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# Iodopropyl-branched polysiloxane gel electrolytes with improved ionic conductivity upon cross-linking†

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**We here report the implementation of poly[(3-*N*-methylimidazolium-propyl)methylsiloxane-co-dimethylsiloxane]iodides as suitable polymeric hosts for a novel class of *in situ* cross-linkable iodine/iodide-based gel-electrolytes for dye-sensitized solar cells. The polymers are first partially quaternized and then subjected to a thermal cross-linking which allows the formation of a 3D polymeric network which is accompanied by a dramatic enhancement of the ionic conductivity.**

Among various alternatives for liquid electrolytes, polymer gel electrolytes (PGEs) still maintain the greatest potential in the perspective of photoelectrochemical device technology, filling the gap between high performance and long term stability. PGEs are solid or quasi-solid ionic conductors prepared by the dissolution of salts in a suitable high molar mass polymer. Notification of the ionic conductivity of a solvent-free polymer electrolyte was first observed in 1973 by Fenton *et al.* in semi crystalline poly(ethylene oxide)-alkali metal complexes.<sup>1</sup> Since then extensive research activity has been initiated among electrochemists worldwide.<sup>2</sup>

The solid-state nature of polymer electrolytes is a great advantage, but the ionic conductivity occurring in the amorphous phase of the polymer is too low to determine an intensive application in most of the electrochemical and photoelectrochemical devices for energy conversion and storage. In order to increase ionic conduction, polymer and salts are generally mixed with a plasticizer or inorganic fillers which can induce local relaxations and segmental motion of the polymeric chains.<sup>3</sup> The role of the polymer is mainly to act as a stiffener, creating a three-dimensional network in which

cations and anions move freely in the liquid phase.<sup>4</sup> A large amount of plasticizers and/or solvents is generally required to achieve high enough conductivity values. This led to deterioration of the mechanical properties needed to ensure that the electrolyte could be manufactured, stored and used.

*In situ* cross-linking of fairly viscous polymeric gels has been revealed as an elegant strategy to guarantee excellent thermal and volumetric stability while keeping an adequately good ionic conductivity.<sup>5</sup> Because of the high flexibility of the Si–O bond, high free volume, good thermal and chemical stability and low glass transition temperature, polysiloxanes offer all the necessary prerogatives to play an important role in the PGEs field.<sup>6</sup>

Starting from these remarks, two different sets of methylimidazolium iodide functionalized silicone polymers have been synthesized and employed in the formulation of curable polymer gel electrolytes. Polymers were obtained by hydrolysis and co-condensation of the starting monomers in the presence of water and *p*-toluenesulfonic acid as a catalyst. The obtained polymers had molecular weights in the range of 10<sup>5</sup> Da and were thus equilibrated in the presence of hexamethyldisiloxane, affording 20 kDa molecular weight polymers. This procedure allowed the preparation of two families of iodopropyl-branched polydimethylsiloxanes having comparable molecular weight but characterized by two different molar ratios between dimethylsiloxane and iodopropyl-functionalized methylsiloxane units, namely 1/1 and 1/4. The corresponding polymers will be hereafter referred as GL11 and GL14.

These iodopropyl-branched polysiloxanes have then been subjected to partial quaternization with 1-methylimidazole, leading to the formation of polycationic backbones and to the corresponding delivery of iodide counteranions (see the schematic overview of the synthetic procedure reported in Fig. 1).

For each polymer, three different quaternization rates (QR) were selected. Six different batches of ionic conducting hosts were thus obtained and tested, namely GL11\_Q55 (QR 55%), GL11\_Q65 (QR 65%) and GL11\_Q80 (QR 80%), and GL14\_Q55 (QR 55%), GL14\_Q65 (QR 65%) and GL14\_Q85 (QR 85%). The overall synthetic procedure, accompanied by an exhaustive spectroscopic and rheological characterization is reported in the ESI.†

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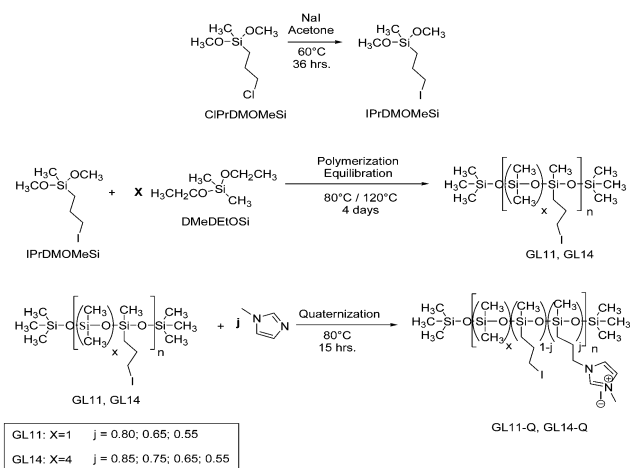


Fig. 1 Synthetic procedure adopted for the preparation of the 3-iodopropyl-branched polysiloxanes synthesized in the present work.

PGEs were thus prepared by dissolving the aforementioned polymers in an ionic liquid consisting of  $I_2$  and LiI in 3-methoxypropionitrile. A stoichiometric amount of bis(3-aminopropyl)-terminated poly(dimethylsiloxane) was then added to the polymeric solutions and acted as a cross-linking agent. The overall amount of polymer has been set at around 40% wt, whereas the specific amount of LiI added to each electrolyte was varied in order to obtain an overall constant value of iodide species of 0.9 M. The concentration of the  $I^-$  species is comprehensive due to the dissociation of LiI present in the ionic liquid, the dissociation of iodopropyl units upon the quaternization process and the contribution associated to cross-linking mechanism. These contributions have been separately calculated in Table 1.

The cross-linking process was executed at 75 °C and analysed in real-time through an oscillatory rheometer. The evolution of storage ( $G'$ ) and loss ( $G''$ ) moduli upon the application of small amplitude oscillatory strain was detected over four hours at the given temperature. Data plots measured on the GL11 series are shown in Fig. 2a. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) respectively describe the elastic and the viscous contributions to the complex modulus of the investigated sample. The point at which  $G'$  exceeds  $G''$  is usually referred to as the gel point; it indicates that an equilibrium between solid-like behaviour and viscous properties has been established.<sup>7</sup> At the initial stage of the process all the PGEs appear as fairly viscous liquids and the  $G''$  results are slightly higher than  $G'$ .

Cross over is already observed to happen in the first 7–8 min for both GL11\_Q55 and Q65 and a few min later in the case of GL11\_Q80. Then an abrupt increment of both of the moduli is detectable which implies a rapid development of the cross-linking

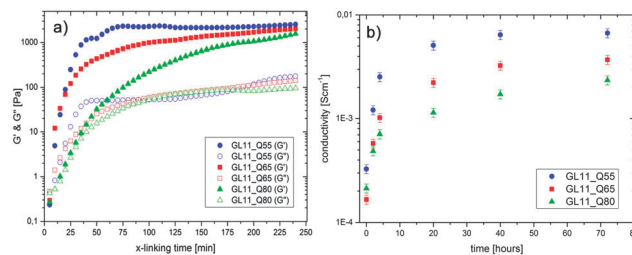


Fig. 2 *In situ* analysis of the cross-linking process at 75 °C of GL11 polymers with three different QR: (a) evolution of the storage and loss moduli upon oscillatory strain; (b) evolution of the ionic conductivity measured in Pt/EL/Pt test cells.

reaction. After only 60 min GL11\_Q55 appears to have completed the cross-linking and it then exhibits a plateau region. A pseudo-plateau region, which is characterized by a relatively slow growth of  $G'$  dominates the process instead in the cases of GL11\_Q65 and Q80. However in all of the cases the elastic modulus reaches a maximum value of around 1.1 kPa after 240 min of curing. As expected, due to the higher density of pending iodopropyl units available for the cross-linking, GL11\_Q55 presents the most favourable conditions for the fast formation of a quasi-solid 3D network.

Evolution of the most relevant electrochemical features of the here disclosed PGEs has also been monitored through an electrochemical impedance spectroscopy (EIS) analysis which has been carried out on Pt/electrolyte/Pt test cells with an active area of the cell of 0.2 cm<sup>2</sup>.<sup>8</sup> In particular, ionic conductivity  $\sigma$  has been obtained using the following equation:

$$\sigma = \frac{1}{R_b} \frac{d}{S}$$

where  $d$  is the thickness of the cell,  $S$  is the area of the electrode in contact with the electrolyte and  $R_b$  is the bulk resistance of the PGE. See the ESI† for more details. The extrapolated values of  $\sigma$  have been plotted in Fig. 2b as a function of the curing time. A surprisingly outstanding behaviour was revealed: all of the PGEs go through an exponential increment of the ionic conductivity as the cross-linking reaction goes on and the viscous gels turn into a 3D viscoelastic solid element. Ionic conductivity increases of almost one order of magnitude after just 5 hours of thermal curing at 50 °C. GL11\_Q55 highlights a greater enhancement with respect to GL11\_Q65 and GL11\_Q80. Lower QRs imply in fact a more extended portion of cross-linkable macromolecules and thus a larger quantity of  $I^-$  delivered during the curing process. It has also been observed that PGEs of the GL14 series exhibit better ionic conductivities with respect to their homologous of GL11 series: this can be easily put into correlation with their correspondingly lower viscosity as well as

Table 1 Chemical composition, viscosity, ionic conductivity and photovoltaic performances upon completion of the cross-linking process

Gel electrolyte	$I^-$ from quaternarization [M]	$I^-$ from curing [M]	LiI [M]	$I_2$ [M]	Polymer content [% wt/wt]	Ionic conductivity upon cross-linking [ $S \text{ cm}^{-1}$ ]				
						$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$V_{oc}$ [V]	FF	PCE [%]	
GL11_Q55	0.34	0.29	0.27	0.15	40	$6.65 \times 10^{-05}$	13.84	0.63	0.67	5.84
GL11_Q65	0.48	0.25	0.17	0.15	40	$3.71 \times 10^{-05}$	13.06	0.65	0.65	5.51
GL11_Q80	0.77	0.19	—	0.15	40	$2.22 \times 10^{-05}$	12.48	0.66	0.65	5.35

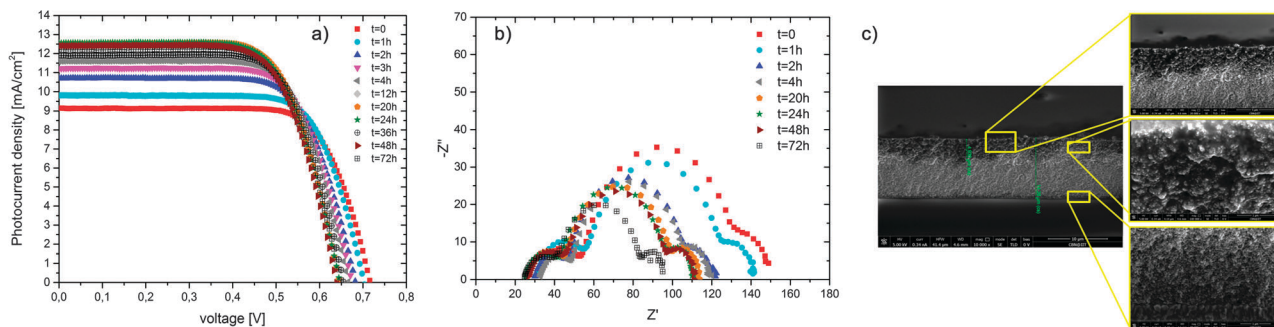


Fig. 3 (a)  $J$ - $V$  curves and (b) EIS spectra @ $V_{oc}$  measured at 25 °C under 1 sun illumination for a dye-sensitized solar cell filled with GL11\_Q80 upon thermal curing at 60 °C. (c) Cross-sectional view of the  $TiO_2$ -mesoporous-electrode/electrolyte interface upon 48 hours of thermal treatment.

to the larger amount of LiI dissolved in the liquid phase. Values of ionic conductivity revealed upon the completion of the thermal curing (72 h at 75 °C) are reported in Table 1. These polysiloxane-based electrolytes have been finally implemented as electron mediators in dye-sensitized solar cells (DSSC) employing an organic sensitizer with high molar extinction coefficient.<sup>9</sup> They have been injected in the form of viscous liquids into the gap between two electrodes and gelation has been made to happen at 60 °C.  $J$ - $V$  and Nyquist plots were then measured at regular intervals after cooling the cells at 25 °C.  $J$ - $V$  curves of the DSSC filled with GL11\_Q80 at different curing times are shown Fig. 3a.

A remarkable enhancement of the current density ( $J_{sc}$ ) was detected as an effect of the thermal treatment:  $J_{sc}$  increased from the initial value of 9.18 mA cm<sup>-2</sup> to 12.48 mA cm<sup>-2</sup> after 48 hours of treatment at 60 °C. This effect can be partially attributed to a more efficient regeneration of the oxidized dye as a consequence of a deeper permeation of the viscous phase into the  $TiO_2$  mesopores. But it cannot be decoupled from the beneficial effects caused by the cross-linking on the ionic conductivity of the solid phase. On the other hand a decrease of the open circuit voltage was detected upon the first 20 hours of curing. Higher iodide concentration (up to 0.19 M) turned into an enhancement of the redox potential of the electrolyte of about 10 mV (as calculated by the Nernst equation). But it can be also ascribed to a reduction of the recombination resistance which has been confirmed from electrochemical impedance spectroscopy analysis. The Nyquist plots reported in Fig. 3b reveal in fact a consistent shrinking of the impedance associated to the second arc (frequency range 1 kHz–10 Hz) in the first 24 hours of curing, which is attested to a reduction of the charge transfer resistance ( $R_{ct}$ ) at the interface  $TiO_2$ /electrolyte. A significant reduction of the diffusion resistance ( $R_{diff}$ ) was even detected from the analysis of the low-frequency arc, which was fitted through a Warburg equivalent circuit element. Plots of the extrapolated values of  $R_{ct}$  and  $R_{diff}$  are shown in the ESI.†

In Fig. 3c we report a cross-sectional view of the  $TiO_2$  mesoporous electrode taken from a disassembled cell upon the completion of the above referred monitoring of the PV performances. The liquid phase intimately fills the micro-/nano-sized pores of the dye-sensitized  $TiO_2$  films thus ensuring excellent pore-filling and thus an adequate regeneration of oxidized dye; the polymeric phase instead does not effectively penetrate the  $TiO_2$  film, it forms a solid-membrane which fills the gap between  $TiO_2$  and Pt where the

remaining portion of liquid comes to be practically retained and gradually penetrates the  $TiO_2$  film up to only a couple of microns.

In summary, a novel class of polymer gel electrolytes has been designed and synthesized, which are classifiable as poly[(3-*N*-methylimidazoliumpropyl)methylsiloxane-*co*-dimethylsiloxane]iodides. They have been partially quaternized with 1-methylimidazole and then subjected to thermal cross-linking which consists of a further quaternization reaction between the residual iodopropyl pendant groups and the terminal aminopropyl groups of a suitable polymeric cross-linker. The amount of unquaternized iodopropyl units is therefore a fundamental parameter which allows the controlling of both the viscoelastic properties and the ionic conductivity of these systems.

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