nature portfolio

Peer Review File

High selectivity framework polymer membranes chemically tuned towards fast anion conduction

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This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
I have examined the updates made by Fang et al. to their manuscript. I appreciate the significant efforts the authors went through to add experiments, correct the data presentation, and revise the discussion. The authors clearly took the revision process seriously, and the paper is greatly improved. I also believe that Nature Communications is a better home for the advances made in this work. I thank the authors for incorporating the advice given by me and the other reviewers. However, for me, the updated manuscript still has two concerning discussions that should be revised. I recognize that a lot has already been done at my request, but I hope the authors agree that these are important points to clarify for the good of their future readers. I believe that these final revisions will make the manuscript suitable for publication.

1. Pulse field gradient NMR and the claim of “barrierless” ion transport
The response to the issue taken with the claim of “barrierless” transport (the first review, point 1) explained that “there remains an energy barrier contributed by pore tortuosity and non-uniform pore size distributions,” but that the local diffusion is what has become barrierless. Therefore, in the manuscript, the authors continue to claim that F- transport is indeed barrierless (abstract, line 30: “resulting in…locally barrierless F- diffusion”). The reasoning behind this claim lies in the fact that the measured diffusion coefficient for F- in the membrane is only 10.5% lower than the measured diffusion coefficient for F- in dilute aqueous solution. I have two concerns about this persisting claim that transport has been achieved without any energy barrier. Because of these concerns, I believe the authors should continue to use their revised language, and say that they pursued very low energy barriers to ion transport, even for F-.

First, the authors claim that PFG NMR measures the local diffusion coefficient of F-, which would need to be done at very low length/time scales. As far as I am aware, PFG NMR measures transport at the length scale of at least 10s of nanometers. How can we be confident that the diffusion coefficients are not semi-local?

Second, aside from the numbers, the logic of the claim doesn’t sit well with me. Even F- in dilute aqueous solution has an energy barrier to transport: resources such as Robinson and Stokes (1965) compile the conductance of ions at various temperatures, allowing for easy calculation of the thermal energy barrier for ion transport in dilute aqueous solution. If the membrane F- diffusion coefficient reached parity with the aqueous solution F- diffusion coefficient, I grant that the authors could claim that the membrane did not add any additional energy barrier for F- transport. However, although these membranes achieve very fast F- transport, the two values are not statistically indistinguishable from one another; even that claim would not be supported by the data.

2. The driving force of concentration gradient–driven salt transport
I thank the authors for sharing some sources regarding the ion dominating concentration gradient–driven salt permeability experiments and for explaining their logic. However, I reiterate that this is not a problem which is current or contentious: the rate-limiting role co-ions play in concentration driven salt permeation across ion-exchange membranes has been decidedly known for decades. Because of this, the discussion around KCl permeabilities in Figure 2c of the manuscript must be adjusted. Large KCl permeability coefficients measured as described in this manuscript do not indicate fast K+ conduction, but rather suggest significant Cl- leakage.

Even though mobile anions are more numerous than mobile cations in the membrane, the cations are known to dominate the salt permeability experiments; in fact, it is because they are the minority species that they are the rate-limiting step. The authors rightly claim that the anions provide an electric field which accelerates the transport of cations, but this is not the dominant factor of salt permeation through ion exchange membranes.

Regarding the sources provided by the authors to support their position: One refers to Diffusion Dialysis (Luo et al, J. Membr. Sci. 2011, 366, 1–16. doi.org/10.1016/j.memsci.2010.10.028). I specifically take issue with the KCl permeability experiments, where the receiving compartment was filled with DI water. For the redox active permeability measurements, with a concentrated receiving compartment solution, the Diffusion Dialysis style analysis becomes more relevant and I believe the authors' claims are reasonable. Two of the other sources provided in the reviewer response didn't make any claims regarding this specific topic, that I could find. The fourth source provided by the authors (Ye et al. Nat. Commun. 2022, 13, 3184. doi.org/10.1038/s41467-022-30943-y) is firmly in favor of co-ion dominant permeation. Ye et al. discuss permeability of cation-exchange membranes (anions are the co-ions) on page 6: "The permeability of a range of potassium salts was investigated to assess the selectivity of sPIM-SBF membranes towards anions with varied physical size and charge density, as the diffusion of the salts is predominantly controlled by the properties of the anions rather than that of the small K+ cation of high mobility."

Instead of these quite recent publications, I refer the authors to established textbooks on ion-exchange materials, which all discuss the concentration gradient–driven permeation of electroneutral salts across an ion-exchange membrane. These sources derive the ambipolar diffusion equation (one way to express it is given below) to describe the effective diffusivity of salt resulting from the individual counter-ion and co-ion diffusivities.

Ds = (D_counter*D_co) * (C_counter+C_co) / (C_counter*D_counter+C_co*D_co)

where Ds is salt diffusion coefficient, D_counter is counter-ion diffusion coefficient, D_co is co-ion diffusion coefficient, C_counter is counter-ion concentration, and C_co is co-ion concentration.

These textbooks comment on the implications of this equation for concentration gradient–driven salt permeability experiments:

• Crank, Diffusion in Polymers, 1968: Chapter 10 Section VII: "The counter-ions usually greatly outnumber the co-ions … Thus, the transport of an electrolyte down a concentration gradient across an ion-exchange resin membrane does not differ much from the simple Fickian diffusion of the co-ions."
• Helfferich, Ion Exchange, 1995: Section 8.3b: "The rate of electrolyte diffusion is controlled by diffusion of the co-ion. This is another example of the general rule that the diffusion rate is controlled by the species which is in the minority. An interesting consequence is that, say, HCl and NaCl diffuse across a cation-exchanger membrane at about equal rates"
• Lakshminarayanaiah, Transport Phenomena in Membranes, 1969: Section 4.5A: "The main conclusion of this study is that the rate of diffusion of the electrolyte is governed by the diffusion coefficient of the co-ion"
• Tanaka, Ion Exchange Membranes: Fundamentals and Applications, 2015: Section 2.4.1: "Electric neutrality in the membrane accelerates the movement of ions having lower diffusivity, and deaccelerates the movement of ions having larger diffusivity. This phenomenon induces the acceleration of co-ions and deacceleration of counter-ions in the membrane. … When the concentration of co-ions is decreased extremely in the membrane, the diffusion flux of the counter-ions is decreased remarkably, owing to the dominant Donnan exclusion … the diffusion velocity of counter-ions is influenced by a small amount of co-ions remaining in the membrane.
• Sata, Ion Exchange Membranes, 2004: Section 2.7 "These equations mean that the flux of electrolyte through the ion exchange membrane is governed by the diffusion coefficient of the co-ion, not the counterion. For example, the diffusion flux of hydrochloric acid should be equal to that of sodium chloride in an ideal cation exchange membrane."

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
The authors address my previous concerns to my satisfaction. I support publication of this manuscript in Nature Communications.

Responses to reviewer comments

For Referee #2

I have examined the updates made by Fang et al. to their manuscript. I appreciate the significant efforts the authors went through to add experiments, correct the data presentation, and revise the discussion. The authors clearly took the revision process seriously, and the paper is greatly improved. I also believe that Nature Communications is a better home for the advances made in this work. I thank the authors for incorporating the advice given by me and the other reviewers. However, for me, the updated manuscript still has two concerning discussions that should be revised. I recognize that a lot has already been done at my request, but I hope the authors agree that these are important points to clarify for the good of their future readers. I believe that these final revisions will make the manuscript suitable for publication.

Reply: We thank the reviewer for their positive feedback and insightful comments/suggestions on our manuscript. We highly appreciate the Reviewer's effort and expertise in this area, and believe their recommendations have improved the quality of this study. The remaining two concerns of the reviewer have been revised according to your comments. Please see our point-by-point response below.

Q1. Pulse field gradient NMR and the claim of "barrierless" ion transport

The response to the issue taken with the claim of "barrierless" transport (the first review, point 1) explained that "there remains an energy barrier contributed by pore tortuosity and non-uniform pore size distributions," but that the local diffusion is what has become barrierless. Therefore, in the manuscript, the authors continue to claim that F^- transport is indeed barrierless (abstract, line 30: "resulting in…locally barrierless F^- diffusion"). The reasoning behind this claim lies in the fact that the measured diffusion coefficient for F^- in the membrane is only 10.5% lower than the measured diffusion coefficient for F^- in dilute aqueous solution. I have two concerns about this persisting claim that transport has been achieved without any energy barrier. Because of these concerns, I believe the authors should continue to use their revised language, and say that they pursued very low energy barriers to ion transport, even for F^-.

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transport, the two values are not statistically indistinguishable from one another; even that claim would not be supported by the data.

Reply: According to the Reviewer's comments, we revised our language and claimed that we pursued very low energy barriers to ion transport, even for F^-.

For the PFG-NMR measurement, we agree with the Reviewer that the length scale of the measurement cannot be simply categorized as a local measurement, even though it may not reflect long-range ion diffusion. The corresponding language has been revised.

We agree with the Reviewer that even though the membrane adds almost no additional energy barrier for F^- transport, the diffusion values are not quite identical. The relevant discussion has been revised.

Q2. The driving force of concentration gradient–driven salt transport

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Reply: We thank the Reviewer for their insightful comments on KCl permeability measurements. We carefully referred to the textbooks you mentioned and learned more basic knowledge about static salt permeation measurements and the underlying mechanisms. The most relevant textbooks are cited (Please see refs #28-30). According to the Reviewer's comments and our understanding, relevant discussions in

Figure 2c have been adjusted in the revised manuscript. Please see page 7 of the revised manuscript(the content was also copied below).

We measured the cross-membrane permeation rates for BTMAP-Vi (a redox-active organic cation) and KCl (**Figure 2c,** Supplementary Figures S13-S15, Supplementary Tables S5-S6), which are dramatically different in size. The QCTF membranes exhibited size-induced selectivity towards cations, allowing a small amount of K^+ permeation while rejecting larger BTMAP-Vi cations. The permeability coefficients of BTMAP-Vi across the QCTF and the P-QCTF were determined to be 4.3×10^{-11} cm^2 s^{-1} and 3.32×10^{-11} cm^2 s^{-1}, respectively. It further decreases to 2.93×10^{-11} cm^2 s^{-1} for M-QCTF, a value that is much smaller than those of Selemion® DSV, Selemion® AMV, Sustainion® X37-50, Fumasep® FAA-3-PE-30, and some PIM-based membranes (**Figure 2c** and Supplementary Figure S14). The permeability coefficients of KCl (predominantly controlled by the diffusion of the minor co-ion (K^+))[28-30] through the QCTF and P-QCTF are 1.82×10^{-7} cm^2 s^{-1} and 2.6×10^{-7} cm^2 s^{-1}, respectively and it is 3.1×10^{-7} cm^2 s^{-1} for M-QCTF. The comparison between the chloride salt permeability coefficients and selectivity of the QCTF membranes versus representative commercial AEMs and previously reported membranes implies that these framework membranes maintain comparable charge selectivity, but deliver significantly higher size-induced selectivity (Supplementary Figure S16 and Supplementary Table S6). By contrast, the KCl permeability coefficient for the control Sustainion® X37-50 membrane (a commercial AEM) is 2.4 times that of the M-QCTF membrane, and the BTMAP-Vi permeability coefficient for Sustainion® X37-50 membrane is at least three orders of magnitude higher than that of the M-QCTF membrane because of sever water swelling (54.6% vs. 1%) and excessive water uptake (172% vs. 8.5%) at 30 °C.

The revised contexts mainly reveal the following aspects.

(1) The minor co-ion diffusions are the rate-limiting step in the salt permeability experiments.

(2) The KCl permeability coefficients measured as described in our manuscript do not indicate fast Cl^- conduction, but rather suggest the permeation/leakage of K^+. By contrast, the membrane can effectively block the permeation of larger cations, e.g., BTMAP-Vi.

(3) The measured KCl permeability coefficients and leakage of K+ ions do not change the nature of our membrane, which is an anion exchange membrane, with a t_- value of 0.95.