

Peer Review File

Local ionic transport enables selective PGM-free bipolar membrane electrode assembly



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors explore the impact of ion transport in enhancing CO₂ conversion efficiency in BPM-based electrolyzers. They do this via both computational and experimental approaches. Their findings indicate that incorporating anion-exchange ionomer enhances local bicarbonate availability and proton transference number, thereby increasing reverted CO₂ levels and improving faradaic efficiency towards CO. The following comments need to be addressed before publication in Nature Communications.

1. On page 4, line 100, the authors discuss local ion transport within the catalyst layers. However, the emphasis of the study predominantly centers on ion transport across the membrane and between the membrane interface and cathode surface, rather than within the catalyst layers themselves. I recommend that the authors amend the description to enhance clarity.

2. What primary factor influenced the CO₂-to-CO performance through the optimization of ionomer types? One possible factor could be the improvement in the local environment, facilitating the transport of CO₂ gas. Another factor highlighted by the authors is the presence of reverted CO₂ at the catalyst-electrolyte interface. Further discussion on these factors is suggested. Are there any experiments that could help distinguish between these two effects?

3. In the field of CO₂RR, the majority of reported performances have achieved over 90% FE for CO production across a wide range of current densities. However, the authors in this study were only able to achieve less than 50% FE at current densities exceeding 200 mA/cm², despite utilizing optimized ionomer. This raises the question: what factors may have contributed to this discrepancy in performance compared to existing research?

4. Enhancing the H⁺ transference number is crucial for maximizing the availability of CO₂ at the cathode layer and improving the efficiency of CO₂-to-CO conversion. Apart from the KOH concentration on the anode side, which influences the H⁺ transference number, are there any other factors contributing to values below 1?

5. In previous work (Xie, K. et al.; Nat. Commun. 13, 3609 (2022)), the authors reported that the use of interposer mainly increased carbon utilization. But from Fig. 4c, the authors did not obtain similar results? Any explanation about this? Did the authors try other interposers rather than PVDF (different thicknesses, material types, etc.) to further enhance the performance?

6. Did the direct attachment of the interposer to the CEL impact the H⁺ transference number? If so, what was the nature of this influence?

7. During the stability test, as mentioned on Page 12, line 311, the authors attributed the degradation of the cell primarily to the instability of the catalyst layer in the acidic environment, particularly where the catalyst layer is attached to the CEL. Have the authors experimented with incorporating a spacer covering the catalyst layer to potentially enhance stability?

8. On Page 12, line 320, the authors highlighted the significance of a certain level of K⁺ crossover for activating CO₂ reduction. However, excessive K⁺ crossover can diminish the H⁺ transference number and promote salt precipitation. How can this challenge be addressed effectively?

9. Figure 5b showed the pressure build up is due to salt precipitation. Why does the use of BPM still have such a significant salt precipitation? The H⁺ on the CEL/CL interface is supposed to couple with (bi)carbonate to regenerate CO₂.

10. The stability of this system remains a significant challenge. Do the authors have any insights or suggestions on further enhancing the system's stability?

Reviewer #2 (Remarks to the Author):

The manuscript highlights some of the challenges associated with use of monopolar ion-exchange

membrane for electrochemical conversion of CO₂. While using bi-polar membrane (BPM) address or avoid these issues, significantly higher potential and longer-term structural stability of BPM yet to be established for larger-scale application. Particularly higher cell potential from configuration with BPM poses severe techno-economic feasibility challenges for such design.

Research work presented in this manuscript provides some insights into ion transference number of the BPM and local ion transport within the catalyst layers. This is a novel study and can provide helpful insights into developing future BPM with reduced potential and improved structural stability. This would be a timely publication in the field considering the research interest on BPM-configured electrolyzers. I recommend publishing this manuscript with minor modifications on following aspects:

#1. Bulk average (physical and transport) properties of CEL and AEL are used in the model. The degree of cross-linking of polymer backbone and extent of functionalization (in both CEL and AEL) are expected to change ion-transference number as well as local ion transport through these layers. Wouldn't it be beneficial to include these aspects into the model?

#2. Does ion transference number and local ion transport have any effect on Ohmic losses associated with the BPM? Any opportunity to reduce such losses?

#3. Is there any penalty in full-cell potential due to pH gradient between cathode and anode? Additional discussion on this aspect will be beneficial.

#4. While BPM configuration help avoiding/minimizing cathode salt precipitation or use of non-PGM anode, the higher full-cell potential makes BPM-configuration less attractive from operational cost perspectives. It would be beneficial for the future readers if a short discussion is added on potential penalty associated with using BPM.

Reviewer #3 (Remarks to the Author):

In the manuscript by Li et al., the authors presented a PGM-free bipolar membrane (BPM) electrode assembly for a CO₂ electrolyzer. Through transport modelling and experiments, the authors found that anion-exchange ionomers in the catalyst layer increased local bicarbonate availability and that increasing the proton transfer number in the BPM increased CO₂ regeneration and limited K⁺ concentration in the cathode region. The uniform local distribution of bicarbonate ions increased the accessibility of reverted CO₂ to the catalyst surface. However, some important issues need to be addressed adequately to reveal new insights or fundamental science to advance the field. The content of the article needs to be major revised and demonstrated for the improvement of the manuscript quality.

1. One of the major advances in this work is the PGM-free BPMEA configuration for a CO₂ electrolyzer, here, the author emphasized the vital role of managing ionic species to improve CO₂ conversion efficiency while preventing acidification of the anodic compartment. However, there are many studies on BPM in the CO₂ electrolyzer. And we also noticed that the author's team had previously applied bipolar membrane electrode assemblies to CO₂ electrolysis and achieved an increase in CO₂ utilization (ACS Energy Lett. 2021, 6, 4291–4298.). Additionally, in this reviewer's opinion, we recommend that the authors compare previous work with similar designs and performance to emphasize the scientific advance and innovation of this study.

2. The author's summary of the current technical barriers to the application of BPMEA electrolytic cells in electrocatalytic CO₂ reduction is incomplete. For example, under the reverse bias, generally, the

BPM needs the water dissociation catalyst which can reduce the overpotential. Therefore, the authors should discuss more about the potential limitations of the BPM configuration.

3. The authors made substantial efforts in this work, with insights into several aspects of CO₂ electrocatalysis, from the reaction system design to the selection of the catalyst (PGM-free anode catalyst). However, I do not think the PGM-free system is a point. Ni/Fe oxides have been widely used as the OER catalysts. The authors should build their paper around the BPM reaction systems.

4. The author believes that there is a difference in equivalents between Nafion and Sustainion. Why not choose the same equivalents for performance comparison? So I think you should choose the same equivalent for ionomers.

5. Authors should perform relevant characterization of the prepared materials, even if they have been reported.

6. Here, we noticed that in the PGM-free BPMEA cell system developed by the author, its stability for 150 hours is unsatisfactory, and its CO selectivity drops significantly. (Energy Technol. 2017, 5, 929.) has reported up to 4000 h and (Nat Commun. 2021, 12, 5223) has reported up to 2400 h. Therefore, the reasons for poor system stability should be taken seriously, such as catalyst deactivation, membrane failure, carbonate deposition, etc., we suggest that the authors provide intuitive experimental evidence to explain this.

7. We believe that the author's pH measurement of the electrolyte after the reaction is incomplete in describing and inferring some ion migration processes during the reaction. Some in-situ testing methods, such as in-situ infrared spectroscopy or Raman, should be established to reveal some pH changes at the CL interface during the reaction.

8. We recommend that the authors add calculation details for parameters such as ionic current, K⁺ and CO₂ crossover rates because the qualitative and quantitative analysis of this parameter is crucial in this study.

Reviewer #1

The authors explore the impact of ion transport in enhancing CO₂ conversion efficiency in BPM-based electrolyzers. They do this via both computational and experimental approaches. Their findings indicate that incorporating anion-exchange ionomer enhances local bicarbonate availability and proton transference number, thereby increasing reverted CO₂ levels and improving faradaic efficiency towards CO. The following comments need to be addressed before publication in Nature Communications.

1. On page 4, line 100, the authors discuss local ion transport within the catalyst layers. However, the emphasis of the study predominantly centers on ion transport across the membrane and between the membrane interface and cathode surface, rather than within the catalyst layers themselves. I recommend that the authors amend the description to enhance clarity.

Response:

Thank you to Reviewer #1 for their time and efforts taken to review our work. From these comments we have made changes to enhance the accuracy and clarity of the manuscript. The following are the detailed response to each comment.

The reviewer is correct that this study is primarily focused on the local ionic transport within the cathode catalyst layer, which is influenced by the ionic transference number across the membrane, the use of the charged polymers and electrolyte at the anode, and the reactions at the interface and catalyst layer. To further emphasize this aspect, we revised the corresponding sentences in the main text, p4:

The results unveil that the ion transference number of the membrane and local ion transport within the catalyst layers serve a pivotal role in eliminating counterion crossover and maximising accessibility of the catalyst surface to the reverted CO₂.

2. What primary factor influenced the CO₂-to-CO performance through the optimization of ionomer types? One possible factor could be the improvement in the local environment, facilitating the transport of CO₂ gas. Another factor highlighted by the authors is the presence of reverted CO₂ at the catalyst-electrolyte interface. Further discussion on these factors is suggested. Are there any experiments that could help distinguish between these two effects?

Response:

The primary factor influencing the CO₂ to CO performance between the two ionomer types is the amount of CO₂ regenerated within the catalyst layers. As described in the main text on p5 and indicated in Fig. 2a-c below:

Anion exchange ionomers promote the transport of generated (bi)carbonates near the gas-liquid interface towards the BPM, while the Nafion rejects this transport and promotes (bi)carbonate accumulation near the generation point. The positive fixed charge of the Sus-CLs case then provides ample HCO₃⁻ available for acidification and CO₂ regeneration near the CEL/CL interface.

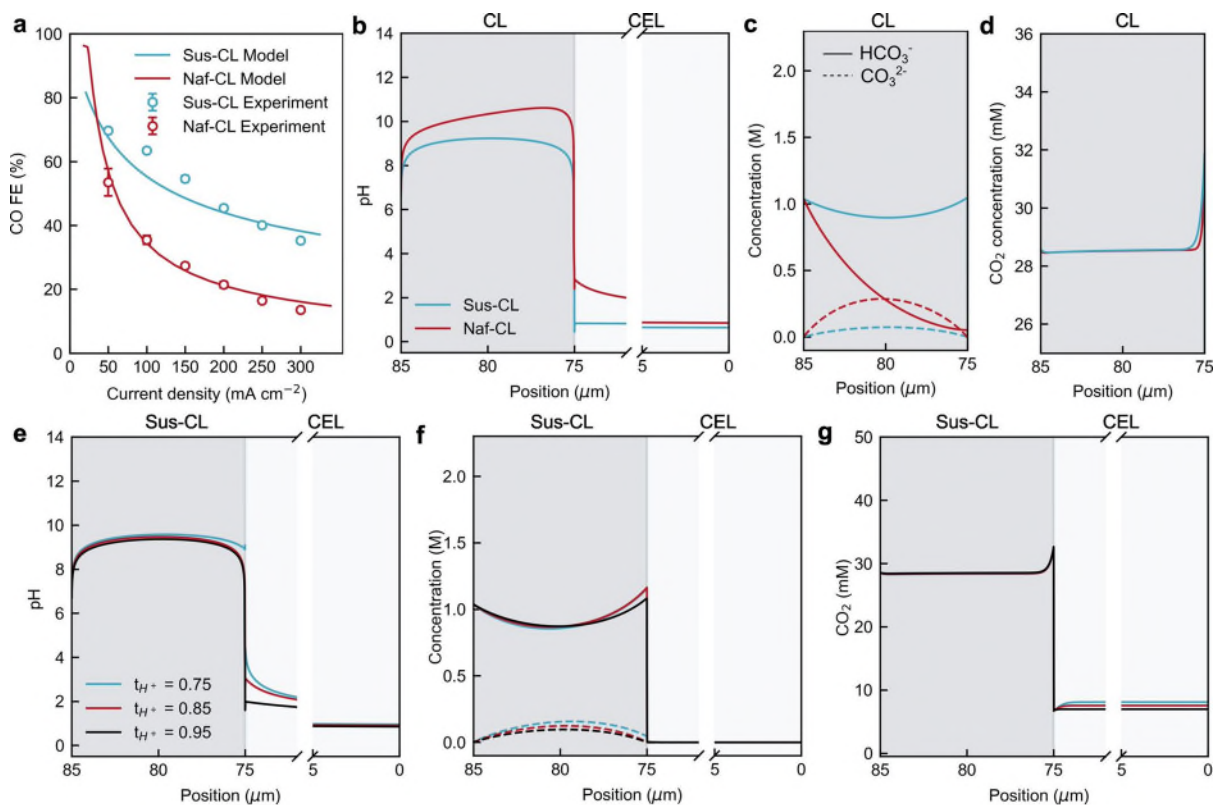


Fig. 1 1D continuum modelling results of the BPMEA. (a) Modelled and experimental Faradaic efficiencies of CO for catalyst layer (CL) incorporated with Sustainion (Sus-CL) or Nafion (Naf-CL) as a function of current densities. Comparison of (b) pH, (c) (bi)carbonate concentrations, and (d) CO₂ local concentration across CLs at 100 mA cm⁻². Profiles of (e) pH, (f) (bi)carbonate ions, and (g) CO₂ local concentration across CEL and Sus-CL as a function of proton transfer numbers. The bipolar junction is located at $x = 0 \mu\text{m}$, and the CEL|CL is located at $x = 75 \mu\text{m}$. The concentration profiles of the CEL for (c) and (d) are presented in Fig. S2, and not shown here for clarity.

To further support this argument, we plotted the CO₂ fluxes in the CLs based with different ionomers, added this data to the revised SI, and included a new discussion in the main text on p9 (see below). This data shows that the CO₂ flux from the CEL is higher when Sustainion is used as the cathode ionomer than Nafion. The positive fixed charges in Sustainion enable fast transport of the (bi)carbonates from the catalyst layer to the CEL surface where they are converted back into CO₂.

The increased CO₂ concentration results in an increase in the predicted CO₂ flux and CO partial current density near the CEL|CL interface as shown in Fig. S7.

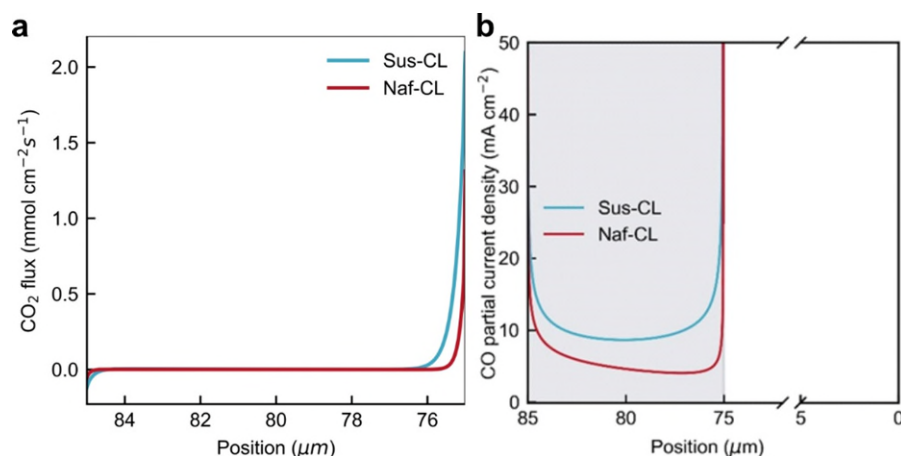


Fig. S1 Model predicted (a) CO₂ fluxes and (b) local partial current density of CO evolution within Sus- and Naf-CL.

Experimentally, the CO₂-to-CO utilization efficiency could serve as an indicator for the local availability of CO₂ in the CLs. The CLs with Sustainion ionomer, regardless of their loadings, show higher utilisation efficiency as compared to CLs with Nafion ionomer. This result is consistent with the predictions from the model prediction that the positively charged polymer facilitates a faster transport of (bi)carbonate for CO₂ regeneration close to the CEL. Detailed discussion is now included in the revised main text, p10:

Therefore, the CO₂-to-CO utilisation efficiency could serve as an indicator for the availability of reverted CO₂ for electrochemical conversion in the CLs. As shown in Error! Reference source not found.e, both CLs based with 15 wt% and 30 wt% Sustainion ionomer exhibit higher CO₂-to-CO utilisation efficiency than the ones with Nafion ionomer at current densities below 250 mA cm⁻². This experimental observation further confirms the beneficial effect of Sustainion ionomer in improving local availability of the reverted CO₂ accessible by catalysts for electrochemical conversion.

3. In the field of CO₂RR, the majority of reported performances have achieved over 90% FE for CO production across a wide range of current densities. However, the authors in this study were only able to achieve less than 50% FE at current densities exceeding 200 mA/cm², despite utilizing optimized ionomer. This raises the question: what factors may have contributed to this discrepancy in performance compared to existing research?

Response:

The inferior CO₂-to-CO performance for the BPMEA to monopolar MEA should largely arise from the acidic but cation-lean reaction microenvironment, which is not ideal for CO₂ reductions. The results of this work imply that its performance can be improved if the local ionic transport can be optimised. The relevant discussion on p4 in the main text is shown below:

Poor management of the local ionic transport and reactions within the catalyst layer usually entails undesired HER and thus low selectivity for CO₂ reduction at the cathode due to the high availability of protons close to the catalyst that appear to be more easily reduced.^{40,46} Product selectivity can be improved by either introducing a stagnant catholyte layer at the cathode/CEL

interface^{38,41} or applying an acid-tolerant and selective catalyst^{39,42}. The abundant cations in the catholyte layer can activate CO₂ reduction but may cause salt precipitation.⁴¹ Recent reports^{39,42} have also shown that acid-tolerant catalysts, such as molecular or metal-nitrogen-carbon catalysts, are more selective than silver catalysts for CO₂ reduction due to their weak binding with protons⁴⁷⁻⁴⁹ but remain far inferior to monopolar IEM-based systems.

4. Enhancing the H⁺ transference number is crucial for maximizing the availability of CO₂ at the cathode layer and improving the efficiency of CO₂-to-CO conversion. Apart from the KOH concentration on the anode side, which influences the H⁺ transference number, are there any other factors contributing to values below 1?

Response:

Another key factor that governs the H⁺ transference number is the applied potential, which drives the water dissociation at the CEL|AEL interface and thus impacts the availability of the H⁺ to be supplied at the CEL. The relevant discussion on p10 is shown below:

The observed CO₂-to-CO utilisation trend as a function of current density could result from an increase in the H⁺ transference number across the CEL of the BPM, because water dissociation dictates the overall ionic current while the co- and counter-ion crossover is mass-transport limited at increased current densities.⁶¹

5. In previous work (Xie, K. et al.; Nat. Commun. 13, 3609 (2022)), the authors reported that the use of interposer mainly increased carbon utilization. But from Fig. 4c, the authors did not obtain similar results? Any explanation about this? Did the authors try other interposers rather than PVDF (different thicknesses, material types, etc.) to further enhance the performance?

Response:

As stated in the previously submitted manuscript, the spacer in this study does not include concentrated salts, so it is different from the one reported in *Nature Communication* (2022) 13, 3609. In this study, instead, the spacer is used as a tool to probe the effect of local H⁺ at the CEL|CL interface on p11-12 of the main text:

In addition to the distribution of (bi)carbonate ions within the CL, we studied the local reaction environment at the CEL|CL interface by introducing a hydrophilic porous spacer (65 um thick) between the CL and CEL. (Error! Reference source not found.a) This configuration is fundamentally different from the previously reported method⁴¹ by Xie et al. that includes concentrated salts within the spacer. In this study, we applied the spacer pre-soaked with ultrapure water before the cell assembly. The ion conduction within the spacer solely depends on the ionic fluxes of protons, (bi)carbonate anions, and K⁺ cations that come from the fixed charge in the CEL and anolyte.

6. Did the direct attachment of the interposer to the CEL impact the H⁺ transference number? If so, what was the nature of this influence?

Response:

The transference number described across the study quantifies the proportion of the ionic transport in the CEL membrane, rather than in the CL. Therefore, the inclusion of the interposer will not change the transference number significantly. Instead, the use of the interposer can be effective in suppressing HER at the CL|CEL interface, as detailed in the original main text on p12:

As shown in Error! Reference source not found.b, the spacer significantly suppresses the HER down to below 15% and boosts the CO FEs up to 91% at 50 mA cm⁻² and 88% at 100 mA cm⁻², which is almost comparable to MEA cells based on monopolar membranes. The comparison of the CO partial current densities vs. cell potentials, as shown in Fig. S8, suggests cells with and without spacer achieve similar CO partial current densities under similar cell voltages. Therefore, the observed CO FE enhancement is mainly attributable to the suppression of HER at CL|CEL interfaces. This finding also indicates that the majority of HER in the absence of spacer occurs at the CL|CEL interfaces due to the direct contact of the CL with excess protons; the spacer increases the retention time for protons to reach the catalyst surface.

7. During the stability test, as mentioned on Page 12, line 311, the authors attributed the degradation of the cell primarily to the instability of the catalyst layer in the acidic environment, particularly where the catalyst layer is attached to the CEL. Have the authors experimented with incorporating a spacer covering the catalyst layer to potentially enhance stability?

Response:

Our result in Fig. S11 indicates that the cell with the spacer included between CEL and CL exhibits much inferior stability as compared to the counterpart with the absence of the spacer. A detailed description of this result in the main text is included below.

The drawback to including the spacer in the BPMEA cell is the large ohmic loss due to the slow ionic conduction across the spacer, as verified by the electrochemical impedance spectroscopic analyses in Fig. S10. The absence of abundant water at the cathode side of the BPMEA accelerates the dehydration of the spacer, which causes further reduction of the ionic conductivity of the spacer and eventually rapid cell voltage overshoot (See Fig. S11).

8. On Page 12, line 320, the authors highlighted the significance of a certain level of K⁺ crossover for activating CO₂ reduction. However, excessive K⁺ crossover can diminish the H⁺ transference number and promote salt precipitation. How can this challenge be addressed effectively?

Response:

In BPMEA, alkali cations, such as K⁺, are essential to maintain the strong alkaline environment for the PGM-free anodes and activate the CO₂ reduction at the cathode. In this case, the crossover of cations from the anolyte to the cathode is nearly inevitable. The strategies discussed in the report published in *ACS Energy Letters* (2023), 8, 1, 321-331 can be effective in addressing the salt precipitation issue, such as the choice of cation identity in the electrolyte and engineering solutions such as introducing pulsed voltage or water pulse. In this study, we

show that, with a periodic ~1 mL water pulse treatment at the cathode, the salt precipitation can be alleviated effectively for at least 24h, as described in the manuscript on p16:

To circumvent this issue, we applied ~ 1 mL pure water pulse to wash off the precipitated salt from the gas channel during operation when an increase in inlet pressure was observed. Unlike the reported hourly water flush to remove the salts at the cathode for the anion-exchange membrane electrode assembly cell^{14,29}, the BPMEA cell requires a much less frequent water pulse, thanks to its high CO₂ utilisation and controlled K⁺ concentrations at the cathode. The water pulse operation also showed negligible impact on the cell potential and CO Faradaic efficiency, as shown in Error! Reference source not found.a.

9. Figure 5b showed the pressure build up is due to salt precipitation. Why does the use of BPM still have such a significant salt precipitation? The H⁺ on the CEL/CL interface is supposed to couple with (bi)carbonate to regenerate CO₂.

Response:

The supply of H⁺ from CEL indeed helps revert (bi)carbonate back to CO₂ and mitigate the potential salt precipitation. This is proved by the discernible improvement of CO₂-to-CO utilisation in Fig. 3e and short-term stability results in Fig. 5b where the pressure build-up only occurs after > 30h operation using 0.1M KOH. Compared to monopolar membrane electrode assemblies using KOH solution, according to our previous study published in *ACS Energy Letters* (2021), 6, 12, 4291-4298, the BPMEA system exhibits a much-improved performance in mitigating salt precipitation. However, the salt precipitation cannot be completely avoided because of the <1 H⁺ transference number, which is described in the manuscript on p10 below. Future work needs to discern the optimal transference numbers to prevent salt formation, maximize CO₂ utilization, and maintain an alkaline environment at anode. This is the effort of a new PhD student that began at TUD.

Therefore, the H⁺ transference number determines the availability of the H⁺ to revert the generated (bi)carbonate species back to CO₂. As the H⁺ transference number is always below 1, it means that some CO₂ converted to (bi)carbonates are never recovered and will either precipitate at cathode or crossover to the anode at periodic intervals.

10. The stability of this system remains a significant challenge. Do the authors have any insights or suggestions on further enhancing the system's stability?

Response:

Improving the stability of the BPMEA cell is currently challenging. Recent advances in pure-water-fed CO₂ electrolysis could indicate some meaningful directions to explore in future, such as the use of new catalyst layers and membrane development. Accordingly, we revised our main text on p13 and p14 as follows:

Such discernible selectivity loss likely originates from an increase in contact area between catalyst and H⁺ and possible deactivation of the catalyst layer in the acidic environment due to the lack of sufficient K⁺ in the CLs. Both could contribute to the rise in the rate of HER and

suppression of the rate of CO₂ reduction. As long-term stability over 1000 h has been demonstrated very recently in pure water-fed CO₂ electrolysis in MEA, where concentrations of alkali cations are also limited, the stability of the CO₂ reduction over BPMEA should be further improved by implementing the advances in designing alkali-cation-lean CLs, such as the use of novel catalyst layers³⁷ and charged polymers².

Reviewer #2

The manuscript highlights some of the challenges associated with use of monopolar ion-exchange membrane for electrochemical conversion of CO₂. While using bi-polar membrane (BPM) address or avoid these issues, significantly higher potential and longer-term structural stability of BPM yet to be established for larger-scale application. Particularly higher cell potential from configuration with BPM poses severe techno-economic feasibility challenges for such design.

Research work presented in this manuscript provides some insights into ion transference number of the BPM and local ion transport within the catalyst layers. This is a novel study and can provide helpful insights into developing future BPM with reduced potential and improved structural stability. This would be a timely publication in the field considering the research interest on BPM-configured electrolyzers. I recommend publishing this manuscript with minor modifications on following aspects:

1. Bulk average (physical and transport) properties of CEL and AEL are used in the model. The degree of cross-linking of polymer backbone and extent of functionalization (in both CEL and AEL) are expected to change ion-transference number as well as local ion transport through these layers. Wouldn't it be beneficial to include these aspects into the model?

Response:

We would like to express our gratitude to the Reviewer for the time and efforts in reviewing our manuscript. The comments have allowed us to constructively modify our manuscript such that our key points are clearer.

The degree of cross-linking is implicitly accounted for in the model by accounting for the change in water uptake (λ) depending on the ion exchange within the ionomer (as shown in Eq. S26). The functionalization of the ionomers was also included by accounting for the different IECs of the ionomers. These aspects of the model change the ion transport in the electrodes in accordance with dilute-solution theory. A more thorough analysis of the non-ideal thermodynamics of the ionomers is beyond the scope of the paper, but can be found in works by Crothers et al. (*Andrew R. Crothers et al 2020 J. Electrochem. Soc. 167 013547*; *Andrew R. Crothers et al 2020 J. Electrochem. Soc. 167 013548*)

2. Does ion transference number and local ion transport have any effect on Ohmic losses associated with the BPM? Any opportunity to reduce such losses?

Response:

The reviewer made a valid point here. We found that the local ionic transport has an impact on the overall cell voltages: the CL with Sustainion ionomer shows lower ohmic loss as compared to the CLs with Nafion ionomer. Accordingly, we included the comparison in the revised Fig. S14a and S14b, as shown below. We also included new discussion in the main text on p13:

The electrochemical impedance data (see Figs. S12 and S13) shows that the choice of the ionomer in the CL has a significant impact on the ohmic loss of the BPMEA. This result is not

surprising because the ohmic resistance is dominated by the ionic transport. As shown in Fig. S14a, the CLs with Sustainion consistently show 1-1.34 $\Omega \text{ cm}^2$ lower ohmic resistance than the CLs with Nafion across the tested current densities. This difference becomes more discernible at high current densities and can be translated into a significant ohmic overpotential of $\sim 0.4 \text{ V}$ at 300 mA cm^{-2} (Fig. S14b). This improvement can be a result of the much lower ionic conductivity of the Nafion ($\sim 30 \text{ mS cm}^{-1}$ in KOH at $25 \text{ }^\circ\text{C}$)⁶⁴ than the Sustainion polymer ($\sim 60 \text{ mS cm}^{-1}$ under similar conditions).³¹

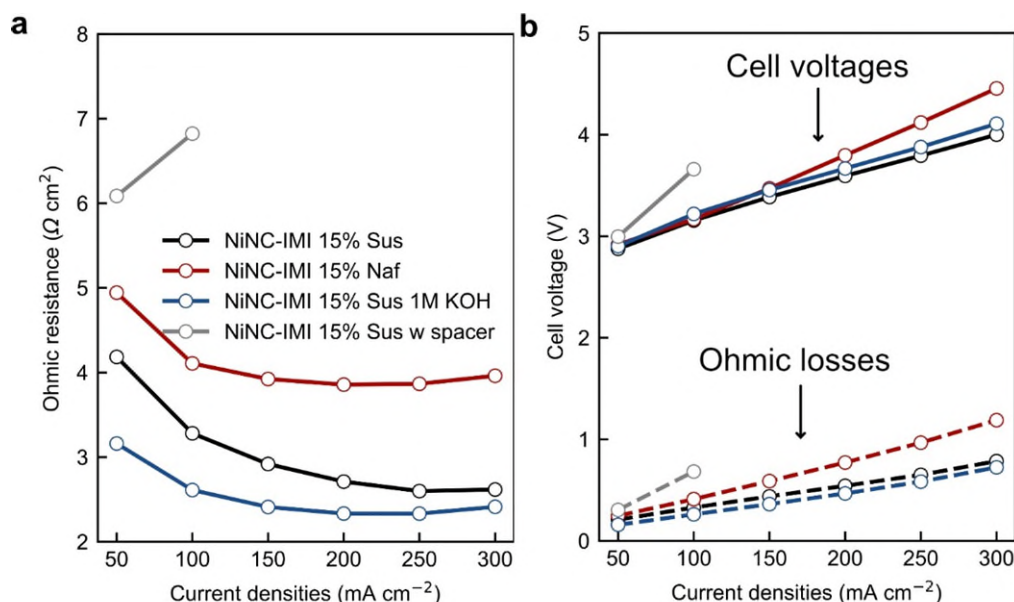


Fig. S2 Comparison of (a) the ohmic resistances and (b) cell voltages (solid line) and ohmic losses (dashed lines) of the BPMEA as a function of current densities for CLs based with NiNC-IMI 15 wt% Sus, NiNC-IMI 15 wt% Naf, NiNC-IMI 15 wt% Sus using 1M KOH, and NiNC-IMI 15 wt% Sus with spacer at CEL|cathode interface. The rest of the samples used 0.1 M KOH as the anolyte.

3. Is there any penalty in full-cell potential due to pH gradient between cathode and anode? Additional discussion on this aspect will be beneficial.

Response:

The pH gradient between the cathode (lower pH) and anode (higher pH) determines the Nernstian shift, which positively affect the full cell potential. However, it is difficult to directly determine the pH of the cathode and anode due to the changes of the pH across the 3D-structured cathode and anode. To address this issue, we estimated the averaged pH of the cathode using our models and new discussion in the main text on p13.

Additionally, the Nernstian shift, arising from the pH gradient between the cathode and anode, should also serve a role in influencing the observed cell voltages. As it is challenging to determine the pH accurately at the BPMEA cathodes due to the experimental limitations and pH variations across the CL structures, we estimated the impact of the local ionic transport on the Nernstian shift using our models and compared the results in Fig. S15. Due to the higher estimated pH over the Naf-CLs (see Fig. 2b as an example), the Nernstian shifts for the Naf-CL case then exerts slightly more negative impact ($< 0.1 \text{ V}$ c.f. $\sim 0.4 \text{ V}$ difference for ohmic loss) on the overall cell voltages across the tested current densities than Sus-CL cases. This

modelling result, together with the impedance analyses discussed above, indicate that the impact of the ionic transport on cell voltages is more closely related to the ionic conductivity of the CLs than the Nernstian shift.

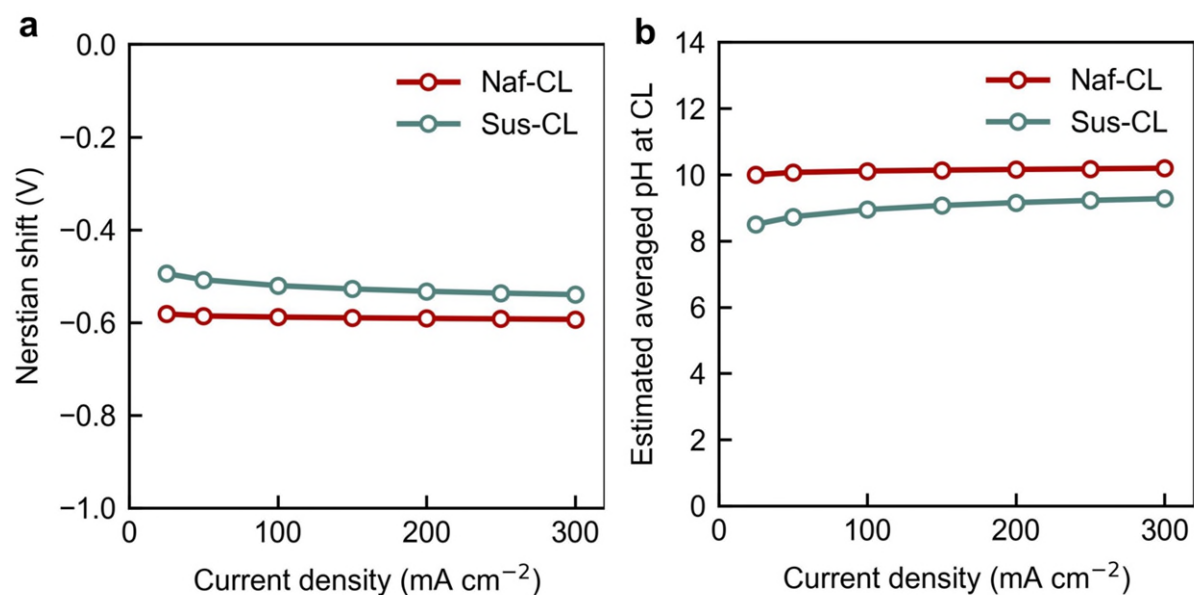


Fig. S3 Comparison of the (a) averaged Nernstian shift and (b) pH values caused by ionomers in the catalyst layers at different current densities estimated from models. Note: the more positive values of the Nernstian shift lead to reduced cell voltages.

In the supplementary information, we included description of the method:

The Nernstian shift can be determined as:

$$\eta_N = \frac{2.303 \times RT}{F} \times (pH_A - pH_C) \quad \text{Eq. 45}$$

Because of the experimental limitations and the local variations of pH across the catalyst layers, it is challenging to accurately determine the pH and the Nernstian shift of the cell. Instead, we used the model to estimate the averaged pH values of the cathode CL and calculate the Nernstian shift caused by the cathode CLs using the equation above.

4. While BPM configuration help avoiding/minimizing cathode salt precipitation or use of non-PGM anode, the higher full-cell potential makes BPM-configuration less attractive from operational cost perspectives. It would be beneficial for the future readers if a short discussion is added on potential penalty associated with using BPM.

Response:

We have included some new discussion on these points in the main text on p13:

The local ionic transport has an impact on the BPMEA cell voltage. Most of the current BPMEAs require higher cell voltages than monopolar MEAs to drive the same current densities due to the high overpotential for water disassociation (WD) at the bipolar junction. Recent

reports have indicated that WD kinetics can be effectively improved by using proper catalysts at the bipolar junction⁶² and optimising the operating conditions (e.g., increasing temperature)⁶³, which has been widely discussed in the literature and is beyond the scope of this study. Instead, this study investigates how the local ionic transport across the CLs influences the overall cell voltages.

Reviewer #3

In the manuscript by Li et al., the authors presented a PGM-free bipolar membrane (BPM) electrode assembly for a CO₂ electrolyzer. Through transport modelling and experiments, the authors found that anion-exchange ionomers in the catalyst layer increased local bicarbonate availability and that increasing the proton transfer number in the BPM increased CO₂ regeneration and limited K⁺ concentration in the cathode region. The uniform local distribution of bicarbonate ions increased the accessibility of reverted CO₂ to the catalyst surface. However, some important issues need to be addressed adequately to reveal new insights or fundamental science to advance the field. The content of the article needs to be major revised and demonstrated for the improvement of the manuscript quality.

1. One of the major advances in this work is the PGM-free BPMEA configuration for a CO₂ electrolyzer, here, the author emphasized the vital role of managing ionic species to improve CO₂ conversion efficiency while preventing acidification of the anodic compartment. However, there are many studies on BPM in the CO₂ electrolyzer. And we also noticed that the author's team had previously applied bipolar membrane electrode assemblies to CO₂ electrolysis and achieved an increase in CO₂ utilization (ACS Energy Lett. 2021, 6, 4291–4298.). Additionally, in this reviewer's opinion, we recommend that the authors compare previous work with similar designs and performance to emphasize the scientific advance and innovation of this study.

Response:

We appreciate the immense time and efforts in reviewing the manuscript. His or her comments have greatly improved the clarity and quality of our work. Below are the detailed responses to the comments.

From the reviewer's comments we have now compared our results against the relevant literature data in terms of polarization curve, product Faradaic efficiency, partial current densities in the revised Fig. S5 (see below) in the SI. The comparison further indicates that the CO₂ conversion rate is strongly correlated with the choice of the charged polymer in the CL, such as the model ionomer used in this study, which has a profound impact on the local ionic transport in the CL. Meanwhile, our work performs well in terms of the polarisation curve and CO₂RR partial current densities as compared to prior reports. A detailed discussion is now included in the main text on p8, and summarised as below:

When compared with those reported in the literature, as shown in Fig. S5, the BPMEA cells using CLs with 15% Sustainion ionomer, as studied in this work, show the lowest cell voltages and are among the best reported CO partial current densities at cell voltages below 4 V. It is interesting to note that, regardless of the catalyst and polymer materials used in the CLs, the NiNC-IMI CLs with 15% Sustainion ionomer show the same CO partial current densities - cell voltage relations to the CLs based on cobalt tetraaminophthalocyanine catalysts grafted on the positively charged polymer, as very recently reported by Li et al.⁵⁷ Both cases are superior in CO partial current densities to most of the reported CLs based with Nafion^{41,42,46,58,59} or no ionomers⁴⁰ for BPMEAs at below 4 V cell voltages. Such similarity in these two positively

charged CLs indicate that, the CO production rate at relatively low cell voltages should be strongly correlated with the presence of positively charged polymer (i.e., Sustainion ionomer or other positively charged polymer) in the CLs, which exerts a profound impact on the ionic transport.

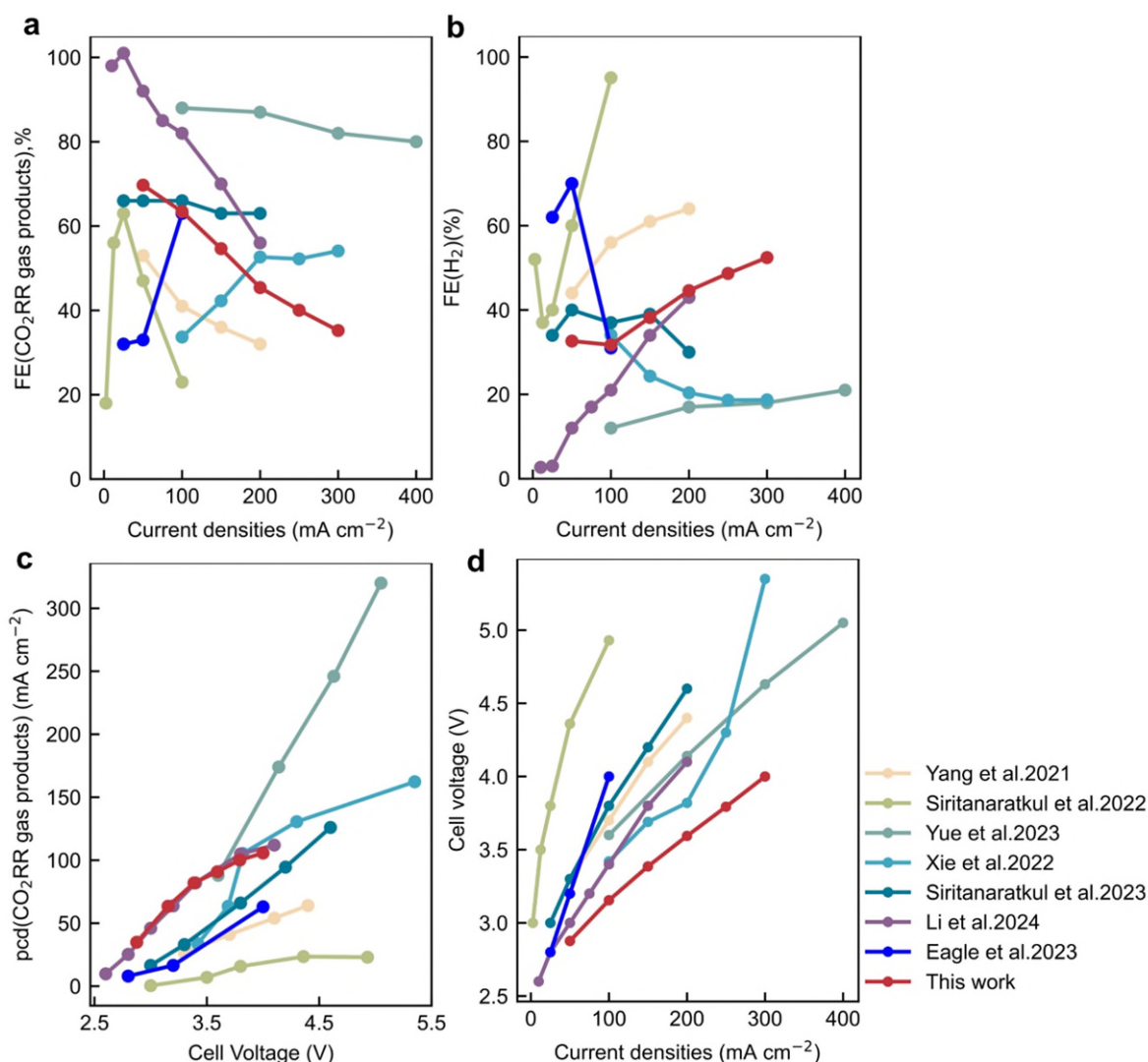


Fig. S4 Comparison of (a) FEs for CO₂ reduction reaction (CO₂RR) gaseous products, (b) FEs for H₂, (c) partial current density of CO₂RR gaseous product, and (d) cell voltages of BPMEA with NiNC-IMI 15% Sus CL as cathode with recently reported literature data by Yang et al.¹³, Siritanaratkul et al.^{14,15}, Yue et al.¹⁶, Xie et al.¹⁷, Li et al.¹⁸, and Eagle et al.¹⁹.

2. The author's summary of the current technical barriers to the application of BPMEA electrolytic cells in electrocatalytic CO₂ reduction is incomplete. For example, under the reverse bias, generally, the BPM needs the water dissociation catalyst which can reduce the overpotential. Therefore, the authors should discuss more about the potential limitations of the BPM configuration.

Response:

To further characterise the limitations and complexities of BPM systems for CO₂RR, we have included additional discussions and results related to the influence of ionic transport on cell voltages in the revised manuscript:

Effect of ion transport on BPMEA cell voltages

The local ionic transport has an impact on the BPMEA cell voltage. Most of the current BPMEAs require higher cell voltages than monopolar MEAs to drive the same current densities due to the high overpotential for water disassociation (WD) at the bipolar junction. Recent reports have indicated that WD kinetics can be effectively improved by using proper catalysts at the bipolar junction⁶² and optimising the operating conditions (e.g., increasing temperature)⁶³, which has been widely discussed in the literature and is beyond the scope of this study. Instead, this study investigates how the local ionic transport across the CLs influences the overall cell voltages.

The electrochemical impedance data (see Figs. S12 and S13) shows that the choice of the ionomer in the CL has a significant impact on the ohmic loss of the BPMEA. This result is not surprising because the ohmic resistance is dominated by the ionic transport. As shown in Fig. S14a, the CLs with Sustainion consistently show 1-1.34 $\Omega \text{ cm}^2$ lower ohmic resistance than the CLs with Nafion across the tested current densities. This difference becomes more discernible at high current densities and can be translated into a significant ohmic overpotential of $\sim 0.4 \text{ V}$ at 300 mA cm^{-2} (Fig. S14b). This improvement can be a result of the much lower ionic conductivity of the Nafion ($\sim 30 \text{ mS cm}^{-1}$ in KOH at $25 \text{ }^\circ\text{C}$)⁶⁴ than the Sustainion polymer ($\sim 60 \text{ mS cm}^{-1}$ under similar conditions).³¹

Additionally, the Nernstian shift, arising from the pH gradient between the cathode and anode, should also serve a role in influencing the observed cell voltages. As it is challenging to determine the pH accurately at the BPMEA cathodes due to the experimental limitations and pH variations across the CL structures, we estimated the impact of the local ionic transport on the Nernstian shift using our models and compared the results in Fig. S15. Due to the higher estimated pH over the Naf-CLs (see Fig. 2b as an example), the Nernstian shifts for the Naf-CL case then exerts slightly more negative impact ($< 0.1 \text{ V}$ c.f. $\sim 0.4 \text{ V}$ difference for ohmic loss) on the overall cell voltages across the tested current densities than Sus-CL cases. This modelling result, together with the impedance analyses discussed above, indicate that the impact of the ionic transport on cell voltages is more closely related to the ionic conductivity of the CLs than the Nernstian shift.

3. The authors made substantial efforts in this work, with insights into several aspects of CO₂ electrocatalysis, from the reaction system design to the selection of the catalyst (PGM-free anode catalyst). However, I do not think the PGM-free system is a point. Ni/Fe oxides have been widely used as the OER catalysts. The authors should build their paper around the BPM reaction systems.

Response:

We agree with the reviewer that Ni/Fe oxides have been reported in numerous CO₂RR works. These studies however either frequently refresh the anolyte, or for the BPM CO₂RR cases they do not measure the pH or composition of the anolyte over time. Thus, previous works have not assessed the validity of using a PGM-free anode. This work provides an experimental demonstration of the capability of the BPMEA system in stabilising the pH and PGM-anode while running CO₂ electrolysis at high rates without replenishing the anolyte. We further characterize our anolyte after operation which is unique versus previous works that have never tested the hypothesis of BPM's allowing for alkaline anolytes.

We believe this proof-of-concept is important to the field as it points out a meaningful research direction for industrially viable system design that is not constrained by material availability. Our results also uncover the important role of ionic transport in the catalyst layers in determining the reaction microenvironment of this BPMEA system and potentially other electrochemical conversion systems, which constitutes the key novelty of this work.

4. The author believes that there is a difference in equivalents between Nafion and Sustainion. Why not choose the same equivalents for performance comparison? So I think you should choose the same equivalent for ionomers.

Response:

The previous work (Electrochimica Acta (2023), 461,142613) led by our co-authors show that the equivalent weight of the ionomer plays a minor role in determining the CO₂RR performance of the NiNC CLs in MEA cell configurations. Therefore, in this study, the ionomer materials are screened by setting the mass loading as the standard.

Accordingly, we further clarify this point in the revised main text, p7:

Considering the reported minor effects of ion-exchange capacities on selectivity and stability of NiNC CLs⁵⁴, this study chose the CLs with these ionomer loadings are used as model electrodes.

5. Authors should perform relevant characterization of the prepared materials, even if they have been reported.

Response:

The characterization of the prepared NiNC-IMI catalyst materials and the relevant electrodes has been well reported in the recent report published by our co-authors in *Nature Chemical Engineering* (2024), 1, 229-239. For easy access to this information, we included the key properties of the materials in the revised Fig. S4 in the SI.

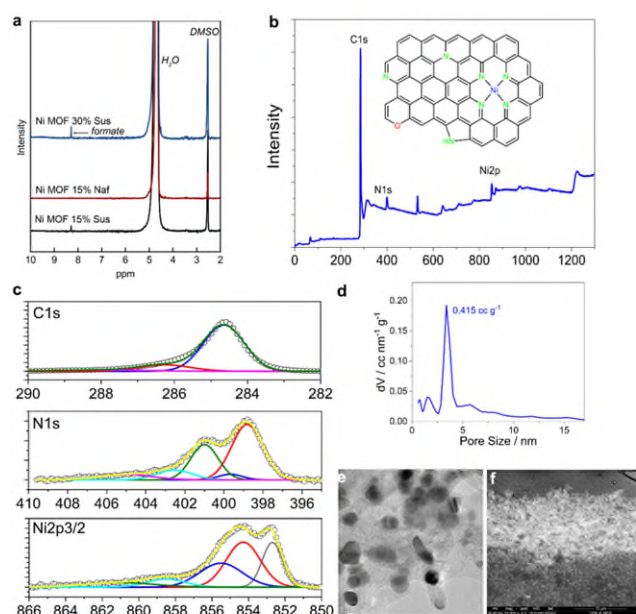


Fig. S5 (a) NMR spectra of the analyte after the test. X-ray photoelectron spectroscopy (b) survey and (c) high-resolution spectra of C1s, N1s, and Ni2p3/2 of NiNC-IMI catalyst survey, accompanied by a schematic illustration highlighting distinct functionalities. The Ni-Nx motifs, identified as the Ni states between binding energy between 856 and 854 eV, is proposed as the active site for electrochemical CO₂ reduction. (d) The pore size distribution of the catalyst was evaluated using N₂ physisorption and BET analysis. (e) Transmission electron microscopy image showcasing the as-prepared catalysts. (f) Cross-sectional image illustrating the catalyst layer after spray coating on the electrode. Related data and images for (b)-(f) have been presented in our previous publication by Brückner et al.⁹

6. Here, we noticed that in the PGM-free BPMEA cell system developed by the author, its stability for 150 hours is unsatisfactory, and its CO selectivity drops significantly. (Energy Technol. 2017, 5, 929.) has reported up to 4000 h and (Nat Commun. 2021, 12, 5223) has reported up to 2400 h. Therefore, the reasons for poor system stability should be taken seriously, such as catalyst deactivation, membrane failure, carbonate deposition, etc., we suggest that the authors provide intuitive experimental evidence to explain this.

Response:

The Reviewer pointed out a meaningful future research direction for BPMEA development. Most of the recently reported BPMEA systems, such as *Li et al. Angewandte Chemie International Edition, 2024, 10.1002/anie.202400414*, and *Siritanaratkul et al. Journal of the American Chemical Society, 2022, 144, 17, 7551-7556*, show poor stability or results even for very short term (usually less than 24 h) stability tests. Our results indicate that the stability issues mainly arise from the changes in the microenvironment for the catalyst layer that became more acidic and lean in K⁺ concentration in the CLs along with the duration of the operation. Accordingly, we included new discussions in the revised main text, p13 and p14:

Such discernible selectivity loss likely originates from an increase in the contact area between the catalyst and H⁺ and possible deactivation of the catalyst layer in the acidic environment

due to the lack of sufficient K^+ in the CLs. Both could contribute to the rise in the rate of HER and suppression of the rate of CO_2 reduction. As long-term stability over 1000 h has been demonstrated very recently in pure water-fed CO_2 electrolysis in MEA, where concentrations of alkali cations are also limited, the stability of the CO_2 reduction over BPMEA should be further improved by implementing the advances in designing alkali-cation-lean CLs, such as the use of novel catalyst layers³⁷ and charged polymers².

By comparing the ohmic resistances obtained from electrochemical impedance (Fig. S16), we found that the degradation of the cell potential should be related to the increase of the polarization resistance over either the cathode or anode rather than the deterioration of the BPM.

7. We believe that the author's pH measurement of the electrolyte after the reaction is incomplete in describing and inferring some ion migration processes during the reaction. Some in-situ testing methods, such as in-situ infrared spectroscopy or Raman, should be established to reveal some pH changes at the CL interface during the reaction.

Response:

To understand the ion migration for the BPMEA, in addition to measuring pH at the electrolyte, we also conducted titration to determine the ionic crossover rates for the short-term stability test. This test provides statistically reliable data for the calculation because the long-term ion-crossover process could lead to significant change of the ions in the anolyte. A detailed calculation is now provided in the revised SI and presented in the response to the following comment.

It is presently challenging to accurately probe the local pH at the cathode experimentally due to the cell configuration used in our study and the local variations of pH across the complex 3D structure of the electrode. For example, infrared and Raman spectroscopy can be useful in probing electrochemical interfaces in small volumes, but they are currently limited in providing spatial details over the 3D-structured CLs and probing MEA cells under investigation in this work. Such limitations could make it difficult to provide meaningful information about the ion migration during the reactions.

Instead, we used the models to estimate the averaged pH at the cathodes in Fig. S15a, and found that the ionomer in the CLs has a minor impact on the Nernstian shift. We have included a new relevant discussion in the main text on p13 (see below).

Additionally, the Nernstian shift, arising from the pH gradient between the cathode and anode, should also serve a role in influencing the observed cell voltages. As it is challenging to determine the pH accurately at the BPMEA cathodes due to the experimental limitations and pH variations across the CL structures, we estimated the impact of the local ionic transport on the Nernstian shift using our models and compared the results in Fig. S15. Due to the higher estimated pH over the Naf-CLs (see Fig. 2b as an example), the Nernstian shifts for the Naf-CL case then exerts slightly more negative impact (< 0.1 V c.f. ~ 0.4 V difference for ohmic loss) on the overall cell voltages across the tested current densities than Sus-CL cases. This modelling result, together with the impedance analyses discussed above, indicate that the

impact of the ionic transport on cell voltages is more closely related to the ionic conductivity of the CLs than the Nernstian shift.

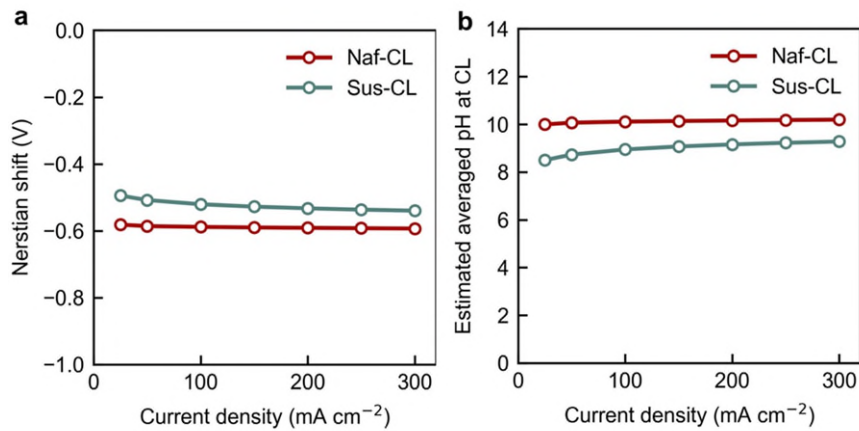


Fig. S6 Comparison of the (a) averaged Nernstian shift and (b) pH values caused by ionomers in the catalyst layers at different current densities estimated from models. Note: the more positive values of the Nernstian shift lead to reduced cell voltages.

8. We recommend that the authors add calculation details for parameters such as ionic current, K⁺ and CO₂ crossover rates because the qualitative and quantitative analysis of this parameter is crucial in this study.

Response:

Accordingly, we have included these calculation details in the revised methods on p15 in SI, and shown below:

The proportion of current associated with K⁺ and CO₂ crossover over total ionic current in the stability test was calculated using the following equations:

$$\text{crossover ratio} = \frac{z_{\text{ion}} \times F \times \Delta n_{\text{ion}}}{J \times 3600 \times t} \quad \text{Eq. S56}$$

$$\Delta n_{\text{ion}} = V_{\text{anolyte, before}} C_{\text{ion, before}} - V_{\text{anolyte, after}} C_{\text{ion, after}} \quad \text{Eq. S57}$$

The ionic current is the same to the total current J . z_{ion} is the number of charges for the ions: 1 for K⁺ and 2 for carbonate ions. Δn_{ion} represents the change in number of moles of the ions, which is a function of volume of the anolyte before ($V_{\text{anolyte, before}} = 1 \text{ L}$) and after ($V_{\text{anolyte, after}} = 0.987 \text{ L}$) stability test as well as concentrations of the ions before ($C_{\text{ion, before}}$) and after ($C_{\text{ion, after}}$) stability test. The concentrations of K⁺ and carbonate ions are determined from titration described above.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed referee comments; the work is suitable for Nature Communications in its present form.

Reviewer #2 (Remarks to the Author):

The updated manuscript properly address the aspects raised earlier by the reviewer. I recommend accepting this manuscript for publication in Nature Communications.