed to the motion of the liquid electrolyte in the PEO matrix. Considering the analogue of constrained materials, the liquid electrolyte partially covers the vacancies in the structure. The $T_1$ and $T_2$ values of $^7$Li in the electrolyte which is within the vacancies $(T_{1,2v})$ are expected to be very similar to those measured in the liquid samples. However the Li ions which are found in near contact with the surface of PEO show a different longitudinal and transverse relaxation time $(T_{1,2s})$ due to the interaction with the ions of PEO, so in general $T_{1,2s} < < T_{1,2v}$. Thus, both relaxation rates can be described as a sum of the two contributions:31

$$
\frac{1}{T_{1,2}} = \frac{n}{T_{1,2s}} + \frac{1-n}{T_{1,2v}}
$$

where $n$ is the proportion of Li nuclei which are near to the PEO–liquid interface, hence they present different relaxation rates. Within such a scheme, $T_1$ and $T_2$ are expected to depend strongly on the size, roughness and fractal dimension of the vacancies, as well as the percentage of voids occupation by the electrolyte. Furthermore, any Li in solid phases would show very short relaxation time which could be clearly distinguished.

In addition, $T_1 < < T_2$, indicating that the liquid electrolyte has a correlation time $\tau_c \approx \omega_0^{-1}$ i.e. $>2 \times 10^{-9}$ s.36 Thus eqn (4) shows that $T_2$ follows the trend of $T_1$ on a different scale. Indeed, the $T_1/T_2$ ratio of samples G1 and G3 (without filler) remains similar to that of the corresponding liquid ones. Comparing now the electrolytes with and without fillers we observe: (a) relative coincidence in their $T_1$ values and (b) substantial decrease of the spin–spin $T_2$ relaxation time for the filled ones, in accordance with the literature.37 The similar $T_1$ values imply that the proportion $n$ of Li nuclei which are adjacent to the solid matrix is similar for the two types of electrolytes. The introduction of the filler is expected to affect $n$ in two ways. Firstly, it establishes an expanded structure with increased voids size which reduces fractality and effectively decreases $n$. On the other side, it extends the effective surface of the polymer by increasing roughness which is anticipated to augment $n$. Therefore, the similar $T_1$ values for the filled and non-filled electrolytes are rather due to a compensation of the two mechanisms which influence $n$.

The $T_2$ decrease observed for the filled electrolytes has been attributed to the increased quadrupole interaction (QI) between the $^7$Li nuclear quadrupole moment and the electric field gradients (EFGs) in the local Li environment.37 The strength of the QI increases when EFGs which the Li nuclei experience, increase. For the filled electrolytes the electric field varies rapidly when Li moves from the polymer to the titania sites and this can justify a more rapid relaxation rate and a decreased $T_2$ value.

The reduced diffusion of Li in the polymer gels relative to the liquid standard counterparts has been attributed to the restricted atomic motion by the polymer matrix and has been observed in several systems.33,38 In this context, the decay of Li magnetization vs. echo delay in the gels can be deduced by the corresponding Li self-diffusion coefficients measured in the liquids and the application of the following equation:39–41

$$
M(t) = M(0) \exp \left[ -\frac{2\tau}{T_2} - \frac{8\lambda^2 G^2 l^4}{D_n} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^6} \left( 2\tau - 3 - 4\exp(-D(2n+1)^2 \pi^2 l^2 / 2\lambda^2) + \exp(-D(2n+1)^2 \pi^2 l^2 / 2\lambda^2) \right) \right] / D(2n+1)^2 \pi^2 l^2 / \lambda^2
$$

where the restriction of the atomic motion in the solid boundaries is taken into account by introducing the parameter $l$ which represents the mean voids size.

Magnetization recovery data of Fig. 6 have been fitted to eqn (5) using the self-diffusion coefficients of the liquids in Table 3. Values of $l$ around 1.2 $\mu$m have been deduced for sample G4 (and 3 $\mu$m for sample G2 which is considered less reliable since it cannot be directly related to the AN-liq). The above values agree, in the order of magnitude and slightly surpass the ones directly determined for the space of the voids from the AFM images.

### 3.7. Diffusion and Ionic dissociation in the polymer gel electrolytes

The fundamental difference between the parameters (diffusion coefficients) measured by NMR and those (conductivities) measured by impedance spectroscopy is that the former is determined by the motion of nuclear spin carrying atoms irrespectively of their state of association in the form of paired or isolated ions (self- or effective diffusion) while the latter correspond only to the isolated ions (ionic diffusion). As for the apparent diffusion coefficient ($D^*$) of the electroactive species, measured by linear sweep voltammetry, it is related to the self- (or effective) diffusion coefficient ($D$) through the Dahms–Ruff’s equation:32–44

$$
D^* = D + k_{ex} \delta^2 C_0 / 6,
$$

where the second term accounts for the electron hopping self-exchange mechanism, $k_{ex}$ is the self-exchange rate and $\delta$ an average distance between the considered iodide and triiodide redox centers at the time of electron transfer. For liquid and gel electrolytes with diffusion in the range $10^{-5}–10^{-6} \text{cm}^2 \text{s}^{-1}$, even very fast electron self-exchange reactions contribute only in a minor way to transport i.e. the right hand term in eqn (6) is small compared to $D^*$.44 and

$$
D^* \approx D_{10}
$$

In this way, it is possible to relate the diffusion coefficients resulting from NMR data to those obtained by electrochemical analysis.

Conductivities (Table 2) and diffusions (Table 3) of the various electrolytes can be related by assuming that the apparent diffusion coefficients of iodide and triiodide are the same which is justified within a 20% error by several authors.28,45 Under this assumption, $\Gamma^-$ and $\Gamma^-$ ($\Gamma^- \cdot \Gamma^-$) are indistinguishable and the system resembles a 1 : 1 electrolyte. Within this frame, the modified Nerst–Einstein equation can be applied38,46 and the ionic conductivity is given by the following simple form

$$
\sigma = \frac{NAe^2}{kT} (D^+ + D^-)
$$

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where $D^+$ and $D^-$ is the diffusion of the cations and the anions, i.e. $D_{Li}^+$ and $D_{Li}^-(D_{AN})$ correspondingly; $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $N$ is the number of cations per unit volume and $A$ is the cations–anions dissociation ratio. The above relation holds equally well for the polymer gel electrolytes whereas effective diffusion coefficients of the ions are used in this case. $^{5,34,38}$

Eqn (8) can be solved by combining conductivity and diffusion values from Table 2 and 3. In this way, the degree of ion dissociation, $\Lambda$, is found and presented in Table 3, too. $\Lambda$ for the PC electrolytes is about 60% and it is hardly influenced by the electrolyte gelation. Values for $\Lambda$ in the range of 50–65% were measured by Aihara et al. $^5$ for PEO based gel electrolytes with LiBF$_4$ or lithium bis(trifluoromethanesulfonylimide salts in PC and these are considered relatively high comparing to other solvents. $^{38}$ Hence, in terms of the ion dissociation, PC based electrolytes behave very well. This is justified by (a) the large dielectric constant of PC which favors dissociation (see Table 1) and (b) the relatively low salt concentration in the PC gels.

Moreover, the diffusion of the $i$ ion is related to its effective hydrodynamic Stokes radius ($r_{s,i}$) through the Stokes–Einstein equation. $^{46}$

$$D_i = \frac{k_B T}{6 \pi \eta r_{s,i}} \quad (9)$$

where $\eta$ is the solvent viscosity.

Eqn (9) indicates that the larger diffusion coefficients of the AN-electrolytes than the PC-ones are basically justified by the different viscosity coefficients of the two solvents (see Table 1). Applying eqn (9) for the cations–anions of the same electrolyte we estimate the ratio $\kappa = r_s(Li^+)/r_s(I^-)$. Calculated values of $\kappa$ are presented in Table 3. Apparently, $r_s$ values of the $I^-/I_3^-$ ions are smaller than the $Li^+$ ones (apart from the AN-gel G2 to be discussed later). This is surprising since the ionic radius of the free lithium ion (0.60 Å) is smaller than that of iodide (2.16 Å). $^{46}$ To interpret this apparent inconsistency, we suggest that some AN or PC molecules are solvated around the Li atoms increasing their effective hydrodynamic radius, while the anions diffuse almost without salvation, in accordance to ref. 23. Similar results of $\kappa$ to those calculated in our liquid samples were also recorded in ref. 47 for LiI dissolved in N,N-dimethylacetamide. Using filled gel electrolytes for the solution usually increases the difference between the cation and the anion $r_{s,c}$. $^{48}$ In fact, such an increase of $\kappa$ was observed in our PC gel electrolyte.

Very high salt concentration, as that realized in the AN electrolytes, leads to association of the ions. Furthermore, the abrupt evaporation of the solvent creates partially filled pores where interactions of the ions with the polymer and restriction in the solid boundaries are realized. $^{49}$ while on top, isolated solution islands may be formed. In this way, the conductivity and the apparent diffusion of triiodide are strongly suppressed while the Li diffusion coefficient is not, because the nuclear spin magnetization is insensitive to the macroscopic isolation of the conduction paths. The above arguments justify the apparent (not real) decrease of the $\kappa$ and $A$ values observed for sample G2 in Table 3.

### 3.8. Efficiency of the polymer gel electrolytes in DSSCs

As a prime practical application proving the importance of this work, the influence of the morphological, diffusive and conducting properties of the novel polymer gel electrolytes on the performance and efficiency of DSSCs was evaluated. In this context, the various PEO based and liquid electrolytes were incorporated into DSSCs (see Experimental section) and characteristic operational parameters of the cells have been extracted from the $I$–$V$ curves obtained under 1.5 AM illumination. Cumulative short circuit photo-current ($J_{sc}$), open circuit voltage ($V_{oc}$), filling factor ($FF$) and overall power conversion efficiencies ($EF$) parameters are presented in Table 4. The $FF$ factor characterizes the quality of the cell and is defined as the ratio of the cell produced maximum power divided by its maximum ‘theoretical’ power, $V_{oc} \times J_{sc}$ while $EF$ accounts for the percentage of solar (light) power that the cell can transform to electrical power. $EF$ values which reach 10% have been reported up to now, using sealed DSSCs filled with liquid electrolytes. $^{50}$ However, the PEO based electrolytes, Table 4, show lower conversion efficiencies. This is consistent with our results reported in Table 2 and 3, where liquid electrolytes present optimum ionic properties (significantly enhanced values of ionic conductivities and diffusion coefficients) with respect to the PEO based ones. Generally, liquid electrolytes present very good efficiencies but the corresponding DSSCs require (a) the deposition of blocking layers (dense titania films) in-between the working glass electrodes and the TiO$_2$ porous film, because otherwise the electrolyte penetrates the film, damaging the cell by a short circuit $^6$ and (b) the sealing of the cell in order to avoid the evaporation of the solvent. The PEO formed electrolytes G1 and G3 obtain high viscosity and provide the advantage of a non liquid contact to the working electrode, without affecting the porous nanostructured titania anode (substrate). In this way, recombination between the electrons and the $I^-/I_3^-$ redox couple is suppressed, $V_{oc}$ and $FF$ significantly increases in accordance to ref. 51 and $EF$ reaches a value of 2.2 and 1.1 for G1 and G3, respectively.

The addition of the filler improves further the efficiency due to the morphological and the consequent ionic conducting changes induced. The better efficiency is due to the decisive enhancement in the short circuit photocurrent $J_{sc}$, reported for samples G2 and G4 in Table 4, by about 60% relative to the unfilled G1 and G3 ones. This increase is directly related to an analogous enhancement of the ionic conductivity which has been shown in Table 2 for the same samples. The relatively low conductivities and $J_{sc}$ of the filler free electrolytes results from their close packed structure revealed by AFM and confirmed by NMR relaxation rate and diffusivity (Table 2 and 3) analysis as well as the consequent severely restricted ionic

### Table 4 Characteristic parameters: short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$) and solar conversion efficiencies ($EF$), of DSSCs operating with various gel electrolytes

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>$FF$</th>
<th>$EF$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>5.7</td>
<td>0.64</td>
<td>0.60</td>
<td>2.2</td>
</tr>
<tr>
<td>G2</td>
<td>9.3</td>
<td>0.58</td>
<td>0.53</td>
<td>2.9</td>
</tr>
<tr>
<td>G3</td>
<td>3.6</td>
<td>0.61</td>
<td>0.50</td>
<td>1.1</td>
</tr>
<tr>
<td>G4</td>
<td>6.0</td>
<td>0.53</td>
<td>0.45</td>
<td>1.4</td>
</tr>
</tbody>
</table>
conduction. In addition, at the photoelectrode/electrolyte interface, the ionic motion is further limited by the transport in the TiO₂ nanoporous network. Consequently, the efficiency of the electrolytes is restrained by their limited percolation into the titanium dioxide porous network. In fact, balancing the gyration radius of the polymer coils with the titania pore size is essential in order to achieve maximum efficiency of the electrolytes.

Introduction of the filler results in extension of the polymer structure (see Fig. 1) and less restricted ionic motion, which proved essential for the achievement of high efficiency in DSSCs, in combination with the benefits of the solid-like character of the polymer gel electrolyte. In this way, an overall $EF$ of about 2.9% and 1.4% is achieved for the filled AN and PC based gel electrolytes, respectively, even though $V_{oc}$ and $FF$ slightly decline as the cost of their increased ionic conductivity. The above extracted $EF$ values compare very well with previously reported ones using gel-type electrolytes and can be improved by optimizing the cell’s preparation. Unfortunately, the AN gel electrolytes which present the best efficiency, still suffer severely from stability problems, while in this aspect, PC gel electrolytes clearly outperform, by $1.4\%$ and $2.9\%$ for the filled AN and PC electrolytes, respectively, even though $A_\text{eff}$ $D_{\text{SSC}}$ and $I_\text{3}/C_\text{0}$ the ionic motion is further limited by the transport in the TiO₂ nanoporous layer.

References