

**“Effect of Ferrierite Zeolite on Methanol Permeability of Poly(ether ether ketone)
(PEEK) Proton Exchange Membrane”**

Comments to the Authors:

[Reviewer 1]

The results and discussion section of the manuscript should be clearly enriched for publication. The proton conduction and methanol permeability characterization of the full set of membranes described in the manuscript should be appeared and properly discussed. In particular, the characterization of composite membranes at various sulfonation degree values (not only 0.53) and as a function of temperature (similarly to the mechanical properties study from 303 K-393 K) are claimed to support the stated conclusions. More specifically, the following issues should be reconsidered by the authors to improve the quality and understanding of the paper:

1. Introduction section:

The molecular representation of the PEEK monomeric unit before and after the sulfonation process to illustrate the proton conduction mechanism will be gratefully acknowledged. The authors pointed out the water retention properties of the composite membrane provided by the inorganic filler (3rd paragraph). However, the water adsorption properties of the ferrierite zeolite (with a SiO₂/Al₂O₃ molar ratio = 55 according to the text) as single material have not been experimentally evaluated. In addition, the water uptake values have not been evaluated for any of the composite membranes prepared. These additional experiments would help to discuss the proton conduction enhancement of the composite membranes.

ANSWER: In this work, the water uptake was measure by this method: the dried membranes were soaked in de-ionized water at 27 °C for 24 h. Then, the membranes were removed from the water, quickly dry-wiped with absorbent paper to remove any surface moisture, and then immediately weighed to determine their wet mass (W_w). In the case of the Ferrierite zeolite as a single material, it is in the powder form and it is difficult to measure the wet mass simply by wiping the water out.

2. Experimental section:

2.1 Materials:

The SiO₂/Al₂O₃ molar ratio of the zeolite supplied by Zeolyst CP914 (checked on the web page) is 20 (not 55).

ANSWER: We checked the specification sheet, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is 55 and we made a correction on page 3.

2.3 Preparation of composite membrane:

The units used to express the composition of the composite membranes, i.e. % v/v, are confusing since both raw materials, ferrierite and PEEK are in powder form. The inorganic filler content in the composite membrane could be also expressed in %wt (referred to the PEEK powder) for comparison purposes with published literature.

ANSWER: The compositions of the composite membrane were reported in % v/v. The effect of adding the zeolite into the composite membranes is through the surface area per unit volume; the 'weight' of the zeolite has nothing to do with mechanism of the improvement even though it is convenient to compare with other work.

[The S-PEEK polymer, 1.0 g, was dissolved in 20 mL of dimethylsulfoxide (DMSO) with mechanical stirring for 8 h until the polymer solution was homogeneous. Then, the zeolite Ferrierite was added to the polymer solution at five different percentages (5, 10, 15, 17, and 20 %v/v) to obtain the composite membranes [17]. The mixture was stirred for 4 to 6 h. Then, the solution was cast onto a glass plate and dried at 100 °C for 4 days under a vacuum.]

2.4 Characterization:

The textural properties of the zeolite has been determined by N_2 physisorption analyses and not by BET. BET refers to the Brunaur Emmett and Teller equation commonly used to fit the experimental physisorption results and calculate the so called BET surface area from the adsorbed gas quantity. Moreover, the estimation of microporous volume and micropore size is carried out by using the BJH method. Concerning the channel dimensions (i.e. pore size) of ferrierite zeolite, the authors assume 3.61 Å (see Results section pp 7, 5th paragraph). Particularly on this point further explanations are required due to this value is slower than those reported on the IZA web page (5.4*4.2 and 3.5*4.8 along 001 and 010 directions respectively).

ANSWER: In this work, we used the BET method. We described the method on Page 5. The actual pore size of the zeolite was measured and found to be 3.61 Angstroms.

2.5 Degree of Sulfonation by Titration

According to section 2.2, the PEEK powder sulfonation is carried out with concentrated sulphuric acid. However, before titration the resulting membrane is acidified with an excess 0.1 M HCl solution. Particularly on this point further explanations are required for a proper understanding of the HCl doping step.

ANSWER: The HCl doping process was used to improve the saturation of protons on the sulfonic acid groups along the polymer chain. The protons on the sulfonic acid groups can be easily exchanged with other cations. Here, we tried to raise the number of protons on the sulfonic acid groups.

2.7 Water Uptake Measurements

The values of the polymer membrane weight before soaking in de-ionized water should be also included and compared with W_d values to assess about data reproducibility and standard deviations.

ANSWER: The weight of the dry membrane used in the water uptake measurement varied between 0.2-0.3 g and was described in page 6.

2.8 Electron and Proton Conductivity

The electrical and proton conductivity values reported are those obtained with polymer membranes with 0% and 10% water uptake respectively. The authors should clearly indicate how the water uptake capability of the membrane is controlled. The as denoted “electron conductivity” values are those exhibited by membranes with 0% of water uptake at 50% RH (see Table 1). Thus, the experimental conditions seem a contradictory due to in presence of humidity the sulfonated PEEK membranes are hydrophilic enough for water uptake. In fact, the electron and proton conductivity values reported in Table 1 and 2 are quite similar. This behavior differs from the desired properties required for PEMs, i.e. high proton conductivity values and low electrical conductivity values. The authors are encouraged to provide with the fundamentals that motivate them to denote the conductivity values exhibited by 0% water uptake membranes as “electron” conductivity values. A new figure describing the electrochemical cell (temperature and humidity control, mass flow rates, volume of the chamber) and the experimental set-up (through plane or in plane conductivity measurements) will be gratefully acknowledged.

ANSWER: We changed the text from the electron conductivity to the proton conductivity. It is possible to still have a small amount of water for the 0% uptake.

3.5 Methanol Permeability

The methanol permeability characterization of the full set of membranes described in the manuscript should be appeared and properly discussed. In particular, the characterization of composite membranes at various sulfonation degree values (not only 0.53) and as a function of

temperature (30°-50°-70°C) are claimed to support the stated conclusions. It seems unclear why the methanol coefficient (cm²/s) varies with time on stream unless the membrane properties change with time due to swelling. Therefore, a new figure including the variation of CB (and if appropriate also CA) as a function of time for the full set of membranes would help to understand the variation of methanol permeation rate expressed in mol/(cm²s) as a function of time and the different permeation regimes we have until the steady state is reached.

ANSWER: In this work, we selected the 0.53 DS and 0.71 DS membranes for the methanol permeability study and compared with the values of Nafion 117. There were mistakes for the calculation of methanol permeability. Figures 9 and 10 now are methanol concentration plots, not methanol permeability and the methanol permeability (P) was by using the slope of the methanol concentration versus time plot.

[Reviewer 2]

Reviewer comments for ie-2011-006005: Rejection or Major revision This manuscript deals with sulfonated poly(ether ether ketone) (SPEEK)-zeolite composite membranes for direct methanol fuel cells. Unfortunately, the referee failed to find new information on the research.

1. Direct sulfonation of PEEK has been utilized for proton exchange membrane fabrication. Since direct sulfonation often results in side reactions such as chain cleavage and crosslinking and uncontrolled sulfonation in random sites of aromatic rings, many research groups have usually conducted monomer sulfonation-subsequent polymerization instead of direct sulfonation. Though the main stuff of the manuscript is the SPEEK-zeolite composites, a lot of portions in the manuscript are associated with SPEEK itself. It makes the referee and the readers not to concentrate the idea of manuscript.

ANSWER: In this work, we did not synthesize the S-PEEK, The PEEK 150XF was purchased from Victrex. So, the post-sulfonation is the only possible way to do. In this manuscript, we focus mainly on the S-PEEK properties, then adding the zeolite to improve some properties.

2. The direct mixing of zeolite powder causes their self-aggregation in the SPEEK membrane matrix as shown in Figure 4. It usually leads to non-selective cavities and lowers or eliminate the intrinsic advantages of functional inorganic particles in the corresponding composites. It is common to obtain low methanol permeability after adding inorganic particles. It is not new information.

ANSWER: The self-aggregation of the zeolite powder always occurs when adding in a large amount. However, we selected the Ferrierite zeolite because there were few literatures reporting on this zeolite

and we were interested to study as an additive for using in the proton exchange membrane applications.

3. Methanol permeability means how much methanol can be permeated per a unit time and is an intrinsic property of each membrane material. However, the authors showed the changes of methanol permeability as a function of measuring time in Figure 9 to Figure 11. Those Figures seem to suggest that methanol permeability can be changeable depending on methanol exposure times. It is beyond the concept of methanol permeability.

ANSWER: Figures 9 and 10 are now concentration plots vs. time, not the permeability data. In this work, we selected the 0.53 DS and 0.71 DS membranes for the methanol permeability study and compared with the values of Nafion 117. There were mistakes in the calculation of methanol permeability in the previous manuscript; the methanol permeability (P) was calculated by using the slope of the methanol concentration versus time.

We corrected the text and figures on Page 11, and 21-23.

4. The authors seem to have wrong information on electrochemistry, and proton conductivity concept and measurement. Proton exchange membranes (PEMs) should be highly proton-conductive. Simultaneously, the PEMs should be insulator for electrons. The authors used the terms of electron conductivity in Table 1 and 2. Even the author measured the resistance at 0% water uptake, the measured conductivity must be proton conductivity because hydroscopic sulfonated polymers easily absorb water molecules from atmosphere which act as proton transport medium. Moreover, the authors should measure the proton conductivity in liquid water since the application target is DMFC application.

ANSWER: We changed the text from the electron conductivity to the proton conductivity. It is possible to still have a small amount of water for the 0% uptake and what we measured was proton conductivity.

5. Minor comments:

1) DMFC is not for transport application.

ANSWER: The DMFC applications were modified on Page 2.

It is only suitable for portable devices.

2) The ultimate goals for DMFC in Page 3 line 12 should be changed into the term of “the major requirements of proton exchange membrane materials for DMFC”

ANSWER: We modified the text on Page 3 as suggested.

The referee regrets not to recommend the manuscript for publication in Industrial Engineering & Chemical Research owing to the reasons mentioned above.

[Reviewer 3]

Review: Effect of Ferrierite Zeolite on Methanol Permeability of PEEK Proton Exchange Membrane
The authors present a study on the synthesis and performance of sulfonated poly(ether ether ketone) (S-PEEK) membranes and S-PEEK/Ferrierite composite membranes. PEEK is first sulfonated with concentrated sulfuric acid. Ferrierite is mixed with sPEEK and solution cast into thin membranes. While the membrane fabrication appears successful, the membrane performance is highly questionable. In particular, the authors' membrane exhibit a high electronic conductivity (the electronic conductivity is nearly as high as the proton conductivity). Electronic conductivity will short circuit any DMFC operated with these membranes. This is highly undesirable. Due to these questionable results, along with other comments below, it is recommended that this paper be rejected for publication.

Comments:

1) Page 4, line 3-4. Please clarify whether the ferrierite is being added relative to the casting solution's volume or to the final, cast membrane's volume.

ANSWER: The ferrierite zeolite was added relative to the solution in various amounts. We reported the % v/v to be the volume of the zeolite divided by the volume of the polymer. The text was modified in page 4.

2) Page 6, section 2.8. How was electronic conductivity measured? Electronic conductivity should be zero for the membranes. It is unusual to measure such a property. If electronic conductivity and proton conductivity were taken from the same data set, how were they distinguished?

ANSWER: We changed the text from the electron conductivity to the proton conductivity. It is possible to still have a small amount of water for the 0% uptake and what we measured was proton conductivity.

3) Page 8, section 3.2. DS (the degree of sulfonation) and IEC should be related by a simple mathematical expression based on the MW of the repeat unit. Do the DS and IEC agree with the theoretical calculation?

ANSWER: Yes, they do.

4) Page 8, section 3.3. DS is not a good characterization of Nafion 117. Use IEC instead.

Furthermore, why is the swelling of S-PEEK smaller than Nafion given its significantly higher IEC? This makes no sense.

ANSWER: In this work, both DS and IEC data were reported. The swelling of S-PEEK is smaller than Nafion because the polymer main chain contains a high amount aromatic rings, thus the S-PEEK chain is stiffer with a lower swelling degree than Nafion.

5) Page 9, line 7 and Table 1. How can there be 0% membrane water uptake (Table 1) when the membrane is exposed to 50% relative humidity?

ANSWER: The 0% water uptake membrane was dried in a vacuum oven before the measurement even though it could absorb water from the ambient.

6) Page 9, section 3.4. Again, why is the electronic conductivity so high? And how does a higher DS change the electronic conductivity?

ANSWER: The texts in Tables 1 and 2 should be the proton conductivity, not the electron conductivity. We made the correction.

7) Page 9, section 3.4. The author's claim that the zeolite is enhancing water uptake. The authors should provide experimental evidence of this (i.e. compare the water uptake of membrane's with and without zeolite).

ANSWER: The zeolite hydrophilic property is rather well known. Because of its surface is negatively charged and its high cation exchange capacity brings about high hydrophilicity.

8) Page 9, section 3.4. What other evidence is there of poor zeolite distribution? The distribution does not look particularly poor on the SEM and there is no visual evidence of defect voids. It is more likely that the zeolite is reducing proton conductivity of the membrane by a simple dilution effect. The zeolite should have essentially no proton conductivity.

ANSWER: There is no other evidence. The only evidence shown in this work is the SEM images in figure 4a and b. The S-PEEK/10%v/v zeolite composite membrane was observed to have a non-uniform distribution and an agglomeration of some particles within the S-PEEK membrane (Figure 4b).

9) Page 9, section 3.5. Why is methanol permeability changing in time? It should not take more than 9 hours for the permeability of N117 to stabilize. The measurement technique appears to be in error. Also, the measured permeability of N117 is significantly higher than what others report in the

literature. The measured permeability ranges from 8×10^{-6} to 1.3×10^{-5} for N117. A value between 1 and 3×10^{-6} cm²/s is more typical for N117.

ANSWER: Figures 9 and 10 are now concentration plots, not the permeability data. In this work, we selected the 0.53 DS and 0.71 DS membranes for the methanol permeability study and to compare with the values of Nafion 117. There were mistakes in the calculation of methanol permeability in the previous manuscript. The methanol permeability (P) was by using the slope of the methanol concentration versus time.

We corrected the text and figures on Page 11, and 21-23.

10) Selectivity (ratio of proton conductivity to methanol permeability) is of critical importance for DMFC membranes, but is never discussed or determined by the authors.

ANSWER: We quoted the selectivity values in tables 1 and 2.

11) Figure 11. The addition of 5 vol% ferrierite appears to have no effect on MeOH permeability.

Why?

ANSWER: In this work, the methanol permeability of the composite membranes increases with zeolite content since a larger amount on zeolite loading leads to a non-uniform dispersion, and some agglomerates create voids in the polymer membrane. The 5 vol% ferrierite has a good dispersion in S-PEEK matrix which seems to have no effect on the methanol permeation.

12) Table 1 and Table 2. Why were the conductivities measured at such low water contents? In a DMFC the membrane will be exposed to a liquid methanol/water mixture. Therefore it would be better to measure conductivity in liquid water. Furthermore, the proton conductivities are exceptionally low and not practical for DMFC operation.

ANSWER: In this work, we measured only the membrane with a low water content and compare it with 0% uptake membrane. It is not possible to measure the proton conductivity in a liquid water.