Supporting Information:

# Cation only Conduction in New Polymer/$SiO_2$ Nano Hybrids: $Na^+$ Electrolytes

Irune Villaluenga,[a,b,c] Xavier Bogle,[d] Steve Greenbaum,[d] Izaskun Gil de Muro,[a] Teófilo Rojo[a,b] and Michel Armand[*b]

[a]CIC ENERGIGUNE, Albert Einstein 48, Miñano, Spain.
[b]Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU, Bilbao 48080, Spain.
[c]Current address: Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA and Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA.
[d]Department of Physics & Astronomy, Hunter College of the City University of New York, New York, NY 10065, USA.
E-mail: marmand@cicenergigune.com
Telephone: (+34) 945 297 108
Fax: (+34) 944 035 699

## General Information:

Methylene dichloride and triethylamine were transferred *via* needle and syringe under inert atmosphere (argon). Chemical shifts are given in δ-scale as parts per million (ppm). $^{13}C$ and $^{19}F$ NMR spectra were measured on a Bruker Avance II 300 NMR spectrometer and a Bruker Avance III 400 (with CP-MAS) NMR spectrometer. The organic content was measured by analysis thermogravimetric (Netzsch STA 449C Instrument) under argon at a linear heating rate of 10ºC/min from 25 ºC to 800 ºC. The size of hybrid nanoparticles was evaluated by transmission electronic microscopy (TEM Philips CM200) and light scattering (Malvern Zetasizer 4 spectrometer). Finally, the $^{23}Na$ Linewidth data was performed using a Chemagnetics static broadband probe with 1M NaCl in water as a reference set to 0 ppm. A single pulse sequence used with a π/4 pulse width of 2 μs (this maximizes the signal for a second-order quadrupole broadened spin-3/2 nucleus). The delay time was 0.5 second and 10000 scans were averaged. For the $^{19}F$ measurements a standard pulsed field gradient spin-echo sequence with rf pulse and gradient pulse spacing of 10 ms, gradient duration of 5 ms, and gradient strength of 1000G/cm.

## Synthesis of nanoparticules grafted with the anion of sodium 2-[(Trifluoromethane-sulfonylimido)-N-4-sulfonylphenyl]-ethyl trimethoxysilane ($SiO_2$-anion).

2-(4-Chlorosulfonylphenyl) ethyltrimethoxysilane (organosilane 1, 2 g, Fluorochem®) was added under argon to a solution of trifluoromethanesulfonamide (1 g) and triethylamine (3.38 g, Aldrich) into 30 mL of methylene dichloride. The reaction mixture was stirred and heated at 40ºC overnight. An orange-brown-colored wax (organosilane 2) was obtained after distillation of the solvent[1]. On the other hand, an alkaline stabilized dispersion of commercial silica nanoparticles (LUDOX SM-30, Aldrich) was diluted to 4 wt% particle fraction by addition of aqueous sodium hydroxide solution to pH ~11. Triethylammonium 2-[(Trifluoromethane-sulfonylimido)-N-4-sulfonylphenyl]ethyl trimethoxysilane (organosilane 2) at a ratio of 1.5 g per 1.0 g commercial $SiO_2$ nanoparticles was added dropwise at 100ºC. Following the reaction solution was heated for 12 hours at 100ºC. After 24 hours, an excess of $Na_2CO_3$ in hot water was added to grafted $SiO_2$ nanoparticles to remove the triethylamine. After

removing the water, the product was dialyzed with a cellulose acetate (supplier, Aldrich) for several days in water to remove any remaining free organosilane. Finally, MP-TsOH (macroporous polystyrene sulfonic acid) columns (Symta) were used to remove any remaining triethylamine of dialyzed $SiO_2$ nanoparticles. $SiO_2$ nanoparticles functionalized with Na salt ($SiO_2$-anion) were obtained after distillation of the solvent. $^{13}C$ NMR (solid state): δ 14.03, 28.94, 127.44, 141.26, 145.77. $^{19}F$ NMR: δ -78.35 ppm(s).

**Synthesis of nanoparticules grafted with PEG and the anion of sodium 2-[(Trifluoromethane-sulfonylimido)-N-4-sulfonylphenyl]-ethyl trimethoxysilane ($SiO_2$-PEG-anion).**

First, organosilane 2 was synthesized by experimental conditions explained above[1]. Second, an alkaline stabilized dispersion of silica nanoparticles was diluted to 4 wt% particle fraction by addition of aqueous sodium hydroxide solution to pH ~11. [Methoxy(polyethyleneoxy)propyl] trimethoxysilane (0.75 g, Mw ~ 470, Specific Polymers®) and triethylammonium 2-[(Trifluoromethane-sulfonylimido)-N-4-sulfonylphenyl]ethyl-trimethoxysilane (0.75 g, organosilane 3) were added to 1.0 g commercial $SiO_2$ nanoparticles dropwise at 100ºC. Following the reaction solution was heated for 12 hours at 100ºC. After 24 hours, an excess of $Na_2CO_3$ in hot water was added to $SiO_2$ nanoparticles functionalized to remove the triethylamine. After removing the water, the product was dialyzed for several days in water to remove any remaining free organosilane. Finally, $SiO_2$ nanoparticles functionalized with polymer and anion were obtained after distillation of the solvent. $^{13}C$ NMR (solid state): δ 7.18, 12.57, 20.78, 26.67, 56.59, 67.75, 124.38, 125.63, 140.40, 144.34. $^{19}F$ NMR: δ -78.25 ppm(s).

**Synthesis of new polymer/$SiO_2$ nanohybrid electrolytes.**

A dispersion of $SiO_2$ nanoparticles functionalized with the anion of Na salt and/or PEG was prepared in methanol and water. The dispersion of grafted $SiO_2$ nanoparticles was added to a mixture of polyethylene glycol dimethyl ether (PEGDME, 0.050g, $M_w$ ~ 250) and polyethylene oxide (PEO, 0.050g, $M_w$ ~ $5x10^6$) at ratio 1:1 in weight. After mixing, samples were dried in the convection oven at 80ºC overnight and for at least 24 hours under vacuum.

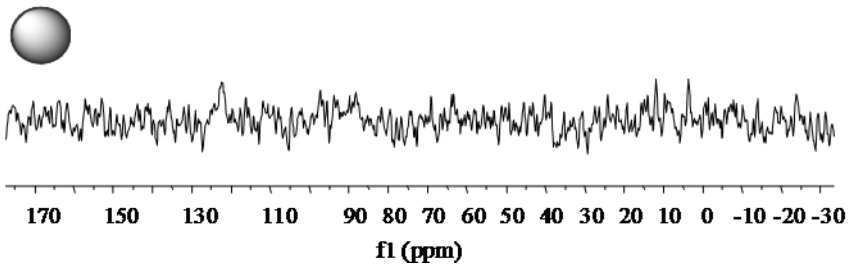
| Polymer electrolytes | PEO/PEGDME (w/w) | EO/Na |
|---|---|---|
| EP-$SiO_2$-anion (EO/Na ~ 40) | 1 : 1 | 40 |
| EP-$SiO_2$-anion (EO/Na ~ 20) | | 20 |
| EP-$SiO_2$-anion (EO/Na ~ 10) | | 10 |
| EP-$SiO_2$-anion (EO/Na ~ 6.5) | | 6.5 |
| EP-$SiO_2$-PEG-anion (EO/Na ~ 40) | 1 : 1 | 40 |
| EP-$SiO_2$-PEG-anion (EO/Na ~ 20) | | 20 |
| EP-$SiO_2$-PEG-anion (EO/Na ~ 10) | | 10 |
| EP-$SiO_2$-PEG-anion (EO/Na ~ 6.5) | | 6.5 |

**Table S1.** Composition of the polymer electrolytes.

**Electrochemical measurements.**

The ionic conductivity measurements of the polymer electrolytes were carried out by AC impedance spectroscopic technique using a Solartron 1260 over the frequency range from 1Hz to 1MHz with a signal level of 10 mV. The conductivity measurements of polymer electrolytes were carried out by sandwiching the samples between two stainless–steel (SS) electrodes. The temperature dependence of the ionic conductivity was performed in a temperature range from 25 to 80 °C. The electrochemical window of the polymer electrolytes was evaluated at 1mV/s scan rate and room temperature by cyclic voltammetry. For these measurements, the polymer electrolytes were sandwiched between two stainless–steel (SS) electrodes in a Swagelock® cell.

**a**

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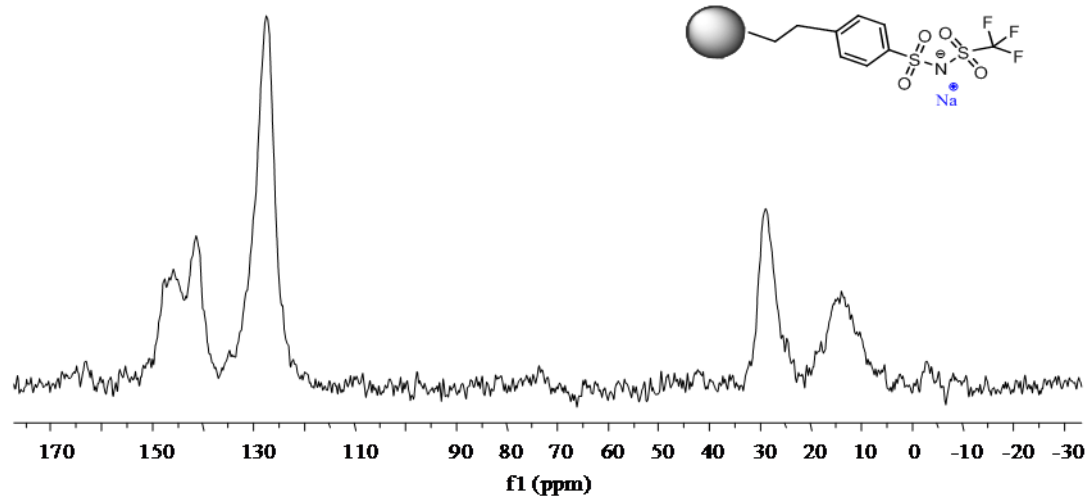


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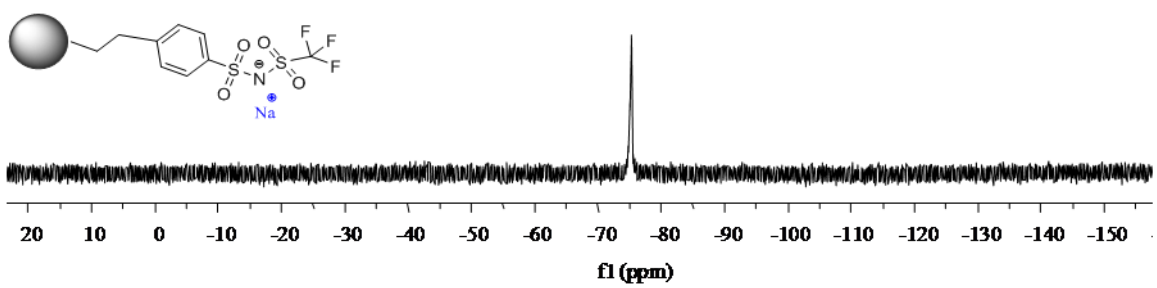

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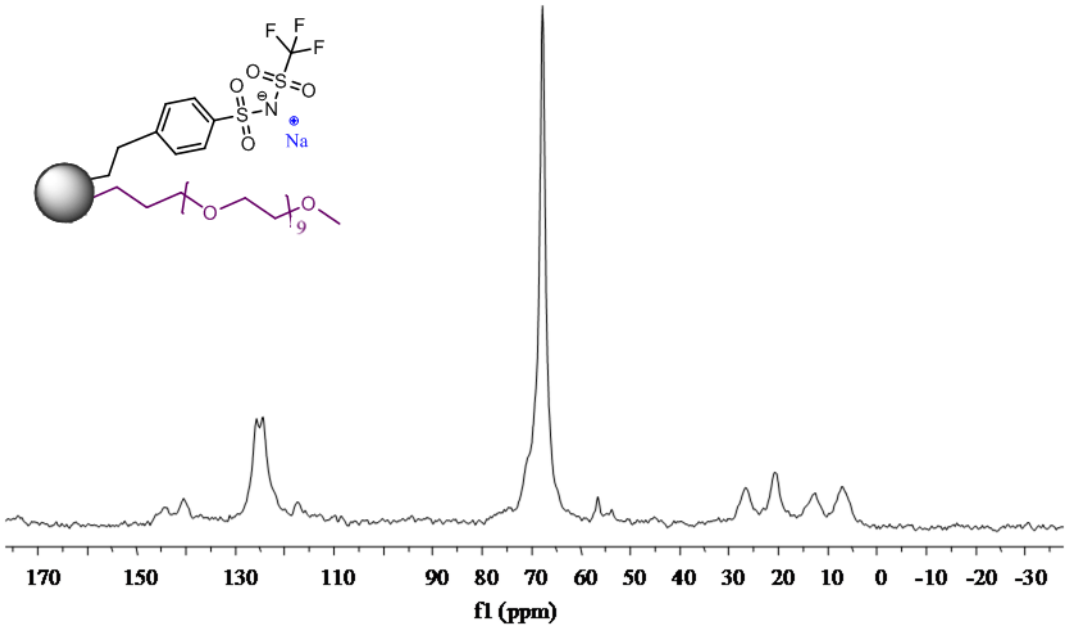


**e**

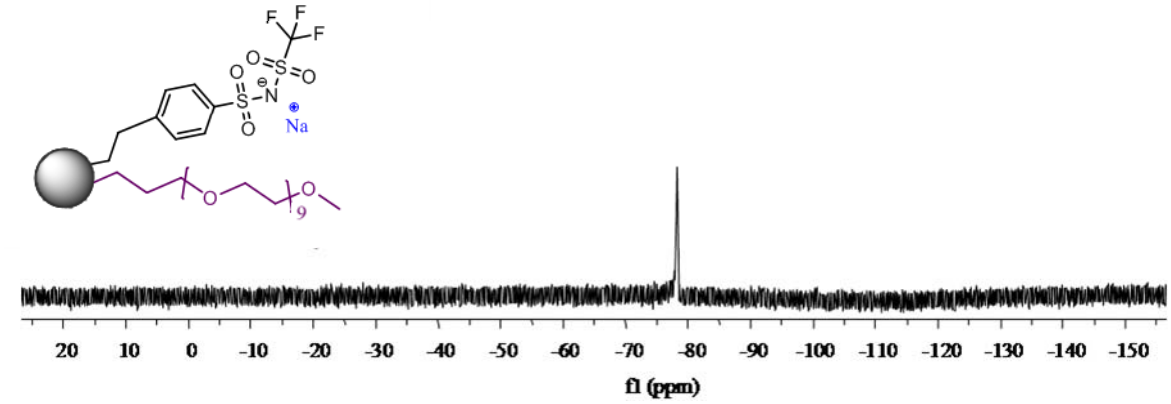


**Fig. S1.** $^{13}C$ NMR and $^{19}F$ NMR spectra of all $SiO_2$ nanoparticles. a) $^{13}C$ NMR Spectra for commercial $SiO_2$ nanoparticles. b) $^{13}C$ NMR Spectra for $SiO_2$-anion nanoparticles. c) $^{19}F$ NMR Spectra for $SiO_2$-anion nanoparticles. d) $^{13}C$ NMR Spectra for $SiO_2$-PEG-anion nanoparticles. e) $^{19}F$ NMR Spectra for $SiO_2$-PEG-anion nanoparticles.

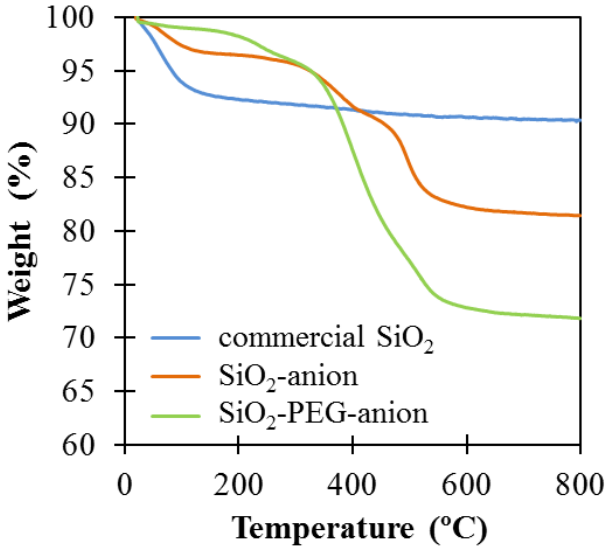


**Fig. S2.** TGAs of all $SiO_2$ nanoparticles.

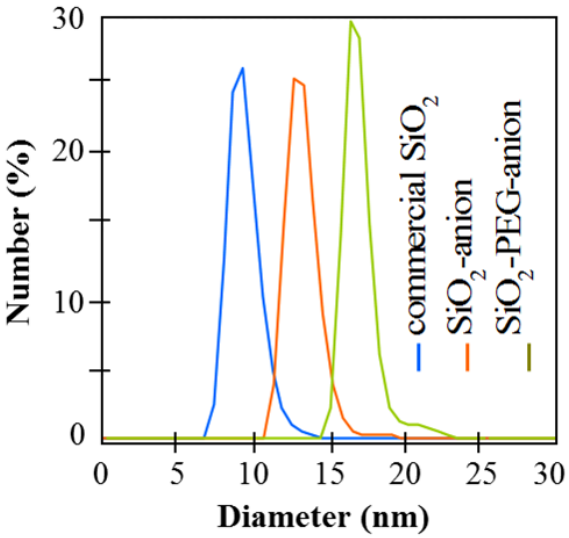


**Fig. S3.** DLS measurements of commercial $SiO_2$ nanoparticles, $SiO_2$-anion and $SiO_2$-PEG-anion.

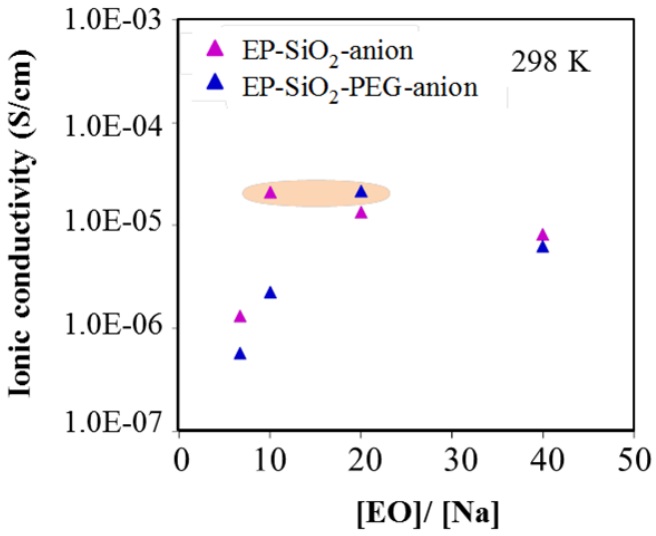


**Fig. S4.** Ionic conductivities of EP-$SiO_2$-anion and EP-$SiO_2$-PEG-anion electrolytes at room temperature, which has the highest Na concentration of the series were studied in this research.

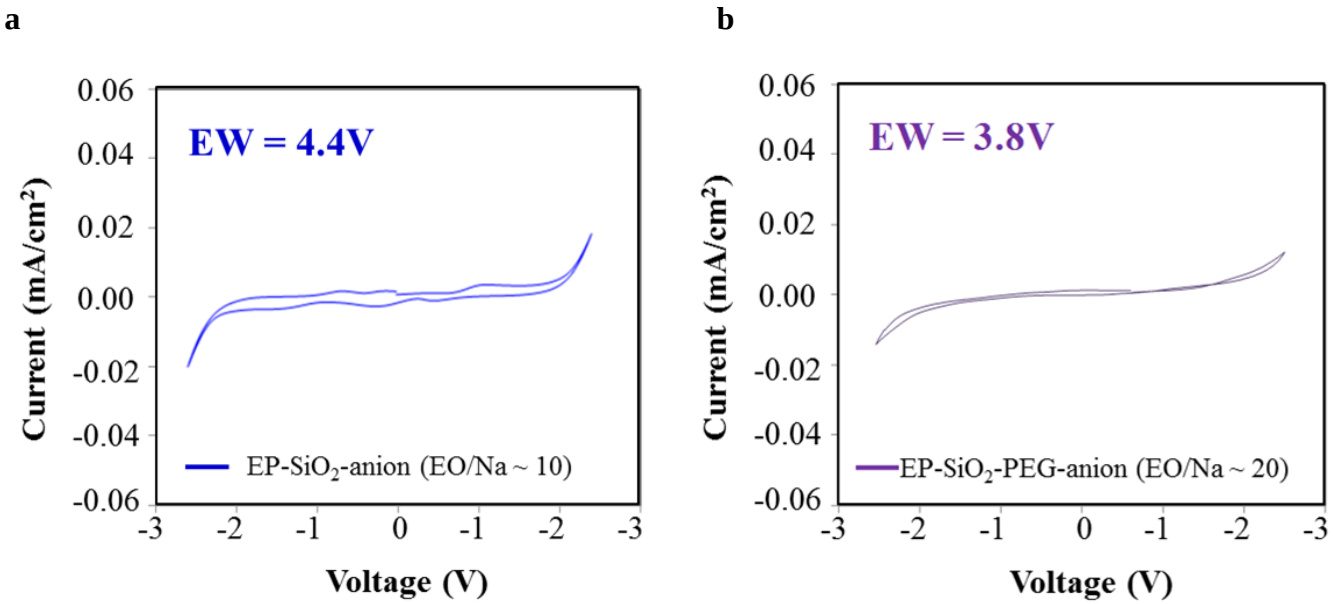


**Fig. S5.** The electrochemical windows of the two polymer electrolytes, a) EP-$SiO_2$-anion (EO/Na ~ 10) and b) EP-$SiO_2$-PEG-anion (EO/Na ~ 20), with highest ionic conductivity.

Reference:

1 A. El Kadib, P. Hesemann, K.Molvinger, J. Brandner, C. Biolley, P.Gaveau, J.J.E. Moreau, D. Brunel, *J. Am. Chem. Soc.*, 2009, **131**, 2882.