nature portfolio

Peer Review File

# Tailoring high-performance bipolar membrane for durable pure water electrolysis

Corresponding Author: Professor Liang Wu

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Yu and co-workers report a new class of bipolar membranes prepared from cation exchange and anion exchange ionomers of the same backbone chemistry: poly(phenylene alkylene). The authors use an earth abundant water dissociation catalyst, tin oxide ($SnO_2$), which was recently shown by Boettcher and co-workers to be highly active in BPMs (Nature Materials 2024). However, the work by Boettcher and co-workers used a cation exchange membrane (CEM) and an anion exchange membrane (AEM) of different backbone chemistries (unlike the work here). However, Boettcher and co-workers did make an all-hydrocarbon BPM (Nexar (Kraton Corporation)-Orion). This article is notable because it uses a BPM of the same polymer backbone chemistry, and this BPM shows one of the best water electrolysis performances (I believe the 2nd best value in the literature) and the best durability (up to 1000 hours). The remarkable durability is a product of using the same polymer backbone chemistry. Not only does the BPM show durability in a water electrolyzer, but it can be folded, crumpled, etc. and retain its integrity. Overall, I find the article suitable for Nature Communications after a revision.

1) The derivative in the y-axes for Figure 2b and Figure S9b should have units on it.
2) I understand why the authors decided to benchmark their BPM against the commercial variants by Fumatech and ASTOM corporation (Neosepta); however, these BPMs are not suitable for water electrolysis because they are not designed to operate at high current density. Using high current density can cause blistering in these materials. I suggest the authors make this point in their revised manuscript. I do appreciate how they have benchmarked their results against other experimental BPMs in the literature.
3) I feel like the Spider chart (Figure 3e) is inappropriate as there is no agreed upon metrics for the Rwd, Rohm, E, etc.
4) Regarding the impedance analysis, I feel that the electric circuit equivalent model used by the researchers, which was developed by Mallouk and co-workers, is incorrect or creates confusion. It is well-known that a plethora of electric circuit equivalent models can fit Nyquist plots. I don't know the differences (physics interpretation) for the reaction rate dissociation constant (kd), found from the Gerischer element, and the resistance for water dissociation ($R_{wd}$). These values both relate to the kinetics of water dissociation. Why are two circuit elements needed to describe water dissociation?
5) How were the ionic transport times determined from the depletion layer? Does this also hail from Gerischer element?
6) In Figure 4, the placement of panel d becomes before panel c. Please reverse them.

Reviewer #2

(Remarks to the Author)
The authors report high-performing and durable BPM design for water electrolysis. In my view, this is a very interesting study, therefore I recommend publication after addressing my comments below.
1. The authors argue that the benefit of using reverse bias BPM electrolyzer for water electrolysis application is to leverage the kinetic benefits of alkaline OER and acidic HER. That will make sense on the surface, however, it does come with penalty of voltage loss in water dissociation. Compared to emerging technology for instance, anion exchange membrane water electrolysis, which essentially has the same anode compared to BPM water electrolyzer but an alkaline HER reaction. Of course, it is well known that alkaline HER is more sluggish compared to acidic HER. If the voltage penalty from water dissociation significantly surpasses the voltage penalty by switching from acidic HER to alkaline HER, then BPM water electrolyzer will never be as efficient as anion-exchange membrane water electrolyzer. Now the question is that, does it really make sense to spend effort developing BPM water electrolyzers? From what is shown here, the onset of water

dissociation reaction (figure 4a) is at minimum of 0.75 V, which I believe is much higher than the voltage penalty by switching from acidic HER to alkaline HER. The authors should comment on this aspect in the manuscript and compared the base BPM water electrolyzer performance with anion exchange membrane water electrolyzer under similar condition to show how much of a performance gap needs to be bridged.
2. I am a little confused on how the EIS is measured, for instance, in figure 3d. The measurement was done in a 4-electrode setup (figure s8) with two identical reference measuring the transmembrane potential, however, the current was applied between the anode and cathode. Theoretically, it is still possible to apply a current perturbation and measure the voltage response. However, in practical case, this is rather challenging. I imagine one would need to potentiostat to do so and it has to be perfectly coordinated? Any case, more illustration and experimental details and measured data should be shown.
3. Figure 4d, it looks like there is quite a bit Sn redistribution after 800 h durability operation, yet, negligible impacts on cell performance is observed. Does it mean the WD catalyst ($SnO_2$) has no impact on performance? Any evidence on that? From what I know in many literature, the WD performance is very sensitive to WD catalyst loadings. Also, the authors conclude the Sn redistribution is due to migration of catalyst nanoparticles. Can the author show if the $SnO_2$ particles have changed morphology before and after operation? It will be important to know if this is just due to migration or due to any sort of dissolution and redeposition. Simply based on Sn Pourbaix diagram, Sn is not stable in neither acid or base condition.
4. I am also confused on how the authors can achieve an onset of ~ 1.5V for water electrolysis in figure 5d, while the onset of WD reaction is about 0.75V for the BPM developed. The onset of water electrolysis should at least be 1.23V+0.75V assuming there is no loss for anode and cathode reactions.
5. Page 10, from the EIS measurement shown in figure 3d, the authors conclude that the highly integrated BPM junction and well-performed $SnO_2$ catalyst explains the performance superiority of the TPSn-BPM compared to Neosepta BP1 and FumaTech BPM. First, there looks to be a few typo in the legend of figure 3d: for instance FumaTech BPM not Fumatech FBM? Second, did I understand it correctly that the Neosepta BPM and Fumatech BPM did not use the same $SnO_2$ catalyst? If so, how can we know how much of the performance improvement is due to the BPM by itself and how much performance improvement is due to the WD catalyst difference? Can it be just due to the catalyst difference so the BPM doesn't matter? Lastly, I feel unclearly about what the "highly integrated" exactly means. This looks to be the most interesting aspect of this work, however, it is not well understood how and why the "highly integrated" is achieved.

Reviewer #3

(Remarks to the Author)
Dear Editor,

The manuscript ”Tailoring high-performance bipolar membrane for durable pure water electrolysis” by Yu et al. describes the bottom-up fabrication of a $SnO_2$ catalyzed bipolar membrane based on quaternary ammonium and sulfonic acid functionalized poly(arylene alkylene)s. The work is highly relevant, as new bipolar membranes that can support high current densities at low resistance could open new avenues in water electrolysis and $CO_2$ capture and utilization. The authors take an interesting approach by combining a good water dissociation catalyst with anion/cation exchange membrane layers combining high conductivity, fast water diffusion and good stability. The bipolar system shows good performance stability over 1000 h at device level in water electrolysis mode, which is a significant advancement of the technology. The work is mostly scientifically sound, but I would recommend the authors to address the feedback below in a revised version:

- The modeling section is rather superficial, and it is unclear how the modeling results are used to guide the experimental work and how it contributes to the interpretation of the experimental results. The scientific value of this part is thus quite limited. I encourage the authors to make more active use of the modeling and simulation results, and to extend this part if that is needed to support the discussion around the experimental results.
- Figure 3c: The comparison with the literature data in this figure is not straightforward, because the results in the different studies depend largely on the specific conditions used. There is not much scientific value in such a comparison. I would recommend the authors to move this figure to the supplementary information, and to include details about the specific experimental conditions behind the literature data points (including references to the original work).
- Figure 3e: It is unclear how this plot should be interpreted. It looks like an attempt to compare different parameters of the in-house made BPM with commercially available reference materials. I would recommend the authors to plot this in a way that allows for quantitative scales on the different axis. It is also unclear how the water dissociation constant, water dissociation electric intensity and ion transport time through the depletion region are obtained. It is stated in the experimental part in the supporting information that they are extracted from the EIS data, but there are no details about how this is done. This must be described.
- Figure 5f: Please provide details about specific test conditions. Is this recorded in pure water or in aqueous acid/base?
- Heading “Discussion” should be “Conclusion”

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I appreciate the authors' response letter and revised manuscript. I recommend the article for publication in Nature Communications without any further revisions.

Reviewer #2

(Remarks to the Author)
The authors have addressed most of my previous comments. I suggest the publication without further review needed. One minor comment is about the statement that: Current
studies on PEMWEs and AEMWEs often use acidic or alkaline feeds to optimize reaction kinetics,
which can lead to accelerated degradation of the electrolyzers. PEMWEs do not need acidic feeds but pure water.

Reviewer #3

(Remarks to the Author)
The authors have carfefully considered the feedback from the reviewers, and taken appropriate actions to revise the manuscript. The discussion is scientifically sound and the conclusions are well supported by experimental data. The bipolar membranes with anion/cation exchange layers derived from poly(arylene alkylene)s, as described in this work, combine excellent polarization performance and performance stability. The results are of significance for various electrochemical applications where bipolar membranes are used, including acid/base generation, electrolysis, and CO2 capture/conversion. I am willing to support publication in the present form.

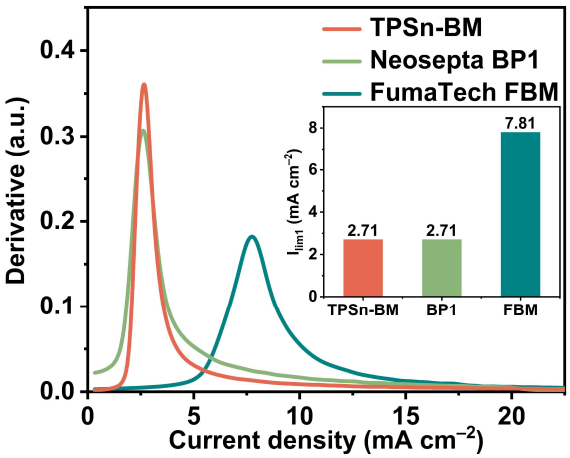
**For Reviewer #1**

***General:*** Yu and co-workers report a new class of bipolar membranes prepared from cation exchange and anion exchange ionomers of the same backbone chemistry: poly(phenylene alkylene). The authors use an earth abundant water dissociation catalyst, tin oxide ($SnO_2$), which was recently shown by Boettcher and co-workers to be highly active in BPMs (Nature Materials 2024). However, the work by Boettcher and co-workers used a cation exchange membrane (CEM) and an anion exchange membrane (AEM) of different backbone chemistries (unlike the work here). However, Boettcher and co-workers did make an all-hydrocarbon BPM (Nexar (Kraton Corporation)-Orion). This article is notable because it uses a BPM of the same polymer backbone chemistry, and this BPM shows one of the best water electrolysis performances (I believe the 2nd best value in the literature) and the best durability (up to 1000 hours). The remarkable durability is a product of using the same polymer backbone chemistry. Not only does the BPM show durability in a water electrolyzer, but it can be folded, crumpled, etc. and retain its integrity. Overall, I find the article suitable for Nature Communications after a revision.

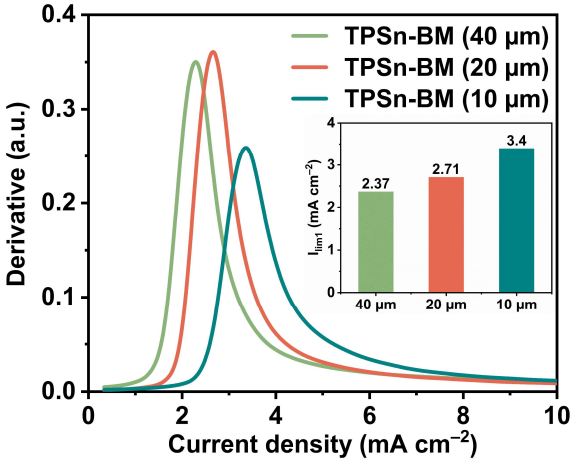
**Reply:** We greatly appreciate your positive feedback and profound comments to improve the readability and clarity of our manuscript. We have carefully considered your suggestions while revising the manuscript, and the changes made in the revised manuscript are highlighted.

***Q1:*** The derivative in the y-axes for Figure 3b and Figure S9b should have units on it.

**Reply:** Thanks. We have added units to the Figures 3b and S9b, as depicted in Fig. 3b in the revised manuscript (page 10) and Fig. S9b in the revised supplementary information (page 23), respectively.




**Revised Fig. 3b** The derivative curves of dU/dI as a function of current density of TPSn-BM and two commercial BPMs.




**Revised Fig. S9b** The derivative curves of dU/dI as a function of current density of the TPSn-BMs with different thicknesses.

***Q2:*** I understand why the authors decided to benchmark their BPM against the commercial variants by Fumatech and ASTOM corporation (Neosepta); however, these BPMs are not suitable for water electrolysis because they are not designed to operate at high current density. Using high current density can cause blistering in these materials. I suggest the authors make this point in their revised manuscript. I do appreciate how they have benchmarked their results against other experimental BPMs in the literature.

**Reply:** We appreciate your insightful comment regarding the benchmarking of our BPM against the commercial FumaTech FBM and Neosepta BP1. We agree that these BPMs are not specifically designed for high current density applications, which could indeed lead to performance issues such as interfacial blistering. In our revised manuscript, we have made the following adjustments to address your concern. We have discussed three main factors that restricting the performance of the existing commercial and research BPMs (on page 3). In light of your suggestion, we therefore compared the electrolyzer performance and stability of our BPM with numerous advanced BPMs reported in literature (including other electrolysis applications adopting BPMs). We have added related discussions in the revised manuscript, and hope these revision will enhance the clarity and significance of our findings in relation to the existing literature. We have included the following statement:

**Revised content (on page 16):** Notably, both the commercial Neosepta BP1 and FumaTech FBM are not custom-designed to operate at high current densities. Therefore, a comprehensive comparison of the electrolysis applications between our TPSn-BM and advanced BPMs reported in literature was made as depicted in Supplementary Table 4. The TPSn-BM shows competitive

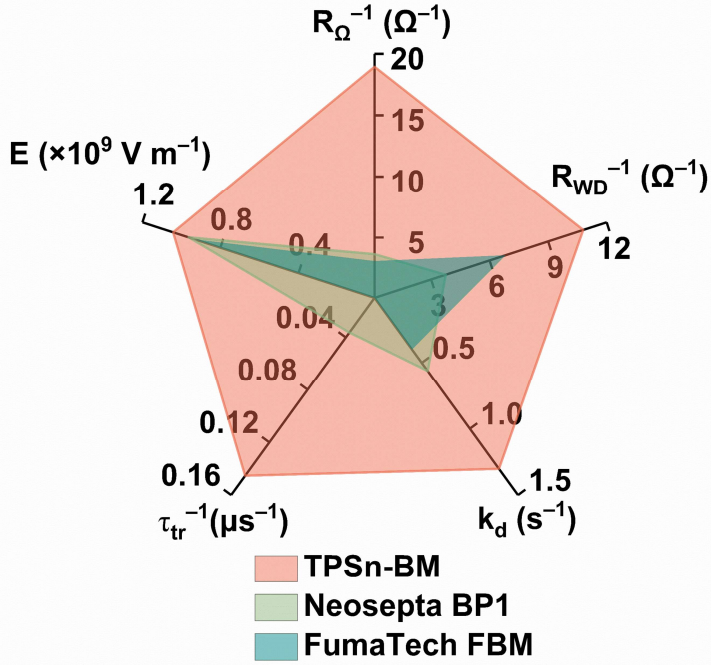
single-cell performance, with appropriate cell voltages for pure water electrolysis that are slightly higher than the BPMs fabricated by the Boettcher's group (e.g., 2.68 *vs.* ~ 2.35 V at current density of 1000 mA $cm^{-2}$).[37]

Supplementary Table 4 Comparison of BPM electrolyzer performance and stability.

| BPM-based application | Current density (mA $cm^{-2}$) | Operating time (h) | Temperature (°C) | Ref. |
|---|---|---|---|---|
| Water electrolysis | 300 ~ 500 | 1000 | 60 | This work |
| Water electrolysis (Acid-base feed) | 20 | 12 | 25 | Ref. 23 |
| Water electrolysis | 500 | – | 60 | Ref. 24 |
| Water electrolysis (Bipolar interface) | 400 | 500 | 80 | Ref. 25 |
| Water electrolysis | 1000 | 4 | 50 | Ref. 26 |
| Water electrolysis | 500 | – | 50 | Ref. 27 |
| Water electrolysis | 500 | ~ 60 | 55 | Ref. 28 |
| Ammonia electrosynthesis | 1000 | 110 | – | Ref. 8 |
| Ammonia electrosynthesis | 1000 | 210 | – | Ref. 9 |
| $CO_2$ electrolysis | 100 | 2.5 | – | Ref. 29 |
| $CO_2$ electrolysis | 300 | 25 | – | Ref. 30 |
| $CO_2$ electrolysis | 150 | 145 | – | Ref. 31 |
| $CO_2$ electrolysis | 300 | 14 | – | Ref. 32 |
| $CO_2$ electrolysis | 150 | 11 | – | Ref. 33 |

***Q3:*** I feel like the Spider chart (Figure 3e) is inappropriate as there is no agreed upon metrics for the $R_{wd}$, $R_{ohm}$, E, etc.

**Reply:** Thanks for your kind suggestion. We have added the explicit values of the $R_{WD}^{-1}$, $R_{\Omega}^{-1}$, $E$, $k_d$, $\tau_{tr}^{-1}$ in the revised Figure 3e, which facilitates the comparison of the relevant parameters between TPSn-BM and two commercial BPMs.




**Revised Fig. 3e** Comprehensive comparison of the water dissociation reaction and mass transport kinetics between the TPSn-BM and two commercial BPMs, where the values of $R_\Omega$, $R_{WD}$, and $\tau_{tr}$ were shown in reciprocal form.

***Q4:*** Regarding the impedance analysis, I feel that the electric circuit equivalent model used by the researchers, which was developed by Mallouk and co-workers, is incorrect or creates confusion. It is well-known that a plethora of electric circuit equivalent models can fit Nyquist plots. I don't know the differences (physics interpretation) for the reaction rate dissociation constant (kd), found from the Gerischer element, and the resistance for water dissociation (R_wd). These values both relate to the kinetics of water dissociation. Why are two circuit elements needed to describe water dissociation?

**Reply:** Thank you for your insightful comments regarding the electric circuit equivalent model used in our impedance analysis. We appreciate your observation about the potential confusion surrounding the use of the Gerischer element and the need for distinguishing between $k_d$ and $R_{WD}$. To clarify, the electric circuit equivalent model developed by Mallouk and co-workers incorporates a Gerischer element that coupling the diffusion boundary layer to a chemical reaction.[1] The rate constant $k_d$, derived from the Gerischer impedance, represents the effective water dissociation rate constant. This parameter describes the complete process including water dissociation at the bipolar junction and the ion transport through diffusion boundary layers. Therefore, the rate constant $k_d$ is influenced by both the catalytic properties and the ionic transport properties of the BPMs. In

contrast, the resistance for water dissociation ($R_{WD}$) extract from the semicircle region of the Nyquist plots specifically describes the water dissociation kinetics at the bipolar junction. This parameter is primarily determined by the water dissociation catalysts.[2] The adoption of both $k_d$ and $R_{WD}$ in our analysis is justified by the comprehensive understanding they provide about the water dissociation process. While $k_d$ accounts for the overall reaction and diffusion dynamics, $R_{WD}$ focuses specifically on the localized kinetics at the bipolar junction. Given that our study focuses on both the catalyst design and monopolar membrane layer engineering, the use of $k_d$ to provide a more nuanced understanding of the water dissociation behavior of the BPMs is warranted.

***Q5:*** How were the ionic transport times determined from the depletion layer? Does this also hail from Gerischer element?

**Reply:** We would like to clarify that the ionic transport times ($\tau_{tr}$) does not originate from the Gerischer element; rather, it is derived from the semicircle observed in the high-frequency region of the Nyquist plots. As outlined in the work of Kim and coworkers,[3] $\tau_{tr}$ reflects how quickly the produced ions are extracted from the ionic depletion layer and is calculated using the following equation:

$$\tau_{tr} = R_{WD} \times C \quad (R1)$$

where $C$ represents the capacitance of the ionic depletion layer, which can be expressed as:

$$C = {R_{WD}}^{(1-n)/n} \times Q^{1/n} \quad (R2)$$

where $Q$ is the pseudo-capacitance, $n$ is the order of (constant phase element) CPE, both of which are extracted from the the CPE element in the equivalent circuit.

We have supplemented the detailed equations in the revised supplymentary information for calculating the relevant parameters from the EIS spectra. The updated content on pages S9–S10 elaborates on the methodology as follows:

**Revised content (pages S9–S10):** EIS experiments were performed using an Autolab workstation (PGSTAT 302N, Metrohm, Netherlands) connected with Nova 2.1.2 software in galvanostatic (30 mA $cm^{-2}$) mode, spanning a frequency range from 100 kHz to 0.1 Hz. The acquired Nyquist plot was fitted using Z-view software based on an equivalent circuit, allowing to describe the ionic transportation and reaction kinetics at the BPM interface layer. This includes parameters such as ohmic resistance ($R_\Omega$, which represents the resistance from the membranes), water dissociation reaction resistance ($R_{WD}$), water dissociation constant ($k_d$), water dissociation electric intensity ($E$), thickness of the depletion region ($\lambda$), and ion transport time through the depletion region ($\tau_{tr}$). The

values for $R_{\Omega}$, $R_{WD}$, and $k_d$ were extracted directly from the equivalent circuit fitting results. The $\lambda$, $\tau_{tr}$, and $E$ were calculated using the following equations:

$$C = {R_{WD}}^{(1-n)/n} \times Q^{1/n} \quad (S5)$$

$$\lambda = \frac{\varepsilon_0 \times \varepsilon_r \times A_{ef}}{C} \quad (S6)$$

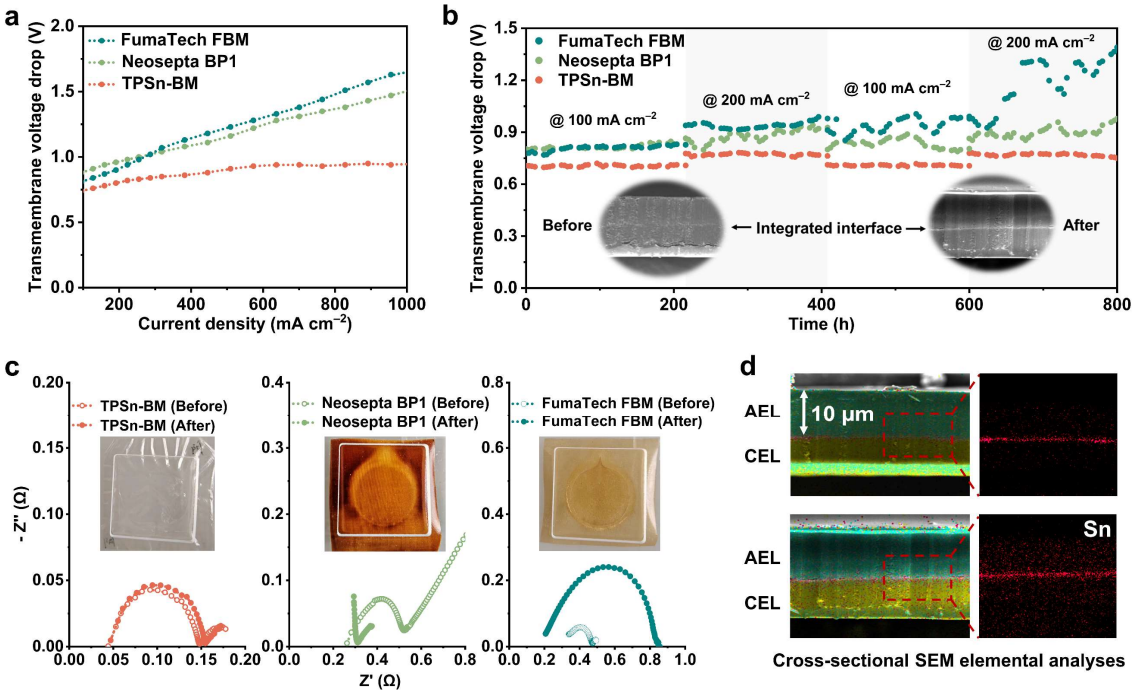
$$\tau_{tr} = R_{WD} \times C \quad (S7)$$

$$\frac{\mathrm{k}_d}{\mathrm{k}_0} = \exp\left[\frac{\alpha \mathrm{F}}{RT}\right] \quad (S8)$$

where $C$ represents the equivalent capacitance of the equivalent circuit, $Q$ and $n$ are the pseudo-capacitance and the order of constant phase element (CPE), as extracted from the CPE element in the equivalent circuit, $\varepsilon_0$ is the vacuum permittivity (8.854 × $10^{-12}$ F $m^{-1}$), $\varepsilon_r$ is the dielectric constant (here is 80 for water), $A_{ef}$ is the effective area of BPMs (here is 3.14 $cm^{-2}$), $\alpha$ is length factor of water dissociation reaction (2.73 × $10^{-10}$ m), $F$ is the faradaic constant (96485 C $mol^{-1}$), $R$ is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$), $T$ is the Kelvin temperature (298.15 K).

***Q6:*** In Figure 4, the placement of panel d becomes before panel c. Please reverse them.

**Reply:** Thanks. Done as requested.




**Revised Fig. 4** High current density performance and long-term stability of the BPMs. (a) *I–V* curves of the TPSn-BM and two commercial BPMs at a relatively high current density range of 100 ~ 1,000 mA $cm^{-2}$. (b) The transmembrane voltage of the BPMs as a function of continuous water dissociation (under dynamic switching current densities of 100 and 200 mA $cm^{-2}$) time. (c) The EIS

Nyquist plots of the BPMs before and after the long-term water dissociation operation. Insets show their photographs after the stability test. (d) SEM cross-sectional elemental mappings of the TPSn-BM before (upper) and after (below) the long-term water dissociation operation.

**For Reviewer #2**

***General:*** The authors report high-performing and durable BPM design for water electrolysis. In my view, this is a very interesting study, therefore I recommend publication after addressing my comments below.

**Reply:** We greatly appreciate your valuable time and positive feedback. According to your comments, we have added more discussions and addressed your concerns point-by-point, as listed below. The changes made in the revised manuscript are highlighted.

***Q1:*** The authors argue that the benefit of using reverse bias BPM electrolyzer for water electrolysis application is to leverage the kinetic benefits of alkaline OER and acidic HER. That will make sense on the surface, however, it does come with penalty of voltage loss in water dissociation. Compared to emerging technology for instance, anion exchange membrane water electrolysis, which essentially has the same anode compared to BPM water electrolyzer but an alkaline HER reaction. Of course, it is well known that alkaline HER is more sluggish compared to acidic HER. If the voltage penalty from water dissociation significantly surpasses the voltage penalty by switching from acidic HER to alkaline HER, then BPM water electrolyzer will never be as efficient as anion-exchange membrane water electrolyzer. Now the question is that, does it really make sense to spend effort developing BPM water electrolyzers? From what is shown here, the onset of water dissociation reaction (figure 4a) is at minimum of 0.75 V, which I believe is much higher than the voltage penalty by switching from acidic HER to alkaline HER. The authors should comment on this aspect in the manuscript and compared the base BPM water electrolyzer performance with anion exchange membrane water electrolyzer under similar condition to show how much of a performance gap needs to be bridged.

**Reply:** Thank you for your thoughtful comments on the efficiency of BPM water electrolyzers (BPMWEs) compared to anion exchange membrane water electrolyzers (AEMWEs). We appreciate the opportunity to clarify several key points regarding their performance and the rationale for our research focus.

As you noted, both the BPMWEs and AEMWEs (or proton exchange membrane water electrolyzers, PEMWEs) have a thermodynamically similar water electrolysis voltage of 1.23 V.[4] The relevant reactions for AEMWEs and their corresponding thermodynamic potentials are as follows:

$$\text{cathode: } 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \qquad E^0 = -0.83 \text{ V vs. SHE}$$

$$\text{anode: } 4OH^- \rightarrow 2H_2O + O_2 + 4e^- \qquad E^0 = 0.40 \text{ V vs. SHE}$$

$$\text{total: } 2H_2O \rightarrow 2H_2 + O_2 \quad E^0_{total} = 1.23 \text{ V vs. SHE}$$

For BPMWEs, the reactions are as foliows:

$$\text{BPM interface: } 2H_2O \rightarrow 4H^+ + 4OH^- \quad E^0_{WD} = -0.83 \text{ V vs. SHE}$$

$$\text{cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \quad E^0 = 0.00 \text{ V vs. SHE}$$

$$\text{anode: } 4OH^- \rightarrow 2H_2O + O_2 + 4e^- \quad E^0 = 0.40 \text{ V vs. SHE}$$

$$\text{total: } 2H_2O \rightarrow 2H_2 + O_2 \quad E^0_{total} = 1.23 \text{ V vs. SHE}$$

This indicates that both technologies have the potential to achieve similar energy efficiencies under optimal conditions. However, AEMWEs primarily achieve high performance by using alkaline feed solutions, which create a kinetics-favorable environment for oxygen evolution reaction (OER). In contrast, BPMWEs present significant advantages for pure water electrolysis. They can operate without the need for additional alkaline or acidic feed solutions, due to the in-situ generation of $H^+$ and $OH^-$ ions during the electrolysis process. This unique capability not only simplifies the system but also optimizes the electro-kinetics for the electrode reactions, which is beneficial for long-duration operation. While we acknowledge that the current performance of BPMWEs may be lower than that of AEMWEs, we believe that the challenges posed by substantial overpotentials for water dissociation at the BPM interfacial layer and mass transport limitations (ions and water) through the monopolar membrane layers are surmountable through the development of high-performance BPMs. We are encouraged by recent advancements, such as the work by Sasmal et al., which demonstrated that tailored BPMs can achieve lower voltages in pure water electrolysis compared to AEM-based systems, although long-term durability remains a challenge.[5] Hence, Our ongoing research aims to address these challenges associated with water dissociation at the BPM interfacial layer and improving mass transport and membrane durability for pure water electrolysis. Accoding to your suggestion, we have added relevant discussions in the revised manuscript.

**Revised content (page 17):** We acknowledge that the water electrolysis performance presented in this study requires further improvement to compete with emerging technologies, such as anion- and proton-exchange membrane water electrolyzers (PEMWEs and AEMWEs), which can achieve higher current densities exceeding 10 A $cm^{-2}$ under similar cell voltage conditions.[41,42] Current studies on PEMWEs and AEMWEs often use acidic or alkaline feeds to optimize reaction kinetics, which can lead to accelerated degradation of the electrolyzers. In contrast, BPMWEs present significant advantages for pure water electrolysis. They can operate without the need for additional alkaline or acidic feed solutions, making them particularly attractive for applications requiring high purity water. The TPSn-BM demonstrates substantial potential for long-endurance pure water

electrolysis, highlighting the unique advantages of BPMWEs in utilizing pure water without additional feed solutions.

***Q2:*** I am a little confused on how the EIS is measured, for instance, in figure 3d. The measurement was done in a 4-electrode setup (figure s8) with two identical reference measuring the transmembrane potential, however, the current was applied between the anode and cathode. Theoretically, it is still possible to apply a current perturbation and measure the voltage response. However, in practical case, this is rather challenging. I imagine one would need to potentiostat to do so and it has to be perfectly coordinated? Any case, more illustration and experimental details and measured data should be shown.

**Reply:** We appreciate your thorough examination of our experimental setup and your interest in understanding the details involved. The EIS measurements were carried out with a potentiostat (Autolab electrochemical workstation, PGSTAT 302N, Metrohm, Netherlands) as we described in the Experimental methods section. The EIS measurements were performed in galvanostatic mode. Upon applying a direct current, an alternating current perturbation was superimposed using the potentiostat, allowing us to measure the voltage response effectively. We understand the concern regarding the need for precise coordination in this setup. The potentiostat indeed facilitates the control of current and voltage, making it possible to accurately capture the impedance response of the system during the measurements.

In response to your suggestions, we have added more detailed description and improved the schematic illustration in the revised supplementary information.

**Revised content (pages S9–S10):** EIS experiments were performed using an Autolab workstation (PGSTAT 302N, Metrohm, Netherlands) connected with Nova 2.1.2 software in galvanostatic (30 mA $cm^{-2}$) mode, spanning a frequency range from 100 kHz to 0.1 Hz. The acquired Nyquist plot was fitted using Z-view software based on an equivalent circuit, allowing to describe the ionic transportation and reaction kinetics at the BPM interface layer. This includes parameters such as ohmic resistance ($R_\Omega$, which represents the resistance from the membranes), water dissociation reaction resistance ($R_{WD}$), water dissociation constant ($k_d$), water dissociation electric intensity ($E$), thickness of the depletion region ($\lambda$), and ion transport time through the depletion region ($\tau_{tr}$). The values for $R_\Omega$, $R_{WD}$, and $k_d$ were extracted directly from the equivalent circuit fitting results. The $\lambda$, $\tau_{tr}$, and $E$ were calculated using the following equations:

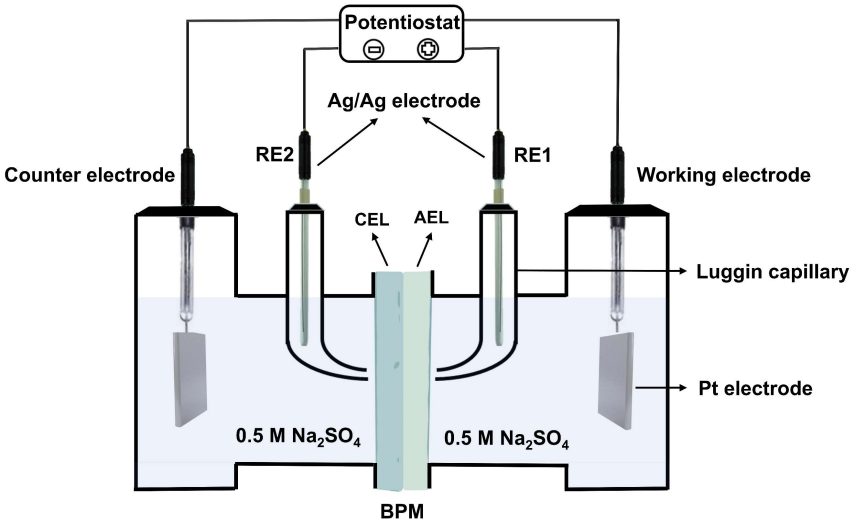
$$C = {R_{WD}}^{(1-n)/n} \times Q^{1/n} \quad (S5)$$

$$\lambda = \frac{\varepsilon_0 \times \varepsilon_r \times A_{ef}}{C} \quad (S6)$$

$$\tau_{tr} = R_{WD} \times C \quad (S7)$$

$$\frac{k_d}{k_0} = \exp\left[\frac{\alpha F}{RT}\right] \quad (S8)$$

where *C* represents the equivalent capacitance of the equivalent circuit, *Q* and *n* are the pseudo-capacitance and the order of constant phase element (CPE), as extracted from the CPE element in the equivalent circuit, $\varepsilon_0$ is the vacuum permittivity (8.854 × $10^{-12}$ F $m^{-1}$), $\varepsilon_r$ is the dielectric constant (here is 80 for water), $A_{ef}$ is the effective area of BPMs (here is 3.14 $cm^{-2}$), $\alpha$ is length factor of water dissociation reaction (2.73 × $10^{-10}$ m), *F* is the faradaic constant (96485 C $mol^{-1}$), *R* is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$), *T* is the Kelvin temperature (298.15 K).




**Revised Supplementary Fig. 8** Schematic illumination of the custom-made four-electrode setup for *I–V* and EIS measurements. During the electrochemical measurements, the BPMs were stuck in the middle of two symmetrical compartments with an effective area of 3.14 $cm^2$, both the two compartments filled with 0.5 mol $L^{-1}$ aq. $Na_2SO_4$. Two Pt electrodes placed outboard act as working electrode and counter electrode. Two reference electrodes (Ag/AgCl) were respectively placed inside the Luggin capillary that contacts the surface of BPMs. During long-term operation, electrolytes of both sides were fully circulated and refreshed to minimize the effects of polarization.

***Q3:*** Figure 4d, it looks like there is quite a bit Sn redistribution after 800 h durability operation, yet, negligible impacts on cell performance is observed. Does it mean the WD catalyst ($SnO_2$) has no impact on performance? Any evidence on that? From what I know in many literature, the WD performance is very sensitive to WD catalyst loadings. Also, the authors conclude the Sn redistribution is due to migration of catalyst nanoparticles. Can the author show if the $SnO_2$ particles

have changed morphology before and after operation? It will be important to know if this is just due to migration or due to any sort of dissolution and redeposition. Simply based on Sn Pourbaix diagram, Sn is not stable in neither acid or base condition.

**Reply:** Thanks for your comments. As noted in the manuscript, we did observe the redistribution of $SnO_2$ catalysts within the BPM after long-term operation. While the mechanism behind this redistribution is complex, we believe that the observed minimal impact on cell performance could be attributed to the inherent robustness of the BPM design and improved interface compatibility, which we have optimized in this study. However, we recognize that further investigation into the relationship between $SnO_2$ catalyst loading and performance is essential, as existing literature indeed highlights this sensitivity.

We acknowledge your request for evidence to differentiate between catalyst migration and potential dissolution/re-deposition. Unfortunately, we currently lack precise *in-situ* characterization technologies necessary to fully elucidate this mechanism. Previous studies have illuminated that the interface issues (blistering and delamination) will reduce the lifespan of BPMs even to less than a hundred hours, and the short-term interface issues are more likely to be attributed to physical losses. At the present study, we have dramatically increased the durability of BPMs to nearly a thousand hours by improving the bipolar interface compatibility. This is an important aspect of our ongoing research, and we aim to incorporate advanced imaging and operando techniques in future studies to investigate changes in $SnO_2$ morphology before and after operation.

Your comment regarding the instability of Sn in both acidic and basic conditions is well-taken. While the Pourbaix diagram indicates that Sn may not be stable under these conditions, our observations suggest that the performance of the BPM can still be maintained despite the redistribution. This could imply that the $SnO_2$ remains functionally active, likely due to the quick migration of $H^+$ and $OH^-$ out of the interface layer under a reverse bias. Further studies are needed to validate this hypothesis and understand the detailed mechanisms involved.

***Q4:*** I am also confused on how the authors can achieve an onset of ~ 1.5 V for water electrolysis in figure 5d, while the onset of WD reaction is about 0.75 V for the BPM developed. The onset of water electrolysis should at least be 1.23 V+ 0.75 V assuming there is no loss for anode and cathode reactions.

**Reply:** Thanks. As we demonstrated in our response to Q1, the theoretically water electrolysis voltage for BPMs is indeed 1.23 V. The reactions in BPMWEs and their corresponding

thermodynamic potentials are as follows:

$$\text{BPM interface: } 2H_2O \rightarrow 4H^+ + 4OH^- \quad E^0_{WD} = -0.83 \text{ V vs. SHE}$$

$$\text{cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \quad E^0 = 0.00 \text{ V vs. SHE}$$

$$\text{anode: } 4OH^- \rightarrow 2H_2O + O_2 + 4e^- \quad E^0 = 0.40 \text{ V vs. SHE}$$

$$\text{total: } 2H_2O \rightarrow 2H_2 + O_2 \quad E^0_{total} = 1.23 \text{ V vs. SHE}$$

The observed onset voltage of ~ 1.5 V reflects not only the theoretical electrolysis voltage but also additional overpotentials due to various factors such as kinetic limitations, ohmic losses, and potentially the pH gradient across the BPM. Thermodynamically, the potential drop associated with the pH gradient across the BPM is compenstaed by the Nernstian shifts in the formal potentials of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). This results in an effective potential requirement similar to that of monopolar membranes under practical operating conditions.[4] Therefore, while the theoretical minimum voltage for water electrolysis is 1.23 V, the practical onset voltage can be higher due to the aftorementioned factors. This difference between the expected voltage and the observed onset voltage reflects the real-world complexities involved in electrochemical processes.

***Q5:*** Page 10, from the EIS measurement shown in figure 3d, the authors conclude that the highly integrated BPM junction and well-performed $SnO_2$ catalyst explains the performance superiority of the TPSn-BPM compared to Neosepta BP1 and FumaTech BPM. First, there looks to be a few typo in the legend of figure 3d: for instance FumaTech BPM not Fumatech FBM? Second, did I understand it correctly that the Neosepta BPM and Fumatech BPM did not use the same $SnO_2$ catalyst? If so, how can we know how much of the performance improvement is due to the BPM by itself and how much performance improvement is due to the WD catalyst difference? Can it be just due to the catalyst difference so the BPM doesn't matter? Lastly, I feel unclearly about what the "highly integrated" exactly means. This looks to be the most interesting aspect of this work, however, it is not well understood how and why the "highly integrated" is achieved.

**Reply:** Thank you for your thoughtful and constructive comments. The correct designation is indeed “FumaTech FBM. ”“FBM” refers to a commercial bipolar membrane produced by Fumatech BWT GmbH, a recognized manufacturer in the field. You are correct in noting that the specific water dissociation catalysts employed in the commercial Neosepta BP1 and FumaTech BPM remain undisclosed due to proprietary reasons. While $SnO_2$ has been recognized as an effective water dissociation catalyst. It is important to emphasize that the performance of BPMs is influenced

significantly by the characteristics of both the catalyst and monopolar membrane layers. Our study confirmed through theoretical and experimental investigations that variations in the thickness and properties of monopolar membrane layers can result in substantial differences in BPM performance, especially regarding long-term stability. To illustrate this point, we referenced the work by by Boettcher and co-workers, who used $SnO_2$ nanoparticles as water disscociation catalyst.[5] Their BPM, which featured different monopolar membrane materials different from ours, exhibited a water electrolysis stability of only 100 hours. This highlights the critical role of monopolar membrane layer engineering in determining the overall performance and durability of the BPM. Lastly, "highly integrated" referes to the tightly integration of the bipolar interface between the anion- and cation-exchange layers (AEL–CEL). A key highlight of our study is that both layers share the same polymeric skeleton, which enhances interfacial compatibility. This compatibility fosters a stable and cohesive interface, contributing to the overall performance and durability of the BPM.

In light of your comments, we will include more detailed explanations and revisions in the manuscript to ensure clarity regarding these critical aspects. We greatly appreciate your effort in reviewing our work.

**Revised and emphasized content:** (1) Commercial Neosepta BP1 (ASTOM Corporation, Japan) and FumaTech FBM (FUMATECH BWT GmbH, Germany) were purchased and used as standard bipolar membranes for comparison purposes (page S4, revised supplementary information).

(2) As shown in Supplementary Fig. 7a, the cross-sectional SEM image suggests a tightly integrated AEL–CEL interfacial junction, which is attributed to the high compatibility between the monopolar membrane layers (page 9, revised manuscript).

(3) Although there have been several studies on BPM electrolyzers for ampere-level pure water electrolysis, their operational lifespan has mostly not been reported, and there are currently no cases (including which ones adopt $SnO_2$ nanoparticles as the water dissociation catalyst) of continuous operation over hundreds of hours (Supplementary Table 4)[37–40].

(4) The exceptional stability of the TPSn-BM results from the synergistic effect of the following two factors: on the one hand, the highly compatible polymeric matrix of AEL and CEL endows TPSn-BM with a tightly integrated dipolar interface; on the other hand, fast water transport is brilliant for alleviating the interface drying incurred by insufficient water replenishment. For verification, changes in the interfacial morphology of the TPSn-BM were illuminated via SEM images. As shown in Fig. 4d and Supplementary Fig. 11, TPSn-BM maintains an unblemished interface layer after the stability test for up to 800 h (page 12, revised manuscript).

**For Reviewer #3**

***General:*** The manuscript ”Tailoring high-performance bipolar membrane for durable pure water electrolysis” by Yu et al. describes the bottom-up fabrication of a $SnO_2$ catalyzed bipolar membrane based on quaternary ammonium and sulfonic acid functionalized poly(arylene alkylene)s. The work is highly relevant, as new bipolar membranes that can support high current densities at low resistance could open new avenues in water electrolysis and $CO_2$ capture and utilization. The authors take an interesting approach by combining a good water dissociation catalyst with anion/cation exchange membrane layers combining high conductivity, fast water diffusion and good stability. The bipolar system shows good performance stability over 1000 h at device level in water electrolysis mode, which is a significant advancement of the technology. The work is mostly scientifically sound, but I would recommend the authors to address the feedback below in a revised version:

**Reply:** We greatly appreciate your positive feedback and profound comments to improve our manuscript. According to your comments, we have added more discussions and addressed your concerns point-by-point, as listed below. The changes made in the revised manuscript are highlighted.

***Q1:*** The modeling section is rather superficial, and it is unclear how the modeling results are used to guide the experimental work and how it contributes to the interpretation of the experimental results. The scientific value of this part is thus quite limited. I encourage the authors to make more active use of the modeling and simulation results, and to extend this part if that is needed to support the discussion around the experimental results.

**Reply:** Thanks for your constructive feedback regarding the modeling section. In our study, we performed numerical simulations in an effort primarily for disclosing the limiting factors affecting BPM performance at high current densities. This was aim at guiding the design of BPMs form a membrane layer engineering perspective. Specifically, we investigated the effects of ion exchange capacity (IEC) and thickness of membrane layers (the two most critical factors determining the mass transport properties) on BPM water dissociation performance. Based on the insights gained from our modeling, we tailored the monopolar membrane layers with relatively higher IEC (which leads to fast water and ions transport capacities) and fabricated the BPMs with relatively thin thickness than that of the commercial BPMs. These measures were confirmed to accelerate the water replenishment at the BPM interface and ion migrate outward the membrane layes, thus

improving the water dissociation efficiency.

In response to your valuable suggestions, we have expanded the discussions about the modeling and numerical investigations in the revised manuscript. Key revision include:

**Revised content:** (1) Modeling and numerical simulations are first performed to analyze the polarization and mass transfer behavior of BPMs, aiming to theoretically instruct the membrane layer engineering (page 4).

(2) Instructed by the numerical studies, we tailored the IEC of the AEM and PEM to relatively higher values of ~ 2.0 and ~ 2.2 (all active sites on the side chain were ionized to obtain the highest IEC values for the present structures), respectively (page 7).

(3) Notably, the fabricated BPMs are thinner than most of commercially available and reported BPMs, which is anticipated to increase the mass (ion and water) transport (as illuminated by the numerical studies) (page 8).

***Q2:*** Figure 3c: The comparison with the literature data in this figure is not straightforward, because the results in the different studies depend largely on the specific conditions used. There is not much scientific value in such a comparison. I would recommend the authors to move this figure to the supplementary information, and to include details about the specific experimental conditions behind the literature data points (including references to the original work).

**Reply:** Thanks for your kind suggestion. We understand that the results from different studies can depend heavily on specific experimental conditions, which may complicate direct comparisons. According to your suggestion, we have provided a detailed water dissociation performance comparison (including references to the original literature) in the revised supplementary information (Supplementary Table 3). Notably, we have decided to retain Figure 3c in the main manuscript, as it illustrates the comparison of transmembrane voltages at a current density of 100 mA $cm^{-2}$ ($U_{100}$) and first limiting current density ($I_{lim1}$). These two parameters are widely recognized as universal indicators for evaluating BPM performance. Typically, these measurements are conducted using unified experimental procedures with a four-electrode setup, which allows for a more standardized comparion. By keeping Figure 3c, we aim to facilitate an intuitive comparison between our BPMs and competitors reported in the literature. We believe this visual representation is beneficial for readers to quickly assess the performance of our BPMs in relation to existing data.

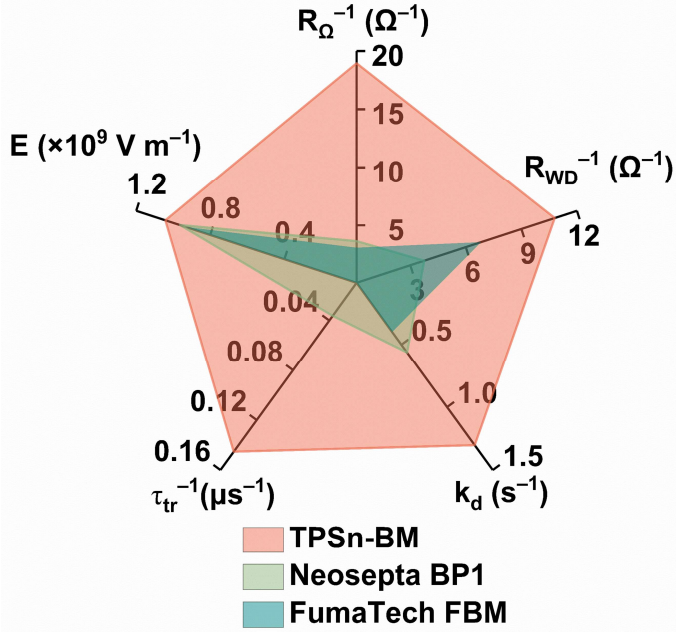
Supplementary Table 3 Comparison of BPM water dissociation performance.

| Parameter | $I_{lim1}$ (mA cm$^{-2}$) | $U_{100}$ (V) | Ref. |
|---|---|---|---|
| TPSn-BM | 2.71 | 0.71 | This work |
| FumaTech FBM | 7.81 | 0.81 | Commercial |
| Neosepta BP1 | 2.71 | 0.88 | Commercial |
| $Fe_2O_3$@GO | – | 0.89 | Ref. 4 |
| PIL-BPM | 9.62 | 1.87 | Ref. 5 |
| BPM-2D | 5.5 | 1.2 | Ref. 6 |
| BPM-3D | 5.9 | 0.95 | Ref. 6 |
| 0.5hFCBM | 5.4 | 0.75 | Ref. 7 |
| MBM | 4 | 0.76 | Ref. 8 |
| CIBM | 3.43 | 1.1 | Ref. 9 |
| SBM-NC2.0 | 5 | 1.4 | Ref. 10 |
| SBM-D1.0 | 1.22 | 2.4 | Ref. 10 |
| SCBM | 6 | 1.1 | Ref. 11 |
| Fe(III)@PEI BPM | 25 | 1.8 | Ref. 12 |
| Co-electrospun 3D bpm | 5 | 1 | Ref. 13 |
| 4GO-BPM | 3 | 1.45 | Ref. 14 |
| LBL film | 3 | 1.6 | Ref. 15 |
| GO-BPM | 0.5 | 2.2 | Ref. 16 |
| MIL 101-BPM | 19 | 4.2 | Ref. 17 |
| EBPM-2 | 10.5 | 2.4 | Ref. 18 |
| Intermediate BPM | 7 | 3.9 | Ref. 19 |
| LBL interface BPM | 8 | 3.8 | Ref. 19 |
| LBL & intermediate BPM | 10 | 2.1 | Ref. 19 |
| BiOCl/BPM (irradiation) | 7 | 5.2 | Ref. 20 |
| BiOCl/BPM (no irradiation) | 7 | 6 | Ref. 20 |
| I-BiOCl BPM | 9 | 5.1 | Ref. 20 |
| BPM-ZrOH | 0.424 | 9 | Ref. 21 |
| BPM-SiOH | 0.5 | 10 | Ref. 21 |
| BPM-TiOH | 0.46 | 12 | Ref. 21 |
| BPM-2000 | 0.48 | 3.6 | Ref. 22 |
| BPM-3400 | 0.53 | 3.5 | Ref. 22 |

***Q3:*** Figure 3e: It is unclear how this plot should be interpreted. It looks like an attempt to compare different parameters of the in-house made BPM with commercially available reference materials. I

would recommend the authors to plot this in a way that allows for quantitative scales on the different axis. It is also unclear how the water dissociation constant, water dissociation electric intensity and ion transport time through the depletion region are obtained. It is stated in the experimental part in the supporting information that they are extracted from the EIS data, but there are no details about how this is done. This must be described.

**Reply:** Thanks for your kind suggestions. According to your suggestion, we have added the explicit values of the different parameters in the revised Figure 3e, which facilitates the comparison between TPSn-BM and two commercial BPMs. In addition, more detailed descriptions of the calculation of these parameters were added in the revised Supplementary Information.




**Revised Fig. 3e** Comprehensive comparison of the water dissociation reaction and mass transport kinetics between the TPSn-BM and two commercial BPMs, where the values of $R_\Omega$, $R_{WD}$, and $\tau_{tr}$ were shown in reciprocal form.

***Q4:*** Figure 5f: Please provide details about specific test conditions. Is this recorded in pure water or in aqueous acid/base?

**Reply:** Thanks for your kind suggestion. The long-term stability tests (Fig. 5f) were carried out with pure water feed. We have provided details about the test conditions in the revised manuscript.

***Q5:*** Heading "Discussion" should be "Conclusion"

**Reply:** Thanks. We would like to clarify that the heading "Discussion" follows the standard

formatting guidelines established by the journal, and we are unable to make changes to the headings. We appreciate your understanding in this matter.

**References**


1. Yan, Z. *et al.* The balance of electric field and interfacial catalysis in promoting water dissociation in bipolar membranes. *Energy Environ. Sci.* **11**, 2235–2245 (2018).
2. Blommaert, M. A., Vermaas, D. A., Izelaar, B., Veen, B. I. & Smith, W. A. Electrochemical impedance spectroscopy as a performance indicator of water dissociation in bipolar membranes. *J. Mater. Chem. A* **7**, 19060–19069 (2019).
3. Kim, B. S. *et al.* Bipolar membranes to promote formation of tight ice-like water for efficient and sustainable water splitting. *Small* **16**, 2002641 (2020).
4. Oener, S. Z., Ardo, S. & Boettcher, S. W. Ionic processes in water electrolysis: The roleof ion-selective membranes. *ACS Energy Lett.* **2**, 2625−2634 (2017).
5. Sasmal, S. et al. Materials descriptors for advanced water dissociation catalysts in bipolar membranes. *Nat. Mater.* (2024). https://doi.org/10.1038/s41563-024-01943-8

**For Reviewer #1**

***General:*** I appreciate the authors' response letter and revised manuscript. I recommend the article for publication in Nature Communications without any further revisions.

**Reply:** Thanks. We greatly appreciate your positive feedback our manuscript.

**For Reviewer #2**

***General:*** The authors have addressed most of my previous comments. I suggest the publication without further review needed. One minor comment is about the statement that: Current studies on PEMWEs and AEMWEs often use acidic or alkaline feeds to optimize reaction kinetics, which can lead to accelerated degradation of the electrolyzers. PEMWEs do not need acidic feeds but pure water.

**Reply:** Thanks. We greatly appreciate your valuable time and positive feedback. We have removed the inaccurate statement.

**For Reviewer #3**

***General:*** The authors have carfefully considered the feedback from the reviewers, and taken appropriate actions to revise the manuscript. The discussion is scientifically sound and the conclusions are well supported by experimental data. The bipolar membranes with anion/cation exchange layers derived from poly(arylene alkylene)s, as described in this work, combine excellent polarization performance and performance stability. The results are of significance for various electrochemical applications where bipolar membranes are used, including acid/base generation, electrolysis, and $CO_2$ capture/conversion. I am willing to support publication in the present form.

**Reply:** Thanks. We greatly appreciate your positive feedback and profound comments to improve our manuscript.