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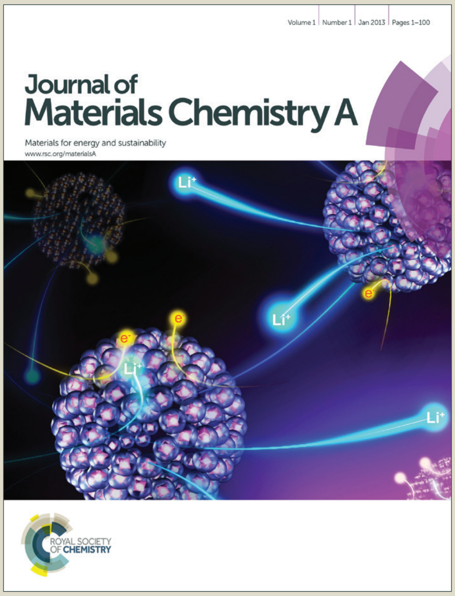

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COMMUNICATION

Single-ion conductor nanocomposite organic-inorganic hybrid membranes for lithium batteries†

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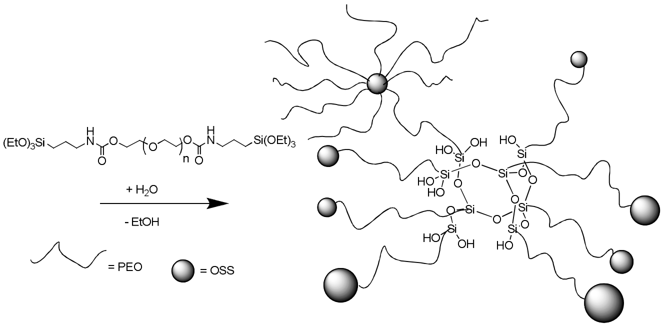
A modified sol-gel synthesis of di-urethanosil resins provides an easy preparation of single-ion conductor membranes, by combining in one pot the in-situ formation of oligosilsesquioxane nanofillers, the cross-linking of PEO chains and the covalent grafting of anion groups. Prototypal membranes demonstrated promising combination of thermal stability, flexibility and lithium ion conductivity performance.

Over the last years, polymer electrolyte membranes (PEM) for lithium batteries have been improved by the design of single-ion polymer conductors (lithium ion transference number $\tau_{Li}^{+} = 1$).[1-6] Actually, low Li^+ transference number electrolytes hinders device performance, as high currents cause anion concentration gradients within the cell, leading to local depletion and therefore high internal resistances that ultimately limit cell lifetime, charging rates, and energy density.[5,6] Different strategies, based on the covalent linkage of anion groups on the polymer network have been proposed to design single-ion conductor PEMs (in which only the lithium cation is mobile), while keeping high mechanical and conducting performances. Some of them focused on single-ion cross-linked comb-branched polymers electrolytes in which anions are fixed to the side chains.[3] Others have been recently proposed, which were based on AB diblock and BAB triblock copolymers, where A is the ionic conductor block and B is the block providing the mechanical strength.[4] Interesting approaches based on nanocomposite membranes were triggered by the use of nanofillers functionalized with covalently linked lithium salt groups.[7] Moreover POSS (polyhedral oligomeric silsesquioxanes) were successfully used in place of silica nanoparticles, as nanofillers and lithium sources.[8]

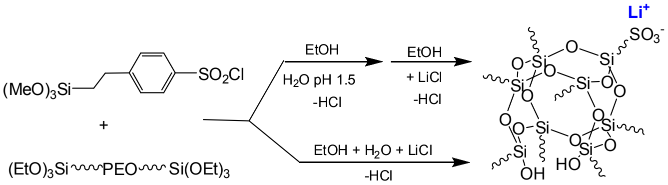
In the present work we propose an original approach combining in one pot the formation of POSS-like nanofillers, the cross-linking of PEO chains and the covalent grafting of anion groups. Indeed sol-gel processing is known to give access to hybrid organic-inorganic nanocomposites in which PEO segments are covalently bonded to *oligosilsesquioxane* (OSS) domains through urethane linkages.[9, 10] Di-urethanosil membranes can be easily prepared from alkoxysilane end-capped PEOs, arising from the reaction of OH-terminated polyethylene glycol and 3-isocyanatopropyltriethoxysilane (Scheme 1).



Scheme 1. Synthesis of di-urethanosil membranes (n ≈ 21)

Ether coordination sites enable the dissociation of lithium salts, while mobile polymer chains assist the transport of Li^+.[11] Nevertheless, in long-chain PEOs the presence of crystalline regions is known to hamper this mobility.[12] Here, the high functionality of the POSS-like nanofiller allows to create a high density of cross-links that makes possible the use of short polymeric chain (1000 g.mol^{-1} average molecular weight) while keeping sufficient mechanical strength. The originality is that lithium sulfonate groups are incorporated during the sol-gel reaction, by means of a precursor bearing a hydrolysable trialkoxysilylated group, so that these salt groups are bonded to the OSS cross-linkers, which further act as lithium cation reservoirs evenly dispersed in the PEO matrix. As far as the counter-ions are covalently bonded to the OSS-domains, the Li^+ transference number is raised to 1 (Scheme 2).

Transparent and flexible membranes were synthesized in one step starting from commercially available 2-(4-chlorosulfonylphenyl)ethyl trimethoxysilane (Scheme 2). The acid needed to catalyze the sol-gel reactions was provided in situ by the HCl molecules released. See electronic supplementary information (ESI) for a typical synthesis.



Scheme 2. Two-step (top) and one step (down) syntheses of SO_3Li-modified di-urethanosil membranes

For a better understanding of the process, a two-step synthesis was also carried out (Scheme 2). The first-step led to SO_3H-containing membranes (hydrolysis of chlorosulfonyl groups into sulfonic acid ones is spontaneous in the presence of water molecules), while the subsequent metathesis reaction with LiCl (second step) led to SO_3Li-containing membranes. In both processes, the complete lithiation was confirmed by acid-base titrations (see ESI). All the membranes were further submitted to a prolonged Soxhlet extraction to eliminate all residual species able to migrate. Both extraction yields and condensation ratios from ^{29}Si MAS NMR (see below) were shown to be rather similar whatever the synthesis way. Thereafter the membrane samples will be labelled as **EO/Li-X**, where X is the molar ratio EO/Li (number of ethylene oxide units per Li^+ cation).

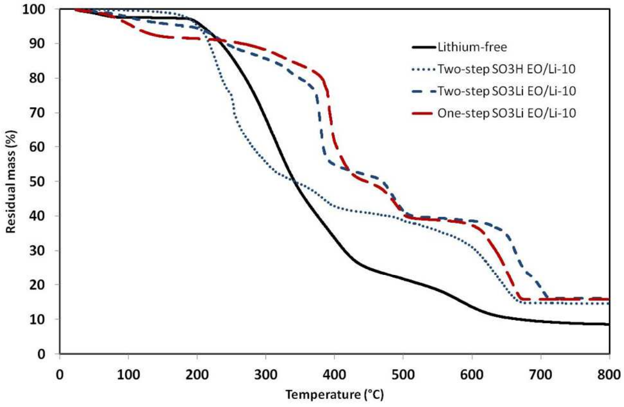


Figure 1 TGA traces of **Li-free** (solid line), two step synthesized **EO/Li-10** (before and after lithium exchange) and one-step synthesized **EO/Li-10**

The thermal stability of all membranes was studied by thermogravimetric analysis (TGA) going from room temperature to 800 °C under air. Figure 1 compares the thermolysis of the pristine urethanosil membrane (**Li-free)**, a modified membrane before (step 1) and after lithium exchange (step 2), respectively, and a one-step synthesized membrane with the same EO/Li ratio of 10. After a weight loss corresponding to removal of residual humidity at about 100 °C, the inception of the thermal decomposition is detected from about 200 °C until the complete oxidation into silica at about 700 °C. For one-step or two-step synthesized membranes, the degradation of **EO/Li-10** samples were delayed by comparison to the non lithiated (SO_3H-modified) membrane.

Table 1 summarizes the data relative to the different membranes. Based on solid-state ^{29}Si MAS NMR, condensation ratios (see ESI) were found to be higher in the modified (sulfonyl-containing) membranes as compared to the pristine urethanosil matrix (**Li-free**), with a significant increase (Figure 2) of T^3 substructures (3 siloxane bonds per silicon atom; near -66 ppm) with respect to T^2 and T^1 ones (2 and 1 siloxane bonds per silicon atom; near -58 and -49 ppm, respectively). This suggests extensive condensation reactions of the sulfonyl-containing silicon precursor onto the OSS nanodomains (Schemes 1 and 2). However the broadness of signals reflects a wide range of Si-O-Si environments in OSS nanodomains and disclosed that the OSS structure discards significantly from symmetrical POSS. Actually, the OSS nanodomains are far from being quasi perfect polyhedra as in the oversimplified depiction of the graphical abstract. They should be regarded as more or less condensed clusters, with random structure, rather than cage-like or ladder-like oligomers.[13]

Table 1. Young Modulus E from DMA, T_g from DSC, condensation ratio from ^{29}Si MAS NMR, ionic conductivities σ and σ_{PC} of solvent-free and PC-swelled membranes, respectively, at 60 °C from impedance spectrometry.

sample	Young Modulus E / MPa	T_g / °C	Condensation Ratio/ %	$\sigma_{60°C}$ /S.cm^{-1}	$\sigma_{PC60°C}$ /S.cm^{-1}
Li-free	6.3	-50	72	-	-
EO/Li-30	2.7	-45	85	$4.9.10^{-8}$	$7.9.10^{-7}$
EO/Li-20	6	-34	90	$4.6.10^{-8}$	$1.4.10^{-6}$
EO/Li-10	6.6	-18	90	$3.5.10^{-8}$	$2.8.10^{-6}$

It is worth noting the low amounts (~8%) of extract after exhaustive Soxhlet extraction with ethanol, which is consistent with the high condensation rates revealed by solid-state ^{29}Si MAS NMR. As a consequence the EO/Li value was not significantly modified by the extraction treatment.[14]

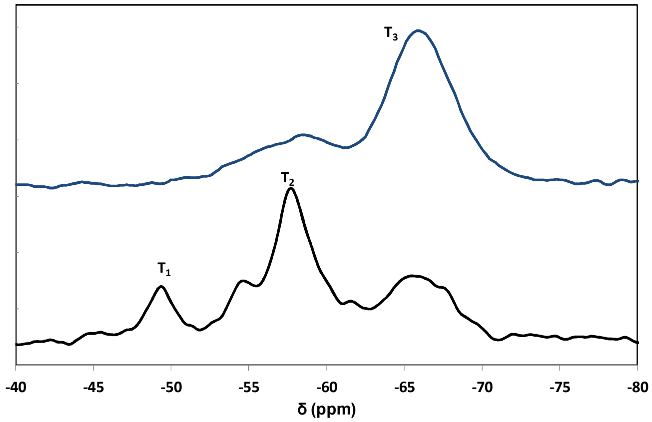


Figure 2 Single-pulse ^{29}Si MAS NMR spectra of **Li-free** (bottom) and **EO/Li-10** (top) membranes

The thermo-mechanical response of the membranes was evaluated through Dynamic Mechanical Analysis (DMA) (Figure 3). It is observed a Giga-Pascal modulus in the vitreous state, common of polymeric materials, a sharp decrease of the modulus in the range 230-270 K, which corresponds to the glassy-to-rubbery transition, and a rubbery plateau, which depends on the network cross-links density. The shift to higher temperature of the main mechanical relaxation with an increase of the salt content confirms its effective incorporation and is due to bonding interaction between PEO ether and Li cation, which decreases the mobility.[12,15] This was also confirmed by differential scanning calorimetry (DSC) measurements, which showed an analogous trends when the ratio EO/Li decreased (Table 1).

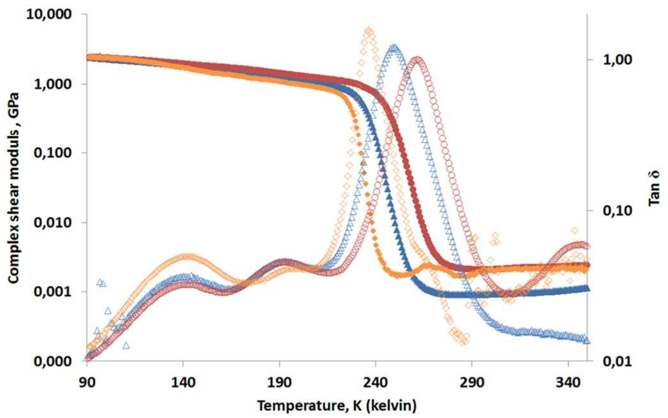


Figure 3: Complex shear modulus (filled symbols) and tan δ (open symbols) as a function of temperature for the **Li-free** membrane (♦), **EO/Li-30** (▲) and **EO/Li-10** (●) samples.

Regarding to the rubbery modulus (Table 1), it is first observed a decrease between Li-free membrane and **EO/Li-30**, which reflects the effect of the sulfonate-functionalized silicon precursor, which competes with the end-chain silicon groups in the sol-gel condensation process, lowering the cross-links density. However the Young modulus increased as the EO/Li ratio decreased from 30 to 10, because of the bonding interaction between Li cation and the PEO which counterbalances the loss of PEO-OSS linkage [16]

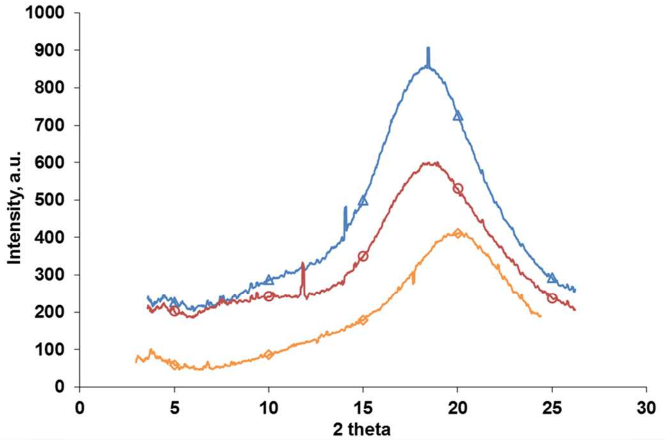


Figure 4: WAXS spectra for the **Li-free** membrane (♦), **EO/Li-30** (▲) and **EO/Li-10** (●) samples.

The 'anti-plasticization' effect observed both with DMA and DSC and attributed to a inter and intramolecular coordination of ether oxygen atoms with the lithium cation is confirmed by Wide Angle X-ray Scattering (WAXS) where a modification of the interchains distance in PEO chains is observed when lithium is added (Figure 4).[17] Note that both DMA and DSC showed that the membranes are completely amorphous.[18] This is in agreement with the high crosslinks density reached.

The stability of membranes against Li metal was checked by repeating several conductivity measurements every 30 minutes with Li/membrane/Li configuration. However the conductivity values were found to have the same order of magnitude with simple steel/membrane/steel configuration. Accordingly, thereafter the study was carried out with the latter configuration.

Figure 5 shows the temperature dependence of the ionic conductivity σ for different EO/Li ratio. It is observed an increase of σ in a monotonically fashion over the entire temperature range investigated. Actually, it would be expected that σ significantly increases when the EO/Li molar ratio decreases from 30 to 10 (open symbol). Actually it is not the case. This can be explained by the above discussed increase in T_g. Note that the contribution of protons to the overall ionic conductivity could be estimated by measuring the conductivity of a lithium-free membrane. This contribution was found to be very low, though the relative amount of silanol groups, based on Si^{29} NMR spectra, was much higher in the Li-free sample as compared to **EO/Li-10** sample (Figure 2).

Swelling single ions membrane is a common way to increase the ionic conductivity.[19] All the membranes were swelled by dipping in propylene carbonate (PC) for 24 hrs. All of them remained free-standing. Solvent uptake for **EO/Li-30**, **EO/Li-20** and **EO/Li-10** were 112, 40 and 33% wt, respectively. However the ionic conductivity of swelled membranes showed a remarkable improvement by one to two orders of magnitudes (filled symbols). This illustrates the powerful plasticizing effect of PC, which spaces the PEO chains apart. Moreover, PC can solvate lithium cations, which results in an increase of the effective charge carrier number. For the two sets of samples the maximum ionic conductivity was obtained for **EO/Li-10**: typically, at 60 °C σ was 3.5 10^{-7} S.cm^{-1} for the solvent-free sample and 2.8 10^{-6} S.cm^{-1} for the swelled one.

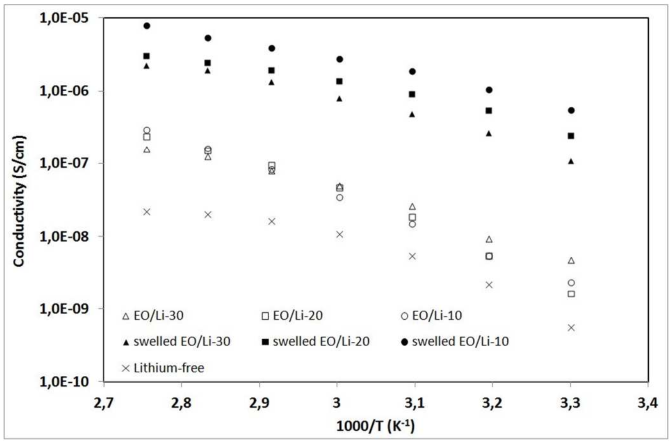


Figure 5 Temperature dependence of ionic conductivity σ for **EO/Li-30**, **EO/Li-20**, **EO/Li-10** samples, before and after swelling with PC (open and filled symbols, respectively). The ionic conductivity of a Li-free and PC-free membrane is given for comparison (crosses).

The curved profile of conductivity plots suggests that the data can be interpreted by the VTF equation. Actually, the best fitting parameters from the VTF equation were found to be consistent with the literature[19,20] (see ESI).

Both the polymer architecture and the ion dissociation are known to influence the ionic conductivity in Li-based PEMs.

Here, phenylsulfonate anion is far from enabling high dissociation levels as anions with extensive charge delocalization as perfluorosulfonimide anions,[4] which gives an explanation for the moderate conductivity observed. However, the proof of concept being given, the performances of the prototypal membranes should be improved in the near future by using more dissociated lithium salt precursors.

Conclusions

A straightforward sol-gel process gives access to flexible hybrid membranes comprising PEO chains and OSS nano-domains functionalized with lithium sulfonate groups. These OSS nano-domains, covalently bonded both to the polymer chains and the lithium sulfonate groups, act as crosslinkers, nanofillers and lithium sources. This nanocomposite character both contributes to the mechanical strength and provides Li^+ charge carriers, while suppressing the contribution of anions to the ionic conduction. The uniform cross-linking at the ends of the PEO chains permits to extensively swell the membranes with PC without a drastic loss of mechanical property. By varying some synthesis parameters, as using more dissociated lithium salt precursors, the approach can be adapted to tune the transport and mechanical properties of electrolyte membranes.

Notes and references

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Electronic Supplementary Information (ESI) available: Materials, syntheses and methods; details on ionic conductivity measurements. See DOI: 10.1039/c000000x/

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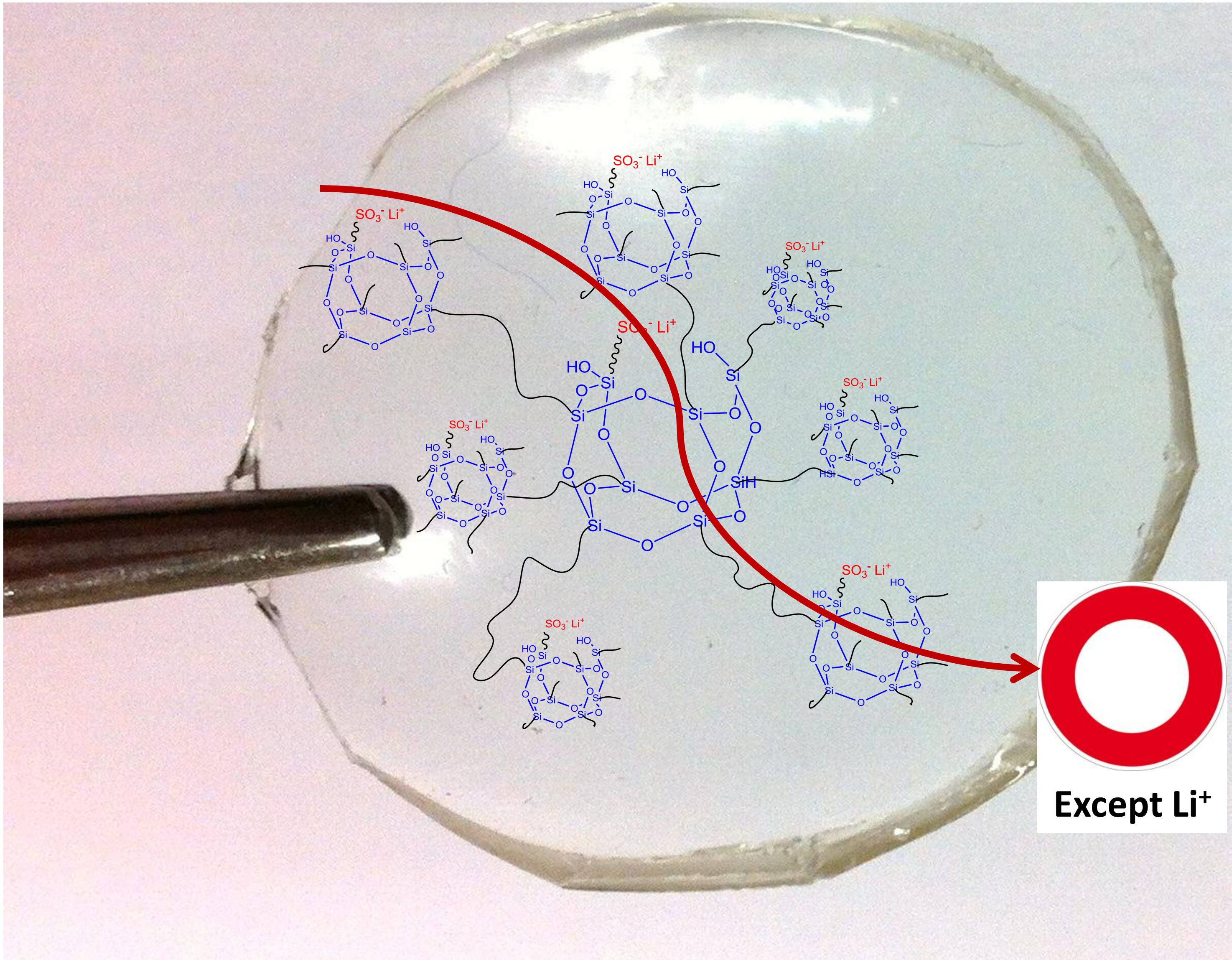
Graphical abstract



A straightforward and versatile sol-gel process for the design and preparation of single-ion conductor flexible membranes