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Abstract: We compare hybrid organic-inorganic polymers, based on sulfonated poly-aryl-ether-ketones (S-PEEK) and different sulfonated and silylated molecules and macromolecules. The synthesis of the membranes and their water uptake and electrical conductivity at 25°C are reported. A decent linear relation between the electrical conductivity and water uptake coefficient is obtained. Other correlations with the chemical composition of the membranes (especially, SO3, Si and OH content) are discussed and directions for future work are outlined.

Cover Letter

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Dear Editor

Attached please find a manuscript submitted at the occasion of the SSI-16 conference.

Title: **Design of organic-inorganic hybrid membranes based on sulfonated polyaryl-ether-ketones: correlation between water uptake and electrical conductivity.**

The authors are: M. L. Di Vona , S. Licoccia, P. Knauth.

In this work, we compare water uptake and conductivity data in large number of hybrid materials in the S-PEEK family and conclusions concerning the membrane usability in PEM fuel cells.

Sincerely

P. Knauth

Design of organic-inorganic hybrid membranes based on sulfonated polyaryl-ether-ketones: correlation between water uptake and electrical conductivity.

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Abstract

We compare hybrid organic-inorganic polymers, based on sulfonated poly-aryl-ether-ketones (S-PEEK) and different sulfonated and silylated molecules and macromolecules. The synthesis of the membranes and their water uptake and electrical conductivity at 25°C are reported. A decent linear relation between the electrical conductivity and water uptake coefficient is obtained. Other correlations with the chemical composition of the membranes (especially, SO_3, Si and OH content) are discussed and directions for future work are outlined.

Keywords: proton conductor, ionomer, PEM fuel cell, S-PEEK

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1. Introduction

Today, more than 80 per cent of the world energy consumption stems from fossile fuels (oil, gas, coal). This overuse can not be sustained given the limited resources and also the amount of greenhouse gases produced. Renewable energies or energy conversion technologies with higher efficiency and less pollutant and greenhouse gas emission must be developed. Polymer electrolyte membrane fuel cells (PEMFC) are nowadays a credible technology for environmentally friendly energy conversion, in electric vehicles and portable applications, with hydrogen or methanol (so-called Direct Methanol Fuel Cells) as fuel [1].

The polymer membrane should simultaneously maintain a large proton conductivity (typically 0.1 S/cm at 90°C), have sufficient chemical, thermal and mechanical stability, low permeability to reactants, low cost and ready availability [2]. A future objective of fuel cell vehicle development is an increase of the operation temperature to around 120°C, which presents several advantages: i) the electrode kinetics are faster, enabling a smaller fuel cell stack for identical power, ii) the cooling system can be simplified with a smaller radiator area, iii) the CO tolerance is enhanced significantly, because the kinetics of CO desorption on Pt is much improved, reducing anode catalyst poisoning [3, 4]. However, there are important technological barriers to be overcome in terms of thermal stability of the polymer membrane. Today, Nafion is mainly used as membrane material: it shows a dramatic decrease of conductivity above 80°C. There is still debate about the origin of this effect, which has been attributed to loss of water or change of polymer morphology. [5,6] Anyway, new generation polymer electrolytes should be operated at intermediate temperatures ($T \geq 120°C$) and at low levels of relative humidity for less expensive fuel cell operation ($RH \leq 25\%$, no need for pressurization of the system).

Strategies explored for ionomer membrane improvement are i) addition of inorganic fillers (e.g. SiO_2, ZrO_2, TiO_2), leading however often to porosity problems, ii) acidic additives (e.g. heteropolyacids), however often leached out during fuel cell operation, iii) organic-inorganic hybrid polymers, or iv) polymer blends. [7,8] Hybrid materials combine inorganic and organic components

at a molecular level: “Class II” hybrids present covalent bonds between the organic and inorganic parts. [9] So-called Organic-Inorganic Polymers (OIP) have carbon atoms forming the main network and inorganic groups in the side chains. Polymer blends are materials with two insoluble polymer components held together by only Van der Waals forces. If the polymer domains are of nanometric size, such a blend can be considered a nanocomposite. This definition is equivalent to that of “Class I” hybrid materials. The fabrication of composites adds a supplementary degree of freedom to the development of fuel cell membranes.

Chemically modified fully aromatic thermoplastic polymers, such as PolyEtherEtherKetone (PEEK) and PolyPhenylSulfone (PPSU), receive considerable attention, because they seem to meet the operating requirements for fuel cell application, such as i) very high thermal stability, ii) oxidation resistance, iii) mechanical strength, iv) easy functionalization. [10] However, a high degree of sulfonation is necessary for sufficiently high proton conductivity, leading to poor mechanical properties and lower morphological stability (high swelling) of the polymers, which become progressively water soluble. Compared to Nafion, sulfonated PEEK exhibits different morphological properties essentially related to i) less acidic sulfonic acid groups (pK = -1), ii) a less hydrophobic nature of the aromatic backbone, iii) wider separation between $-SO_3H$ groups, iv) less separated hydrophilic and hydrophobic domains, v) narrower and highly branched water channels with some pockets and dead ends. [5]

Hybrid systems represent a promising class of materials which allow in principle to control and obtain the appropriate ratio between hydrophilic and hydrophobic domains in order to have at the same time sufficient proton conductivity, mechanical strength and morphological stability. Expected improvements of membrane properties by inorganic groups include: i) higher thermodynamic stability, ii) stabilization of morphology, iii) better mechanical properties and iv) optimized water uptake.

We present in the following different hybrid organic-inorganic materials, explored in the last years, based on sulfonated PEEK and various silicon-containing molecules or macromolecules. The

concentrations of sulfonate groups in the hybrid materials are comparable (DS= (0.88 ± 0.05)), but they contain various amounts of phenyl- and hydroxyl groups, permitting to vary their hydrophobic/hydrophilic character and check the influence on water uptake and electrical conductivity. This review includes: i) composites of sulfonated PEEK (S-PEEK) with sulfonated Diphenyl-silanediol (S-DPSDO), ii) composites of S-PEEK with differently modified PPSU (SiS-PPSU), iii) silylated and sulfonated PEEK (SiS-PEEK and SOSi-PEEK). The SOSi-PEEK polymer contains a certain amount of cross-links between the polymer chains. We will discuss in the following proton conductivity and water uptake in this membrane family and correlations between them and with membrane composition. High proton conductivity is one major requirement for fuel cell membranes, but water uptake is an essential parameter for good operation, in relation to morphological stability and mechanical properties of the membrane.

2. Experimental

The chemical formulas of the different hybrid materials are shown in Table 1.

2.1. Materials Synthesis

Sulfonated PEEK (S-PEEK) was prepared by reaction of PEEK with concentrated sulfuric acid at 50°C for 5 days. [11] The solution was poured in a large excess of ice-cold water, under continuous stirring, obtaining a white precipitate. After standing overnight, the precipitate was filtered and washed several times with cold water to neutral pH. The sulfonated polymer (S-PEEK) was then dried under vacuum for 4-6 h at room temperature. The degree of sulfonation (DS) was evaluated both by ^{1}H NMR and by titration, according to published procedures. Both methods gave according results: DS = 0.9.

Sulfonated Diphenylsilanediol (S-DPSD, DS = 1.0) was obtained by reaction of DPSD with chlorosulfonic acid after dissolution in anhydrous $CHCl_3$, which was then heated to 40°C for 4 h. The solvent was vacuum evaporated and the solid residue was treated with absolute ethanol and

with a saturated solution of $NaHCO_3$. After standing at RT for 12 h, the solid was separated by filtration, washed with water, then with 5 M HCl and dried in vacuum for 4 h. [12]

Silylated and sulfonated PEEK (SiS-PEEK) was prepared under nitrogen by dissolving S-PEEK in a DMSO/THF mixture. [11] The resulting solution was cooled to –60 °C, then an excess of BuLi and N,N,N',N'-tetramethylethylenediamine (TMEDA) was added and the solution was stirred for 8 h at –60°C. $SiCl_4$ was then added and the solution was slowly warmed to room temperature, then kept at reflux overnight. After cooling to room temperature, the precipitate formed was left to settle overnight, then filtered and washed with cold water until no chlorides where present. The product (SiS-PEEK) was dried under vacuum for 4 h. The elementary analysis gave %Si = (1.3 ± 0.1) (reproducible over three samples).

For synthesis of SOSi-PEEK [13, 14], the commercial PEEK polymer was dissolved in chlorosulfonic acid at 50°C. This leads to a chlorosulfonated and cross-linked polymer, called SO-PEEK, soluble in organic solvents such as tetrahydrofurane (THF), where it can then react with butyl-lithium and $SiCl_4$ (see above) to the final sulfonated and silylated PEEK (SOSi-PEEK). The molecular structure of SOSi-PEEK has been characterized by combination of different spectroscopies (NMR, IR, MS). The Degree of Sulfonation of the material (DS = 0.8) and its Degree of Cross-Linking (DCL = 0.2) were determined by NMR spectroscopy.

The synthesis of SiS-PPSU was made in two steps: i) metallation reaction with butyl-lithium followed by electrophilic substitution by phenyl-trichlorosilane, ii) hydrolysis and reaction with concentrated sulfuric acid. [15] First, the original polymer PPSU was added, in N_2 atmosphere, to anhydrous THF. The solution was stirred at room temperature for 1 h, then cooled to -60 °C. After 1.5 h, an excess of BuLi and TMEDA were added and the solution was stirred for 2 h at –60°C. Differently substituted silanes were added at that point depending on the type of polymer to be prepared.

For Si-PPSU-Ph, $PhSiCl_3$ (97%) was added and the solution was slowly warmed to room temperature, then kept at reflux for 2h. After cooling to RT, the precipitate formed was filtered and

washed with water until no chlorides where detected. For sulfonation, the product (Si-PPSU) was added to concentrated H_2SO_4 and the mixture was kept stirring at 50 °C for 5 h, then it was poured in ice-cold water. Elemental analysis gave a very high DS = 2. The precipitate was filtered, washed with water to neutral pH and dried under vacuum for 5 h. For Si-PPSU-OH, $SiCl_4$ was added and the solution was slowly warmed to room temperature, then kept at reflux for 2h. The remaining procedure was similar to the above.

The procedure for membrane preparation was solution casting using solvents with a high boiling point: dimethylsulfoxid (DMSO) or dimethylacetamid (DMA). In a typical experiment, around 250 mg of sample was dissolved in 30 mL of solvent. The resulting mixture was stirred for 4 h, evaporated to 5 mL, cast onto a Petri dish and heated to dryness. After cooling to room temperature, the resulting membranes were peeled off and dried at 120°C overnight, then further dried under vacuum at 80°C for 4 h for complete solvent removal.

2.2. Materials Analysis

The number of water molecules per sulfonic acid group is calculated after 1 h full immersion in water. Excess water was then removed with absorbing paper and the mass change was measured by double weighing before and after equilibration.

Electrical conductivity was measured by impedance spectroscopy (Solartron 1260) at 25° C in air under RH = 100%. The membranes were clamped between two platinum electrodes with a permanent pressure. The amplitude of the applied voltage signal was 100 mV in the frequency range 10 MHz–10 Hz. The resistance *R* was derived from the high frequency intercept with the real axis on a complex plane impedance plot, using the Zview® software. The conductivity σ of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = \frac{d}{RS}$, where *d* and *S* are the thickness and area of the sample, determined before and after the measurements.

3. Results

Figure 1 shows typical water uptake kinetics of different hybrid membranes at 25°C. The values of "water uptake coefficient" λ after 1 h of immersion in water, reported in Table 1, are obtained using the equation:

$$\lambda = \frac{(m_{wet} - m_{dry})}{m_{dry}} \frac{IEC}{M(H_2O)} \quad (1)$$

Here, *IEC* is the ion exchange capacity of the polymer, which can be calculated using the degree of sulfonation (Table 1). *M(H₂O)* is the molar mass of water. In Table 1 are also reported the electrical conductivity of the different membranes at 25°C under RH= 100%. Figure 2 shows a plot of the membrane conductivity *vs.* the water uptake coefficient at 25°C for the different membranes. For the basis compound S-PEEK, a conductivity value under fully dry conditions (λ = 0) is also reported in Figure 2.

4. Discussion

There is no clear correlation of water uptake or electrical conductivity with the concentration of silicon, phenyl and hydroxyl groups as indicated in Table 1. Especially, there is no simple relation with the ion exchange capacity nor with the amount of "hydrophilic" OH or "hydrophobic" phenyl groups. However, the relation between electrical conductivity and water uptake can be described with a linear equation, as shown in Figure 2. Proton self diffusion coefficients *D* can be calculated using the Nernst-Einstein equation:

$$D = \frac{kT\sigma}{e_0^2 IECd} \quad (2)$$

In this equation, *k* is Boltzmann's constant, e_0 is the elementary charge, *T* the absolute temperature and *d* the membrane density, for which an average value of 1.23 g/cm^3 was used. The calculated proton diffusion coefficients reported in Table 1 are in good agreement with data obtained for other

sulfonated polyaryl-ether-ketones [16]. These results are in agreement with the idea that the water uptake is the main parameter for understanding the conductivity of ionomer membranes in the S-PEEK series and that the proton conduction properties are not very dependent on small changes of composition.

It was shown recently that the water uptake properties are strongly related to the mechanical properties of the membranes, especially the elastic modulus has been related to the water uptake and the swelling of the polymer membrane. [17] From these considerations, one might conclude that the membranes in the central part of Figure 2, which combine relatively high conductivity and not too large water uptake coefficients are probably the most suitable for use as fuel cell membranes, i.e. a cross-linked single phase polymer (SOSi-PEEK) and a composite material with a small concentration of a relatively hard second phase (S-PEEK+ 5% SiS-PPSU). Studies of long-time morphological stability of these membranes under fuel cell operation conditions remain however to be done to confirm this expectation.

5. Conclusions

This comparison shows that the main effect on conductivity is related to the water uptake of the membrane, which is in turn sensitive to its elastic modulus. However, a change of concentration of hydrophilic OH and hydrophobic phenyl groups did not have a clear correlation with water uptake and conductivity. Future work should be directed to S-PEEK membranes with a small amount of second phase permitting to improve the elastic modulus of the membranes, such as the S-PEEK/5% (Si,S)-PPSU system.

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Table 1. Chemical formulas of hybrid polymers, ion exchange capacity IEC, molar concentrations of Si, hydroxyl and phenyl groups, water uptake coefficient λ after 1 h immersion in water at 25°C and decimal logarithm of electrical conductivity σ at 25°C under RH= 100%.

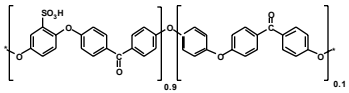
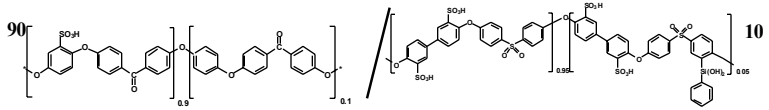
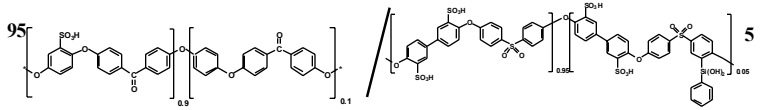
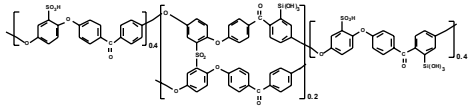
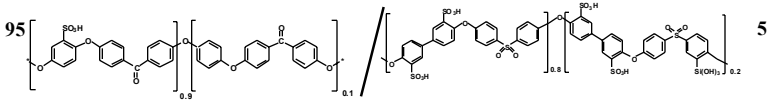
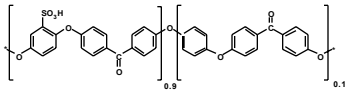
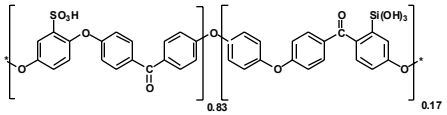
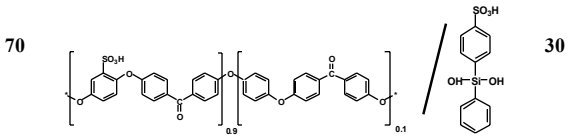
Membrane	Chemical formula	IEC meq/g	Si /mol	OH /mol	Ph /mol	λ	logσ (S/cm)	D 10^{-7} cm^2/s
S-PEEK, dry		2.50	0	0	0	0	-3,40	
S-PEEK/SiS-PPSU 10% Ph		2.39	0.0033	0.0066	0.0033	5	-2,94	1.0
S-PEEK/SiS-PPSU 5% Ph		2.44	0.0016	0.0033	0.0016	12	-1,62	21
SOSi-PEEK/50		1.71	0.5	1.5	0	13	-1,50	40
S-PEEK/SiS-PPSU 5% OH		2.44	0.0065	0.013	0	14	-2,08	7.4
S-PEEK, wet		2.50	0	0	0	16	-1,70	17
SiS-PEEK		2.26	0.170	0.510	0	17	-1,82	15
S-PEEK/ S-DPSD		2.68	0.343	0.686	0.686	18	-1,41	32

Figure 1. Water uptake of hybrid membranes vs. time at 25°C: S-PEEK (■), S-PEEK/S-DPSDO (◆), S-PEEK/SiS-PPSU 5% OH (▼), S-PEEK/SiS-PPSU 5% Ph (●), S-PEEK/SiS-PPSU 10% Ph (▲).

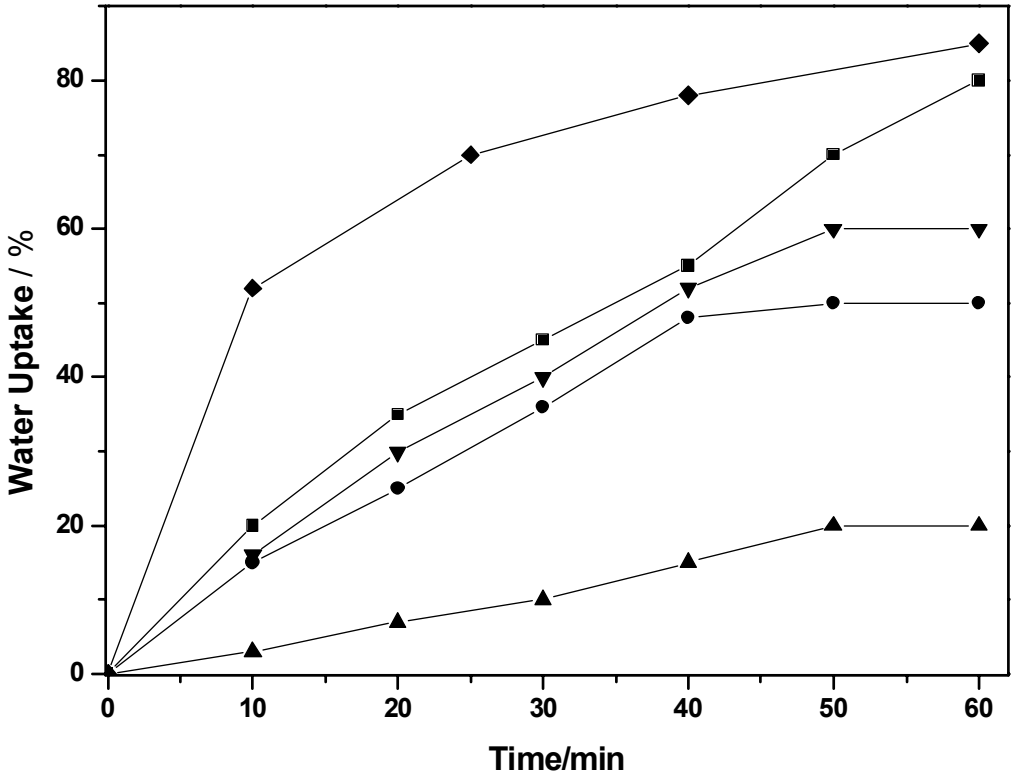
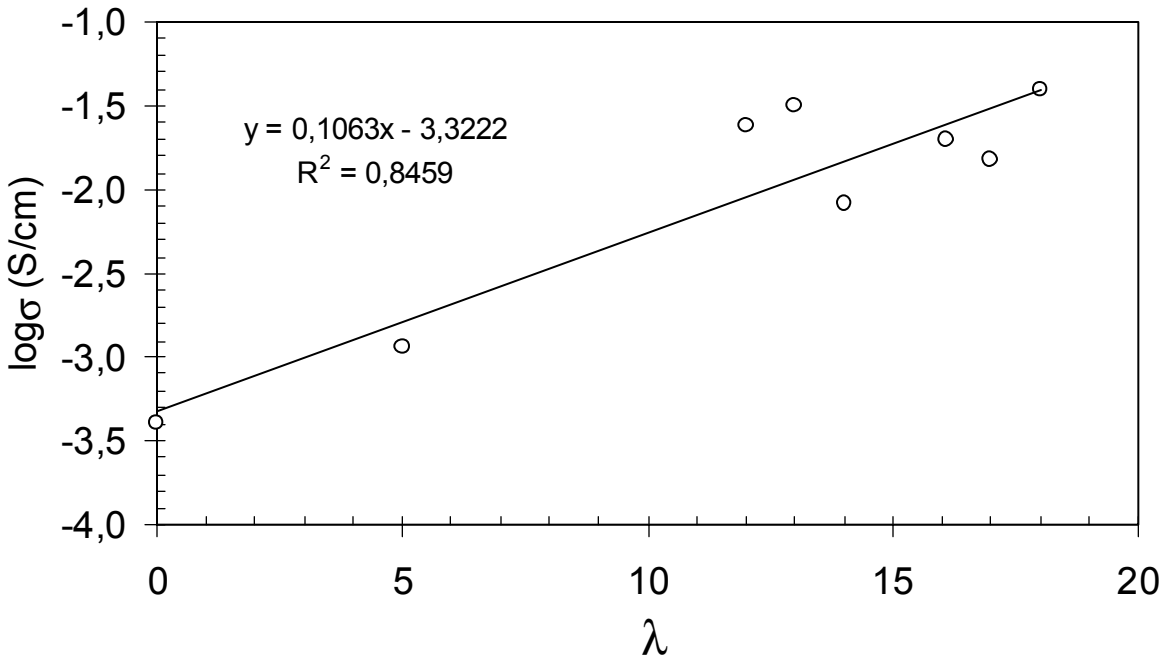


Figure 2. Electrical conductivity vs. water uptake coefficient for different hybrid membranes at 25°C (see table 1).



References

1. S. Cleghon, J. Kolde, W. Liu, Handbook of Fuel Cells-Fundamentals, Technology and Applications, J. Wiley, Chichester (2003).
2. M. A. Hickner, B. S. Pivovar *Fuel Cells*, *5*, **2005,** 213.
3. Q. Li, R. He, J. O. Jensen, N. J. Bjerrum *Chem Mater.*, *15*, **2003,** 4896.
4. N. Gourdoupi, A. K. Andreopoulou, V. Deimede, J. K. Kallistis *Chem. Mater.*, *15*, **2003,** 5044.
5. K. D. Kreuer *J. Membr. Sci.*, *185*, **2001,** 29.
6. M. Casciola, G. Alberti, M. Sgnappa, R. Narducci *J. Pow. Sources*, *162*, **2006,** 141.
7. G. Alberti, M. Casciola *Annu. Rev. Mater. Res.*, *33*, **2003,** 129.
8. S. P. Nunes, B. Ruffmann, E. Rikovski, S. Vetter, K. Richau *J. Membr. Sci.*, *203,* **2002,** 215.
9. C. Sanchez, G. J. De A.A. Soler-Illia, F. Ribot, D. Grosso *C. R. Chimie*, *6*, **2003,** 1131.
10. P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, S. Kaliaguine *J. Membr. Sci.*, *229,* **2004**, 95.
11. M. L. Di Vona, D. Marani, A. D'Epifanio, E. Traversa, M. Trombetta, S. Licoccia *Polymer*, *46*, **2005,** 1754.
12. S. Licoccia, M. L. Di Vona, A. D'Epifanio, D. Marani, M. Vittodello, J. R. P. Jakoukody, S. G. Greenbaum, *J. Electrochem. Soc., 153,* **2006**, A1226.
13. M. L. Di Vona, D. Marani, C. D'Ottavi, M. Trombetta, E. Traversa, I. Beurroies, P. Knauth, S. Licoccia *Chem. Mater.*, *18*, **2006,** 69.
14. D. Marani, M. L. Di Vona, E. Traversa, S. Licoccia, P. L. Llewellyn, P. Knauth, *J. Phys. Chem. B,* 110, **2006**, 15817.
15. M. L. Di Vona, A. D'Epifanio, D. Marani, M. Trombetta, E. Traversa, S. Licoccia *J. Memb. Sci.*, *279*, **2006,** 186.
16. K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, *Chem. Rev., 104*, **2004**, 4637.
17. G. Alberti, *Proceedings Polymer Batteries - Fuel Cells 2007*, p. 34.

*** Ethical Statement**

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Ethical statement

Dear Editor

This manuscript was never published or submitted before.

Sincerely

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