

Hierarchically Conductive Electrodes Unlock Stable and Scalable CO₂ Electrolysis

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This manuscript has been previously reviewed at another journal. This document only contains reviewer comments, rebuttal and decision letters for versions considered at Nature Communications.

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have revised the manuscript to address the previous comments, which were somewhat similar across the Reviewers. The Reviewer thanks them for their effort and it is an improved manuscript. That being said, many of the issues that were deficiencies were not fully corrected and it is recommended that the article is transferred to a less high profile and more specific journal. In particular:

1. The model improvements and justifications for the use of the two electrode potential is not really compelling or justified since the local changes are critical, especially in these complex devices as seen in recent modeling papers.
2. The operational current densities are still relatively low and although good results are obtained for selectivity and for the larger cell size, the CO₂ utilization is still poor. Together the results are not impressive enough or large enough compared to state of the art to be published as a Nature Communication. This is especially true when compared to the Burdyn paper that is now published.
3. The additional data on the durability is good to see although understanding the exact stressors and post mortem analysis would make the paper stronger.
4. The additional data on wettability is lacking as surface contact angle really does not say much for porous media and also the values are essentially the same within error. More characterization is necessary to argue about the claims. Also, the value proposition of ePTFE and wires espoused here is not really addressed well.

Reviewer #3

(Remarks to the Author)

I looked carefully at the 75 hour stability data and I cannot agree with the authors that their system is 'stable'. The FE starts out a little below 40% and drops to around 20% at the end of the 75 hours. The authors speculate this to be due to morphological changes. After the 60 hour mark, the total cell voltage appears to spike up significantly and this is speculated to be due to iridium oxide anode instability. Based on these results, I believe their system actually appears to be 'unstable' and falls below the benchmark by other research groups in the field.

Other than this point, I believe that authors have responded well to the reviewer comments.

Reviewer #4

(Remarks to the Author)

The authors have made significant revisions to address the reviewer questions, including the addition of important extended stability data and more detailed characterization. I consider the manuscript could be suitable for publication after the following remaining points are addressed.

- References are missing: In my version of the revised manuscript, the References section is blank, hence I cannot assess the quality of referencing of prior works.
- Fig.2B. Insufficient experimental detail is given here.
- Fig.2E: The caption doesn't clearly explain what Fig.2E is. Also, its x-axis meaning is undefined. If it shares x-axis label with Fig.2F, this should be better clarified (e.g. remove the gap between E & F).
- Fig.3C: CH₄ FE is shown unitless, which doesn't match what is used throughout the rest of the manuscript (%).
- Stability of Cu catalysts is a known issue, and the same could be true for the Cu wires used here, which are in contact with electrolyte and subjected to high current densities. I therefore expect some degree of corrosion is likely. It would strengthen the manuscript to show some analysis of the wires before and after extended testing (e.g. optical and/or electron microscopy).
- lines 241-242: Mentions of 0.5 cm² are confusing, since that size is not part of Fig.4. Perhaps they mean to refer to Fig.2F - if so, mention that here.
- It is important to explain how the gas quantification was performed, especially in the determination of the gas flow rate out of the cell (needed for proper calculation of product formation rates) which is not equal to the cell inflow rate.
- The 50 cm² HCGDE experimental performance is compared to modeled behavior of an unmodified 50 cm² GDE, which I (and likely readers) find a bit confusing. The key novelty (the improvements caused by the HCGDE approach) would be far more convincing if compared directly to experimental results of an unmodified 50 cm² GDE (without Cu wires, but with all other parameters identical). It is strange that they do not report the actual performance of the unmodified GDE for direct comparison.
- Fig.5: It is potentially misleading to have these two figure parts together, since they are for two very different cell sizes. I would find it more appropriate to combine Fig.5A with Fig.4B.
- The j/V relationships between different cell sizes are somewhat inconsistent in the main text figures, comparing the 4.2 cm² and 50 cm² cells. Namely, j = 100 mA/cm² requires ~4.0 V for the 4.2 cm² tests (Fig.2F & Fig.5B), while the 50 cm² cell reaches 100 mA/cm² at only about 3.3 V (Fig.4D, also consistent with Fig.S18). This is a rather large difference and thus should be addressed in the text. If this is due to the use of different membrane/anode, this should be mentioned and referred to the experimental details.
- Fig.5B: The cell voltage fluctuations sometimes seem to coincide with the moments of C₂H₄ analysis. The authors should consider the possibility that this could be an effect of pressure fluctuation induced by the injection valve of the gas chromatograph.
- line 266: The C-paper GDE tests of Fig.S20 were apparently run at higher current densities (190, 170 mA/cm²) than the HCGDE one (Fig.5B, 100 mA/cm²) which does not really provide a fair basis for comparison of performance (stability or selectivity).
- Table S2 is a valuable collection for comparison. Is there a reason for the missing values in the Total Current Density column? It should be a standard parameter reported in each paper, and it would be valuable to include the values, which are needed in order to relate the actual production rates of C₂+ products.
- Error bars are mentioned but in some places it isn't clearly explained how they are derived (e.g. standard deviation).
- Electrolyte concentration effects: It has been shown that the anolyte electrolyte concentration can influence the selectivity of Cu, even in zero-gap MEA cells (El-Nagar 2023 <https://doi.org/10.1038/s41467-023-37520-x>), and this can result in pronounced changes in the C₂H₄ FE when comparing e.g. 10 and 100 mM concentrations. Here much of the work was conducted under quite low concentrations (10 mM). I suggest the authors consider this and mention its possible implications on further tuning selectivity.

Version 1:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

I find that the revisions have strengthened the manuscript and it is now suitable for publication.

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REVIEWER COMMENTS

Thanks to the comments from reviewers, we have continued to improve our manuscript. Our point-by-point response is included below. Changes to the manuscript and supplementary information between the last version and this version are highlighted in yellow.

Reviewer #1 (Remarks to the Author):

The authors have revised the manuscript to address the previous comments, which were somewhat similar across the Reviewers. The Reviewer thanks them for their effort and it is an improved manuscript. That being said, many of the issues that were deficiencies were not fully corrected and it is recommended that the article is transferred to a less high profile and more specific journal. In particular:

1. The model improvements and justifications for the use of the two electrode potential is not really compelling or justified since the local changes are critical, especially in these complex devices as seen in recent modeling papers.

We do not propose this model as a generalizable model which can be used for any CO₂R electrode, and we acknowledge that more sophisticated models are necessary to model electrodes where these local changes drive performance. We emphasize that the system which we are modelling is different from most other systems modelled in literature. We are modelling large ePTFE electrodes (50cm²) for which ohmic losses are the main drivers of local voltage difference and therefore product distribution. Our model considers only ohmic losses and maps the voltage difference to current density and product distribution, and achieves impressive matching of experimental data without any fitting parameters.

To further demonstrate the adequacy of our model for estimating performance declines at scale, we have collected experimental data for a 50 cm² ePTFE electrode *without* our HCGDE improvements and compared it to the model prediction. As shown in the new Supplementary Figure S15-16, we observe that our model is distinctly able to predict i-V curves and capture the essential trends of the Faradaic Efficiency across length scales for electrodes which are ohmically limited. We have thus validated our model with four experimental points under two experimental conditions: 3x at 4.2cm² with a single side-connection point, and 50cm² with all sides connected.

The fact that our model is able to predict performance to this degree of accuracy without the use of local effects does not limit its validity, rather it implies that these local effects are *not relevant for the specific systems modelled herein*. Again, the driving physics at play here are ohmic losses.

2. The operational current densities are still relatively low and although good results are obtained for selectivity and for the larger cell size, the CO₂ utilization is still poor. Together the results are not impressive enough or large enough compared to state of the art to be published as a Nature Communication. This is especially true when compared to the Burdyny paper that is now published.

Our work is concurrent with that of Burdyny et al, as evidenced by our original submission date at Nature Energy.

The intention of this paper is not to develop a system which itself represents an optimized system for all aspects of CO₂ electrolysis: rather, we develop a tool which is tailored to resolving a pressing issue, though at the same one which is broadly applicable to practically all CO₂ electrolyzers. The reviewer's concerns about current density, selectivity, and utilization can be resolved through implementation of more advanced catalyst systems, but we do not feel it to be necessary in order to convey the important improvements demonstrated herein: a catalyst-, electrolyzer architecture-, morphology-agnostic method of improving conductivity for ePTFE GDEs to enable scaling of any electrode. The HCGDE could be very easily applied to scale most any system which does have leading-edge current density, selectivity, and utilization.

3. The additional data on the durability is good to see although understanding the exact stressors and post mortem analysis would make the paper stronger.

Thanks to the dialogue with the reviewers, we have performed several more experiments and also gained a much stronger understanding of the experiments which were already performed and the physics at play. We have dedicated a section of the Supplementary Information to discussions of stressors and post-mortem analysis which has helped to further strengthen our paper. We appreciate the suggestions. Please see Supplementary Section 7 and Figures S23-S24 for the full description, though a description is provided below:

We have performed an additional 40h stability experiment to show stability on carbon paper substrates at different current densities and have also performed post-mortem characterization of the wetting properties of these electrodes (see Figure S23-S24). We identified that there are two potentially independent instability mechanisms at play in carbon paper electrodes:

The first is a discrete flooding event on the order of ~30 minutes as shown in Figure 1B. This instability mode has been observed before, and has been rationalized as an intrusion of liquid which prevents CO₂R, resulting in hydroxide generation and thus a decrease in membrane resistance, lowering cell voltages and CO₂R FE. (<https://doi.org/10.1016/j.joule.2023.01.013>) We observe that this instability mode becomes present only at higher current densities in our system, as evidenced by our additional stability experiment performed at 100mA/cm² which does not display these same voltage and FE swings.

The second mechanism is a continuous and gradual decay in CO₂R FE. We observe this to occur in both the 100mA/cm² and 170mA/cm² carbon paper experiments, but not the 100mA/cm² ePTFE HCGDE stability experiment. This effect occurs over the course of ~40 hours for both the 100 and 170mA/cm² experiments, resulting in negligible CO₂R FE by the end of the experiment. Due to the gradual nature of this instability, we hypothesize that it is due to gradual restriction of CO₂ gas diffusion to the catalyst due to degradation of GDL hydrophobicity and build-up of low-surface tension alcohol products. Figure S23A reinforces this notion, as the backside of the

carbon paper GDL is noticeably wetted upon disassembly. We also observe the degradation of GDL hydrophobicity in the presence of electrolysis directly in Figure S24.

With regards to this second mechanism, which drives the most relevant losses in efficiency, we have performed post-mortem analysis on the wetting properties of carbon paper electrodes after these extended stability runs. This data can be found in Figure S23. We had initially characterized only the static contact angle, but have since deepened our investigation to consider the advancing and receding contact angles of water on the backside of the GDL. The data, in aggregate, clearly demonstrate a remarkable loss of hydrophobicity of carbon paper electrodes, with a receding contact angle of water which is practically zero. This means that if any liquid, whether water or liquid alcohol products, enters the GDL, it will remain pinned within the micropores of the GDL and be impossible to reasonably remove. This liquid will block CO₂ access to the catalyst, leading to the decreased FE we observe in our experiments.

In comparison, the same characterization for the back-side of the ePTFE HCGDE GDL used in the 70-hour stability experiment shows a minor, if any, change in receding water contact angle. Thus, water and liquid products are significantly easier to remove from the ePTFE GDL. We conjecture that this characteristic is why this second mechanism does not appear to be present in our long-term stability results for ePTFE HCGDE.

This sustained hydrophobicity enables stability of ePTFE, as well as granting further operational control. During our 70-hour HCGDE stability experiment, we periodically flowed a small amount of DI water through our cell to remove precipitation in the gas flow channels which was affecting the gas flow rate, which did not have any observable negative effects on the performance of our cell. The same DI water flow did not beneficially impact the performance for the carbon paper stability experiments.

We also investigated other aspects of our systems to ensure its robustness, including imaging our microwire conductors to verify no obvious corrosion (Figure S25), measuring the resistance of the microwires before and after operation (Figure S26), and have included data verifying the inlet and outlet gas flow rates (Figure S10).

4. The additional data on wettability is lacking as surface contact angle really does not say much for porous media and also the values are essentially the same within error. More characterization is necessary to argue about the claims. Also, the value proposition of ePTFE and wires espoused here is not really addressed well.

We appreciate this insightful comment which has helped to strengthen the post-mortem analysis as described in our response to point #3. While characterizing the wettability of the interior porous media would be the best measurement, it is difficult to do nondestructively. However, we note that the back surface of the GDL of the carbon paper electrodes becomes noticeably flooded as shown in Figure S23A. Complete blockage of the rear of the GDL will effectively block CO₂ diffusion to the catalyst

regardless of the interior wetting state. Thus, we reason that measuring the contact angle on the backside is an imperfect, but in this case, reasonable.

We have deepened this characterization to include the advancing and receding contact angles on these surfaces (Figure S23, 1F), as well as the effect of electrolysis on the carbon paper wettability (Figure S24), both of which help to paint a more complete picture of the electrode wettability. We find that after 40 hours of operation, while the advancing angle remains high for carbon paper, the receding angle becomes essentially zero. This indicates that if any flooding does occur, it will be irreversible, as the liquid wets the carbon paper GDL. The ramifications of this are described in our response to your point #3. Note that we dried these electrodes fully before contact angle measurements, thus eliminating the possibility that alcohol products could affect the measurement. These measurements are still in agreement with the prior measurements which showed “essentially the same within error”, as these prior measurements were effectively measuring the advancing contact angle as droplets were deposited on the surface.

Finally, we have edited the manuscript to include these data and analyses, which we feel help to espouse the value proposition of the ePTFE in maintaining hydrophobicity of the GDL, thus enabling more stable performance. Taken together, the stability of carbon paper is significantly troubled by its loss of hydrophobicity, while ePTFE does not lose its hydrophobicity, making ePTFE an easier GDL material to keep stable and high-performant.

Reviewer #3 (Remarks to the Author):

I looked carefully at the 75 hour stability data and I cannot agree with the authors that their system is 'stable'. The FE starts out a little below 40% and drops to around 20% at the end of the 75 hours. The authors speculate this to be due to morphological changes. After the 60 hour mark, the total cell voltage appears to spike up significantly and this is speculated to be due to iridium oxide anode instability. Based on these results, I believe their system actually appears to be 'unstable' and falls below the benchmark by other research groups in the field.

We agree that our system is not perfectly stable, and have made slight manuscript edits to ensure proper messaging. We now make the following claims in the main text:

- i) Our HCGDE is more stable than our carbon paper electrode: at hour 40, carbon paper has <5% FE, while our HCGDE retains >25% FE. At hour 70, our HCGDE still has >20% FE despite rising cell voltages.
- ii) The trends we see are reflected in the broader literature. The flooding stability of ePTFE has generally been shown to be very good, generally performing better than carbon paper. See Refs 25 and 36.
- iii) Significant challenges we faced in maintaining stability including managing salt precipitation and catalyst morphology changes motivate further work.

Achieving complete stability is difficult and requires the balance of many phenomena which have been covered in many other great works. The generalizability of our HCGDE approach to any catalyst, morphology, and electrolyzer architecture is encouraging in that it enables research groups with benchmark stability performance to scale their electrodes and systems to large sizes and continue to progress towards commercial relevance.

Other than this point, I believe that authors have responded well to the reviewer comments.

Thank you.

Reviewer #4 (Remarks to the Author):

The authors have made significant revisions to address the reviewer questions, including the addition of important extended stability data and more detailed characterization. I consider the manuscript could be suitable for publication after the following remaining points are addressed.

- References are missing: In my version of the revised manuscript, the References section is blank, hence I cannot assess the quality of referencing of prior works.

We apologize for the missing references, the updated manuscript should have them visible for your assessment.

- Fig.2B. Insufficient experimental detail is given here.

We have added a comment to refer to the Supplementary Info where more information can be found!

- Fig.2E: The caption doesn't clearly explain what Fig.2E is. Also, its x-axis meaning is undefined. if it shares x-axis label with Fig.2F, this should be better clarified (e.g. remove the gap between E & F).

We have made these clarifications. Thank you for your close attention.

- Fig.3C: CH₄ FE is shown unitless, which doesn't match what is used throughout the rest of the manuscript (%).

Fixed.

- Stability of Cu catalysts is a known issue, and the same could be true for the Cu wires used here, which are in contact with electrolyte and subjected to high current densities. I therefore expect some degree of corrosion is likely. It would strengthen the manuscript to show some analysis of the wires before and after extended testing (e.g. optical and/or electron microscopy).

Corrosion and morphological issues are significant for copper catalysts as nanometric surface roughness is an important catalyst feature. As the Cu wires do not significantly contribute to the electrochemical reaction, they need only transport electrons, which we expect would be unaffected by morphological changes on a nanometric level.

We perform optical microscopy to verify that no significant changes are seen on the wires on a micrometer to millimeter scale before and after operation. No differences are observed, and images are included in Figure S25.

We also measured the resistance of wire segments to ensure that any possible nano-scale corrosion or restructuring does not significantly affect the contact resistance and therefore overall resistance of the micro wires. As shown in Figure S26, this effect (if any) is small, and does not substantially contribute to the cell voltage.

- lines 241-242: Mentions of 0.5 cm² are confusing, since that size is not part of Fig.4. Perhaps they mean to refer to Fig.2F - if so, mention that here.

We refer to the performance of the 0.5cm² ePTFE GDE in Figure 1D, and have added clarifying references to the main text.

- It is important to explain how the gas quantification was performed, especially in the determination of the gas flow rate out of the cell (needed for proper calculation of product formation rates) which is not equal to the cell inflow rate.

Absolutely. We have added additional text to the Methods section, which also refers to a new Supporting Information figure S10. Here we show that the outflow is indeed not equal to the inflow rate for the 50cm² cell. The remainder of the cells and experiments are operated at sufficiently low conversion/small electrode areas/high gas flow rates such that the gas outflow rate is effectively the same as the gas inflow rate.

- The 50 cm² HCGDE experimental performance is compared to modeled behavior of an unmodified 50 cm² GDE, which I (and likely readers) find a bit confusing. The key novelty (the improvements caused by the HCGDE approach) would be far more convincing if compared directly to experimental results of an unmodified 50 cm² GDE (without Cu wires, but with all other parameters identical). It is strange that they do not report the actual performance of the unmodified GDE for direct comparison.

We appreciate this recommendation. We've performed exactly this experiment as shown in Figure 4 and Figure S16, and it confirms the value proposition of our work. As shown in Figure S16, the model was a very accurate predictor of experimental performance, so all other messaging remains the same. At the 50cm² scale, the HCGDE architecture reaches 300mA/cm² at a cell voltage which is 0.9V lower than that of the unmodified ePTFE electrode. Of course, this difference will only increase for larger electrode sizes.

- Fig.5: It is potentially misleading to have these two figure parts together, since they are for two very different cell sizes. I would find it more appropriate to combine Fig.5A with Fig.4B.

We have adjusted Figures 4 and 5 significantly. Old Figure 5A is now in the supporting information.

- The j/V relationships between different cell sizes are somewhat inconsistent in the maintext figures, comparing the 4.2 cm² and 50 cm² cells. Namely, j =100 mA/cm² requires ~4.0 V for the 4.2 cm² tests (Fig.2F & Fig.5B), while the 50 cm² cell reaches

100 mA/cm² at only about 3.3 V (Fig.4D, also consistent with Fig.S18). This is a rather large difference and thus should be addressed in the text. If this is due to the use of different membrane/anode, this should be mentioned and referred to the experimental details.

We absolutely want to be clear on these points.

Figure 2F: Voltage here is “high” ~4.0V because of excessive ohmic losses. The HCGDE architecture is not used, and the cell is electrically connected as shown in Figure 2A, so electrons must travel further than in Figure 4D

Figure 4D: Voltage here is low, as the HCGDE shortens the electron travel distance.

Figure 5B: Voltage here is higher despite use of the HCGDE because a different membrane/anode are used to achieve longer-term stability. The voltage would be even higher without the use of the HCGDE.

In order to clarify this, we have explicitly referenced the performance in Figure 4 when discussing the performance of Figure 5, as well as commenting on the contributions of the membrane and anode to the heightened voltage. And in the caption for Figure 2F, we have explicitly mentioned the different connection schema.

- Fig.5B: The cell voltage fluctuations sometimes seem to coincide with the moments of C₂H₄ analysis. The authors should consider the possibility that this could be an effect of pressure fluctuation induced by the injection valve of the gas chromatograph.

While this may be possible, we believe it to be unlikely. In Figure S22B, you can see that GC injections occurred every 14 minutes for the first 30 hours, but were paused from hour 30 to 40. In the time without GC injections, the voltage fluctuations continue unaffected. Figure S22C also shows that these oscillations do not occur at lower current density, meaning that the GC intake is not the driving cause.

- line 266: The C-paper GDE tests of Fig.S20 were apparently run at higher current densities (190, 170 mA/cm²) than the HCGDE one (Fig.5B, 100 mA/cm²) which does not really provide a fair basis for comparison of performance (stability or selectivity).

Absolutely. We have performed an experiment with carbon paper at 100mA/cm² to replicate the current densities of the HCGDE experiment. We find the same instabilities are present and relevant (see Fig S22 and discussion in Supplementary section 7). We believe that this has significantly contributed to the rigor of our work and to our understanding of the instability mechanisms.

- Table S2 is a valuable collection for comparison. Is there a reason for the missing values in the Total Current Density column? It should be a standard parameter reported in each paper, and it would be valuable to include the values, which are needed in order to relate the actual production rates of C₂+ products.

This has been updated, fixed, and filled out to completion. Thanks for the attention.

- Error bars are mentioned but in some places it isn't clearly explained how they are derived (e.g. standard deviation).

All error bars are standard deviation and are denoted as such.

- Electrolyte concentration effects: It has been shown that the anolyte electrolyte concentration can influence the selectivity of Cu, even in zero-gap MEA cells (El-Nagar 2023 <https://doi.org/10.1038/s41467-023-37520-x>), and this can result in pronounced changes in the C₂H₄ FE when comparing e.g. 10 and 100 mM concentrations. Here much of the work was conducted under quite low concentrations (10 mM). I suggest the authors consider this and mention its possible implications on further tuning selectivity.

Thank you for bringing this to our attention, this is very interesting indeed. In our work, we do actually work with two different anolyte concentrations: 10mM when using carbon paper IrOx anodes for initial characterization, and 100mM when using titanium felt IrOx anodes for stability trials. This is mentioned in the methods section; increasing the concentration for the titanium felt electrodes was necessary to mitigate ohmic losses through the anolyte. This actually helps to explain the fact that our stability trial with 100mM for the HCGDE had ~40% FE for ethylene at 100mA/cm², while the 0.5cm² experiments with 10mM only reached 40% FE at a current density of 200mA/cm². This has been included in the manuscript as suggested.