



# Electrical conductivity of sulfonated poly(ether ether ketone) based composite membranes containing sulfonated polyhedral oligosilsesquioxane



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## HIGHLIGHTS

- Embedding S-POSS within SPEEK improved PEM conductivity at low loadings.
- The isolated S-POSS electrolyte had conductivities lower than that of the PEMs.
- Insoluble in water S-POSS formed highly conductive interface with liquid water.
- The results were discussed using effective medium theory and bounding models.

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## ABSTRACT

Composite proton exchange membranes (PEMs) intended for fuel cell applications were prepared by embedding of various amounts of dispersed tri-sulfonic acid ethyl POSS (S-Et-POSS) and tri-sulfonic acid butyl POSS (S-Bu-POSS) in thin films of sulfonated poly ether–ether ketone. The electrical properties of the PEMs were studied by Impedance spectroscopy and it was found that their conductivity  $\sigma$  changes with the filler content following a curve with a maximum. The water uptake of these PEMs showed the same dependence. The investigation of initial isolated S-POSS substances revealed the properties of typical electrolytes, which however in both cases possessed low conductivities of  $1.17 \times 10^{-5} \text{ S cm}^{-1}$  (S-Et-POSS) and  $3.52 \times 10^{-5} \text{ S cm}^{-1}$  (S-Bu-POSS). At the same time, the insoluble in water S-POSS was found forming highly conductive interface layer when wetted with liquid water and hence producing a strong positive impact on the conductivity of the composite PEM. Electrical properties of the composites were analysed within the frameworks of effective medium theory and bounding models, allowing to evaluate analytically the range of possible conductivity values. It was found that these approaches produced quite good approximation of the experimental data and constituted a fair basis for interpretation of the observed relationship.

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## 1. Introduction

The extensive attention received by solid polymer electrolytes over last years has resulted in the development of many types of proton exchange membranes (PEMs) having diverse electrical and mechanical properties, different thermal and long term stability

and various efficiencies in a number of applications [1–3]. The strategies that are used to improve PEM properties often proceed along the line of doping an organic polymer with various inorganic components. The former provides structural flexibility and convenient processing while the latter may bring about a range of desirable physical properties such as high conductance along with mechanical and thermal stability [4]. Besides, the composites are distinguished by extended organic–inorganic interfaces that usually have defect structure [5] and provide free volume that can accommodate and retain significant amount of water which allows

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the composite membranes to preserve their conductivity in electrochemical applications.

The dispersion of the second phase can be achieved for instance through formation of inorganic particles by sol–gel reaction in the bulk of the preformed polymer membrane [6], or more conveniently by direct dispersion of a powdered second phase in the casting solution of the polymer. Different inorganic components, such as SiO<sub>2</sub> [6,7], ZrO<sub>2</sub> [8], mixed silicon–titanium, silicon–aluminum oxides [9] nano-clays [10], heteropolyacids [11,12], metal phosphates and sulfo-phenyl phosphonates etc. were used and often found beneficial for the PEM's properties and performance in various applications. However, despite multiple evidences of a positive effect of embedding of inorganic nano-phases into PEM matrices, this technique still did not achieve industrial scale, and is used mainly in R/D laboratories [6].

The addition of inorganic particles to polymer matrices often makes them brittle. One of the methods usually employed to minimize this problem is grafting of organic molecules on inorganic substances [13] allowing a better compatibilization of the filler with the matrix. Recently a new class of hybrid organic–inorganic substances representing a form of nano-silica generally designated as polyhedral oligosilsesquioxane (POSS) emerged as promising fillers for polyelectrolyte membranes. POSS is formed from nano-building blocks R–SiO<sub>3/2</sub> where R can be hydrogen, or an alkyl, alkene, aryl or arylene group [14]. It has a distinct 3-dimensional cubo-octameric siloxane structure where eight reactive organic vertex groups are covalently bound to nanometer size cages. Combining the rigid and thermally stable core with the functionalities of the organic groups may improve the properties of the hybrid materials, such as mechanical strength and toughness and have a positive impact on their processability, making them superior to both organic and ceramic compounds.

Consequently POSS are widely used as nano-fillers that can be embedded into polymers via blending [15–17], copolymerization [18,19] or grafting [20,21], with observed enhancement of chemical, thermal and mechanical stability [22–25].

There are several examples of using POSS as modifiers of PEMs [26–35]. In the work [26] three different highly conductive POSS derivatives were synthesised and embedded in sulfonated polysulfone. Despite the high conductivity of resulting composite PEMs their efficiency in electrochemical applications remains doubtful due to the fact that all three fillers were water soluble and obviously cannot participate on long-term basis in processes involving transport of water molecules (fuel cell, electro dialysis etc). Sandwiching this composite between two layers of pure polymer seemingly may improve its resistance to leaching [27], but for lack of results of long term tests in a real applications, this method still looks unreliable for PEM preparation.

A similar approach was used in works [28,29] where electrospun nanofibers composed of sulfonated polysulfone (ECS) or perfluorosulfonic/ acrylic acid polymers (CSC) hosted fully sulfonated octaphenyl POSS with IEC as high as 4.8 mmol/g. Again, very conductive but water soluble filler greatly improved the conductivity at 120 °C of non-porous membranes obtained from nanofibre mats. As to practical utilization of these composite materials, they still need further investigation. Contrary to the works [26–29] the authors of [30] embedded non-sulfonated branched POSS derivative in perfluorosulfonic acid polymer, which allowed them to reduce methanol crossover and as a result to enhance the composite PEMs' performance in direct methanol FC despite a decrease in their conductivity. The approach used in Ref. [30] seems generally promising in case of less expensive sulfonated arylene polymers; however using Nafion solution for membrane casting hardly may be applied in large scale production due to the high cost of the precursor and also because of the lower stability of cast

perfluoropolymer which has a lower molecular weight compared to extruded Nafion.

A partially sulfonated POSS (three acid functions per cage) was synthesised and embedded in composite membranes based on poly(vinyl alcohol) [31] and poly(ethylene glycol) [32]. Both polymers were reinforced by cross-linking and exhibited a high conductivity, comparable to that of Nafion with much lower methanol permeability. Similar commercial trisulfonic acid isobutyl POSS was used along with two other POSS derivatives in work [33] as a filler for sulfonated poly(ether ether ketone) (SPEEK). Surprisingly non-sulfonated trisilanol phenyl POSS showed a better conductivity and water retention compared to sulfonated POSS. It should be mentioned however that the load of the filler was quite low (2wt.%) in Ref. [33] and the dispersion and spatial distribution of the second phase may play in that case no less important role than its chemical nature. The impact of embedding a non-sulfonated POSS in sulfonated SPEEK was also studied by the same authors in Refs. [34,35].

In all the above cited studies it was observed that the principal function of PEMs, which is to allow proton transfer from anode to cathode, was significantly affected by inclusion of POSS. However the mechanism of conductivity enhancement by this hybridisation still stays undisclosed. In the present work we attempted to clarify the roots of the promoting effect of POSS insertion into partially sulfonated polyarylenes on the example of the composites based on SPEEK containing trisulfonic acid ethyl or isobutyl POSS derivatives. These composites represent a particular interest due to the fact that the chosen POSS substances are water insoluble despite the presence of a substantial content of acid functions corresponding to an ion exchange capacity IEC = 1.64 meq/g for the butyl-form of POSS and 1.84 meq/g for ethyl-POSS. It may be reminded that a good ionic conductor like Nafion has a comparatively lower IEC = 1.0 meq/g. Thus the trisulfonic acid ethyl polyhedral oligomeric silsesquioxane (S-Et-POSS) or its isobutyl derivative (S-Bu-POSS) may represent interesting objects for studies of their properties as promising materials for electrochemical applications. It should be mentioned however, that both substances are consistent viscous masses which prevent them from being used directly in any appliances due to their poor ability to preserve assigned shapes. That makes composites containing this kind of POSS of particular interest as a new concept of structurally stable ionic conductors resistant to water.

In the present work the conductivity of S-Et-POSS and S-Bu-POSS was measured along with conductivities of composite SPEEK based membranes having various contents of these fillers. The influence of water on the electrical properties of these materials was also studied. The main aim of this work was to gain an insight into the mechanism of conductivity in the SPEEK/S-POSS composites which has not been studied in Refs. [33–35]. This required enlargement of the range of concentrations of the filler and stipulated a special study of the conductivity of isolated S-POSS including its interaction with water.

## 2. Experimental information

The composites were prepared by casting from a 10wt. % solution of sulfonated polyether ether ketone (SPEEK) in DMAc mixed at predetermined ratio with S-Et-POSS or S-Bu-POSS pre-dispersed in DMAc. S-Et-POSS and S-Bu-POSS (Fig. 1) were acquired from Hybrid Plastics Inc. (USA) and used as received. S-POSS materials represent viscous thick honey-like substances non soluble in water and scarcely soluble in some organic solvents, which made the process of dispersion in a beaker with magnetic stirred as long as a few hours. Resulting suspension contained elongate particles ~2 by 5 μm in sizes, as was observed in a light microscope, sedimentation of which was very slow.

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