

Emerging technologies: general discussion

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Peter Styring, Waqas Tanveer, Ollie Thomas, Keith Whiston
and Eileen Yu

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George Dowson opened a general discussion of the paper by Alexander J. Cowan: You cite in the presentation how low the gas diffusion rates through ionic liquids can be, where it can take days or weeks for gases to permeate through a bulk ionic liquid. Since this may be a function of the viscosity, would it be worth increasing the temperature of the ionic liquid to increase the gas mobility, even if it costs some gas solubility?

Were temperature changes tracked during your experiments?

Alexander J. Cowan replied: We kept the temperature constant in these experiments to make the system easier to understand, but I agree that this is an interesting idea and should be examined.

George Dowson said: Given the hydrolysis issues of EMIM BF₄, it may be worth trying EMIM PF₆ as an alternative. It is commercially available, well-studied and won't hydrolyse in neutral or mild alkaline water solution.

Alexander J. Cowan responded: Thank you for the suggestion.

Peter Styring remarked: Did you observe any degradation of the ionic liquid and/or the electrode during the reaction, especially at high current densities?

Alexander J. Cowan answered: We did not observe any clear signs of degradation in our electrochemical measurements and an NMR study of the ionic liquid post-electrolysis did not show any evidence of IL breakdown. However, I would highlight that these experiments were relatively short (less than 2 hours)

and we cannot comment on the long-term stability of the system without further experiments.

Peter Styring commented: There is a linear increase in CO₂ uptake with increasing CO₂ pressure. This will affect the reaction kinetics which tend to be first order in most systems.^{1,2}

1 G. R. M. Dowson, D. G. Reed, J.-M. Bellas, C. Charalambous and P. Styring, *Faraday Discuss.*, 2016, **192**, 511–527.

2 S. Supasitmongkol and P. Styring, *Energy Environ. Sci.*, 2010, **3**, 1961–1972.

Alexander J. Cowan responded: Thank you for the comment. We have not determined the reaction order with respect to CO₂ or H⁺ in this system, but this data will help us understand the system.

Katarina Gugujonovic enquired: What about the scalability of this process? What problems can occur when using ionic liquids in a larger scale, thinking about the environmental impact, toxicity, safety issues *etc.*?

Alexander J. Cowan answered: Ionic liquids are being considered as practical CO₂ capture medium. CO₂ capture is not my area of expertise, but from what I have read I cannot see a fundamental reason why they could not be used at scale. Here, we focused on one IL, but the principle may also be applicable to a wider range, including for cheaper ILs.

Ollie Thomas remarked: What do you imagine would be the effect of elevated temperature? Is this something you would like to investigate? Ref. 19 of your paper (DOI: 10.1039/d0fd00140f) suggests that a temperature increase of just 30 K at atmospheric pressure can have a similar effect on the viscosity to elevating the pressure to around 5 MPa.¹ Presumably, elevated temperature would not be as effective as elevated pressure as it would not have the same effect on the bulk CO₂ concentration, but perhaps it would be worth it for simpler, safer operating conditions, particularly since flue gas sources are generally accompanied by a plentiful supply of excess heat. Do you imagine that elevated temperature would lead to selectivity issues? In addition, you suggest that this is a possible strategy for combined CCU. Have you any idea what the effects of contaminants in the gas feedstock would be on both the effectiveness of the process and its safety (*i.e.* corrosive species compromising the pressurised vessel)?

1 A. R. C. Morais, L. M. Alaras, D. L. Baek, R. V. Fox, M. B. Shiflett and A. M. Scurto, *J. Chem. Eng. Data*, 2019, **64**, 4658–4667.

Alexander J. Cowan replied: The temperature was held constant in this study but it is definitely an interesting parameter to study. Our long-term aim is to develop utilisation solutions that can be integrated directly into capture technologies/solvents. Often, the capture process operations have access to available low grade heat, therefore understanding how moderate changes in temperature affect the electrochemical behaviour is really important. The increased temperature will lower the viscosity but, as you note, the increased CO₂ pressure also increases the concentration of dissolved CO₂ as well as lowering the

viscosity. At this stage, we cannot quantify the relative contributions from the improved CO₂ diffusion coefficient and the increased bulk CO₂ concentration, but future studies will examine this.

These (and nearly all CO₂ electrocatalysis) studies are carried out using pure CO₂ (>99%) which is not a good model of flue gas. At this point in time we do not have any data on how impurities will change the catalytic activity, but these are underway in our lab at the moment.

Ali Reza Kamali remarked: Thank you Alex. The work seems very interesting to me, particularly because I have a molten salt background. I was expecting to see some molten salt-based works in this meeting as well, but it was a bit surprising that there was not even one. However, it is good that your work represents the field of ionic melts in this meeting. I also have a question for you – considering you have water in the ionic melt, I am wondering what the typical current efficiency involved in the CO₂ reduction in your system would be like. Do you have any ideas about this?

Alexander J. Cowan responded: We measured the faradic efficiency at low pressure and we achieved 60% for CO and 34% for H₂. At high pressures we cannot measure this value as the cell used has the anode and the cathode in the same chamber, so the possibility of the re-oxidation of the products exists.

Ali Reza Kamali asked: Do you have any idea what could be the solubility of the water that you can have in the ionic liquid?

Alexander J. Cowan responded: Here, we used a 20 mol% solution of EMIM OTF with water and have not attempted to study other ionic liquid in water concentrations. However, this has been examined in detail elsewhere.¹

1 S. S. Neubauer, R. K. Krause, B. Schmid, D. M. Guldi and G. Schmid, *Adv. Energy Mater.*, 2016, **6**, 1502231.

Michael North remarked: What percentage of CO₂ is converted to CO? Will it be necessary to separate CO and CO₂? This is not a trivial separation. However, if the ultimate aim is methanol production, it may not be necessary as many conventional CO to methanol processes actually dope the CO with CO₂ and there is debate in the literature as to which species is actually hydrogenated.

Alexander J. Cowan responded: In these experiments we have used a high pressure electrochemical cell where the anode and cathode are in the same chamber, which prevents the measurement of the conversion yields. Studies at low pressures have reported a range of carbon dioxide conversion yields depending on the conditions, but it is important to note that the practical limit of conversion is likely to be far below 100%. Values of less than 25% on single passes through a reactor are normal. Either some form of product separation, or use of the product in the presence of carbon dioxide, will be required. As you note in the question, this is not necessarily a problem for the production of CO/H₂ mixes in carbon dioxide as this is the feedstock commonly used in methanol production.

Alexander J. Cowan commented: I think that one of the record conversion efficiencies for a single pass has been reported by Prof. Yu and perhaps she is better placed to comment.

Eileen Yu responded: Thank you for the question. By using GDE, we were able to reach 20% total conversion, with the FE for CO being higher than 90%, and for the formate system the FE was around 80%.

Although it is still low, and the energy efficiency can be improved by optimising the anode OER, it opens the possibility to use a recycled stream to further improve the overall conversion.^{1,2}

- 1 H. Xiang, S. Rasul, B. Hou, J. Portoles, P. Cumpson and E. H. Yu, Copper–indium binary catalyst on a gas diffusion electrode for high-performance CO₂ electrochemical reduction with record CO production efficiency, *ACS Appl. Mater. Interfaces*, 2020, **12**(1), 601–608.
- 2 H. Xiang, H. A. Miller, M. Bellini, H. Christensen, K. Scott, S. Rasul and E. H. Yu, Production of formate by CO₂ electrochemical reduction and its application in energy storage, *Sustainable Energy Fuels*, 2020, **4**(1), 277–284.

Waqas Tanveer asked: Studies have found that in co-electrolysis it is mostly water electrolysis which is leading the reaction, while it is CO₂ directing the thermodynamics, and both work in synergy. Did you monitor the temperature effects of how much CO₂ was converted or the CO to hydrogen ratio?

Alexander J. Cowan answered: Thank you for the question. The experiments were carried out at a single temperature (room temperature). In the field, people typically use co-electrolysis to refer to a system where the oxidation of water occurs at the anode and carbon dioxide reduction takes place at the cathode. Proton reduction to make hydrogen is a side-reaction. The CO is generated by electrochemical reduction and there is very strong *in situ* spectroscopic evidence of this in the literature. Under the conditions used it is not generated by the reverse water gas shift reaction.

Waqas Tanveer commented: In terms of scaling up, with the electrolysis cell it is easier to do this from the other side of the cathode, so are you going to do this with the 1 L min⁻¹ electrolysis Cell? Also, how could you separate CO, CO₂ and oxygen? Do you have any plans to separate the gases?

Alexander J. Cowan communicated in reply: Thank you for the question and my apologies if I am misinterpreting it. Is the suggestion that to scale up you should move towards cathodes with distinct sides, such as gas diffusion electrodes? If so, that is not under consideration here due to the complications of the higher pressures used. Currently, we do not plan to separate the gases in our lab, but I note that the separation of these gases is readily achievable with existing technologies.

Volker Sick asked: Have you quantified how the energy needs for stirring the highly viscous ionic fluid compare to the energy needed to build and operate a high-pressure reactor system?

Alexander J. Cowan responded: No, we have not done this, but I agree that it is an important calculation that needs doing.

Walter Leitner asked: IL viscosity as a function of CO₂ pressure has been studied and quantified – is this correlated with the increase, or is it the CO₂ concentration in the liquid phase?

Alexander J. Cowan communicated in reply: Thank you for the question. Unfortunately, we have been unable to find viscosity and CO₂ concentration data for the exact water/ionic liquid combination used in the electrocatalysis study. But from similar water concentrations we believe that the current density is increasingly non-linearly correlated with the estimated CO₂ concentration at different pressures. The current density does directly correlate (linearly) with the volume of expansion, which would, in turn, be expected to correlate with the viscosity, so my belief is that the change in viscosity is key in achieving higher currents. This is also supported by chronoamperometric measurements which show significantly lower levels of current drop with time, indicating increased diffusion coefficients for CO₂ (or H⁺).

Sourav Ghosh remarked: What about the selectivity at high CO₂ pressure?

Alexander J. Cowan responded: Thank you, this is a good question. In these preliminary studies we focused on the fundamental electrochemistry at high pressure to see if the use of a gas expanded liquid would lead to an increased steady state current density due to the improved mass transport properties. Future studies should look at the product distribution. Unfortunately, our high pressure electrochemical cell has the anode in the same compartment as the cathode, so this experiment is not possible with our apparatus.

Peter Styring remarked: Triflate EMIM ionic liquids are expensive. Have you looked at other, cheaper ILs like those based on ammonium salts, for example those in ref. 1?

1 D. G. Reed, G. R. M. Dowson and P. Styring, *Front. Eng. Res.*, 2017, 5, 13.

Alexander J. Cowan replied: At this point we have not examined a wider range of ILs. We have carried out this initial study on one of the most widely used ionic liquids in the CO₂ electrocatalysis community as it was important that its behaviour at atmospheric pressure was well understood before we commenced high pressure studies. I hope that future studies will now go on to look at lower cost ILs under a range of pressure/temperature conditions.

Charles Cummings remarked: Did you investigate the surface of the electrode after cycling or potentiostatic CO₂ reduction? An impedance/SEM study would inform you if you are forming a film (probably from the electrolyte breakdown) which could hinder the available active sites for CO₂ reduction?

Alexander J. Cowan replied: In this preliminary study we did not study the electrode by SEM post-experiment. However, we did take care to ensure that the

applied potential was within the electrochemical stability window of the solvent, so we anticipate that only minimal solvent breakdown will have occurred.

Keith Whiston commented: Have you considered other potential ionic liquids which do not contain fluorine in the anion and which might be more practical for environmental and cost reasons? Have you tried the dicyanamide anion, for example, which should give low viscosity concentrated mixtures with water? These anion systems have been successfully tested in capacitor applications. Also, although you mention that the high viscosity and limited electrochemical window are limitations for other potential IL candidate cations, derivatives of piperidine, hexamethylene imine and even triethylamine would be worth considering on cost and availability grounds.

Alexander J. Cowan replied: Thank you for the question. In the studies at low pressure we examined both EMIM BF₄ and EMIM OTF, which are two of the most commonly studied ionic liquids for carbon dioxide reduction. We chose to work with EMIM OTF as it is resistant to hydrolysis and it has a very large electrochemical stability window. I agree that future studies should be expanded to explore a much greater range of ionic liquids, in particular those which have a lower cost, at both high and ambient pressures, and these are excellent suggestions that I encourage the field to look into.

Charles Cummings asked: Can you fit the peak current in the CVs you showed to the Randles–Sevcik equation to estimate the diffusion constant for a pristine surface and after cycling? This would indicate if a film has formed and is hindering either the kinetics or diffusion.

Alexander J. Cowan responded: In this paper (DOI: 10.1039/d0fd00140f), we related the electrochemical activity to the bulk solvent properties. We measured the expansion, and hence inferred a decrease in viscosity, of the bulk solvent and then correlated this to the current density. However, the question makes an important point and highlights a shortcoming in our study. Our measurement of the solvent expansion does not provide information on the local solvent structure in the EDL and the subsequent effect on the CO₂ diffusion coefficient.

In Fig. 3 of the paper (DOI: 10.1039/d0fd00140f) the peak current shows a linear dependence with the square root of the scan rate for Fig. 3a, both before and after the (short) electrolysis experiments, with a similar slope. We have not attempted to analyse the slope of the plot further. My understanding is that imidazolium ionic liquids rapidly adsorb onto the electrode surface¹ so they will be present even in our first measurements. I am not aware of any studies (spectroscopic or electrochemical) that have attempted to study how the solvent structure at the electrode surface changes with pressure. As the Randles–Sevcik equation should be applied to reversible couples we are now recording how the diffusion coefficient of ferrocene carboxylic acid changes with pressure. This does not directly report on the CO₂ diffusion coefficient but we believe it still will provide a useful insight.

1 G.-H. Deng, X. Li, S. Liu, Z. Zhang, Z. Lu and Y. Guo, *J. Phys. Chem. C*, 2016, **120**(22), 12032–12041.

Huan Doan commented: (1) Can you comment on what would happen if we increase the CO₂ pressure over 5.1 MPa? (2) Did you measure the pH for each CO₂ pressure? I can assume that the pH of water significantly drops in the presence of CO₂. This might help to explain why the current density is higher under the CO₂-expanded liquid than the N₂-expanded liquid. (3) Did you try expanding other mixtures such as ILs in MeOH or DMSO, rather than H₂O reported in your paper (DOI: 10.1039/d0fd00140f)?

Alexander J. Cowan responded: In these experiments we did not examine pressures greater than 5.1 MPa. Our aim was to try to explore how pressure changed the catalysis at pressures that are likely to be relevant to combined capture and conversion systems. We did not measure the pH at each CO₂ pressure, but this is a good suggestion. It is non-trivial to measure pH at high pressure for the bulk electrolyte and even harder to measure the local pH at the electrode surface, but experiments studying the onset of hydrogen evolution on a Pt electrode may offer a way to do this. We have not explored other solvents. The reasons for using water with the ionic liquid is that the anode reaction will need to be water oxidation. Most agree that water oxidation is the only realistic source of electrons/protons if electrocatalytic CO₂ reduction is to be carried out at scale.

Jonathan Ruiz Esquius commented: Based on your experience on the electrocatalytic reduction of CO₂, which area would benefit more from further research; the development of new catalytic materials or the optimization of reactor design and process conditions?

Alexander J. Cowan answered: The short answer is all of the above! We now understand a good amount about metal electrodes for carbon dioxide reduction but the use of complex alloys and transition metal complexes immobilised on electrode supports is still at an earlier stage and these fields hold much promise for improving onset potentials. Similarly, we need to keep working on improving water oxidation catalysts to enable the use of earth abundant elements. The engineering of the electrodes and the design of the electrolyzers is a very active field and from the fundamental electrochemistry studies carried out it is clear that control of the local pH and carbon dioxide concentration is critical if selectivity is to be achieved at a high current density.

Jeffrey Poon asked: A central part of the research premise is the issue of viscosity and CO₂ local concentration limiting the activity (current density) and selectivity (faradaic efficiency). In that case, why not do electrochemistry in supercritical CO₂ instead? Ionic liquids have also been utilised there as a conductivity-enhancer. There is a small body of literature (*e.g.* ref. 1 and 2) that can be expanded upon and the product separation should be much easier (by evaporating excess carbon dioxide).

1 J. A. Branch and P. N. Bartlett, *Philos. Trans. R. Soc., A*, 2015, **373**, 20150007.

2 O. Melchaeva, P. Voyame, V. C. Bassetto, M. Prokein, M. Renner, E. Weidner, M. Petermann and A. Battistel, *ChemSusChem*, 2017, **10**(18), 3660–3670.

Alexander J. Cowan answered: As the question notes, the electrochemical reduction of scCO_2 /ionic liquid systems has been examined in a small number of studies and this is an interesting area of research. I agree that the use of scCO_2 will help with the product/ CO_2 separation but, as noted in a previous answer, this may not necessarily be a problem as CO_2 / CO / H_2 mixes are already used at scale. Our decision to focus on non-super critical CO_2 reduction here was due to a wish to carry out electrochemical measurements under conditions that are most relevant to ionic liquid-based carbon dioxide capture solvents with the ambition of developing an integrated capture/utilisation approach.

Andre Bardow asked: In your presentation, you mentioned the idea of integrating the process with CO_2 capture. Specifically, you considered pre-combustion CO_2 capture due to the high CO_2 pressures needed. In this case, the feed gas would be rich in hydrogen. Could you explain how the presence of hydrogen, or potentially other gases in the feed stream, would affect your process? In addition, I would be thankful if you could clarify the intended downstream separation of your products.

Alexander J. Cowan answered: The comments relating to pre-combustion were due to the number of studies using similar ILs in the pressure range examined here in pre-combustion capture systems. However, I will readily admit that capture is not my area of expertise and it may be that this approach is as (or more!) amenable to post-combustion capture. The separation of CO from H_2 and CO_2 may not be required for use as the $\text{CO}/\text{H}_2/\text{CO}_2$ mix is already commonly used as a feedstock.

Moritz Schreiber commented: There are industrial alkylation processes (in refining) using ionic liquids. So the scale-up and operation of processes using ionic liquids is conceptually feasible.

Liane Rossi asked: How is the selectivity affected by pressure?

Alexander J. Cowan replied: Future studies should look at the product distribution. Unfortunately, our high pressure electrochemical cell has the anode in the same compartment as the cathode so this experiment is not possible with our apparatus.

Haresh Manyar asked: Can you please elaborate further on the nature of the interaction of CO_2 with the ionic liquid at the molecular level, and does the expansion of the liquid volume depend on the strength of the acidity/basicity of the ionic liquid? Furthermore, is this phenomenon of the expansion of volume and reduction in viscosity observed at noticeable levels with other gases such as H_2 or O_2 as well?

Alexander J. Cowan answered: Thank you for the question. We do not have a detailed understanding of how the ionic liquid interacts with the CO_2 either in bulk or at the electrode surface as the pressure is changed. This is an interesting question but unfortunately beyond what we have studied to date. The gas

expansion of relevant ionic liquids by other gases has been studied elsewhere, for example in ref. 1.

1 Z. Lei, C. Dai and B. Chen, *Chem. Rev.* 2014, **114**(2), 1289–1326.

Peter Styring opened a general discussion of the paper by Eileen Yu: Are there any ethical issues with using microbial systems? The public can be nervous about processes using organisms! Are the organisms able to reproduce and what would be the environmental effects if they were released?

Eileen Yu answered: Thanks Peter for the question. Microbes from natural sources, either mixed cultures or pure cultures, have been used in various processes, particularly fermentation for food or beverages. There is no ethical issues and the public do not have any concerns.

Only when genetically modified microbes are produced by synthetic biology will there be concerns. However, if the GM microbes are not able to reproduce, then the risk of GM microbes contaminating the natural environment would be very low.

Deepak Pant asked: You mentioned bacteria being robust catalysts in comparison to electrocatalysts – how do you define robustness? Is it the lifetime of catalyst, the ability to regenerate or process conditions?

Eileen Yu responded: Many thanks Deepak. As mentioned in the session, the robustness here mainly means that the microorganisms are able to regenerate and recover from temporary incidents. Probably robust or resilient could be better terms.

Deepak Pant enquired: Most bacteria used in MES are anaerobic, so it is necessary to expend energy to maintain these process conditions. Traces of oxygen can kill the system – so these are not so robust after all and the working conditions are also limited *e.g.* pH, in ways that chemical reactions do not have. Can you really call them robust?

Eileen Yu answered: Thank you for the question. If a chemical catalyst is poisoned, the activity would deteriorate and, in most cases, it is not possible to bring it back. Whereas microbes might be temperamental, but as long as there are the right conditions it is possible to restore the activity. The reactors in our lab have been running for long time. They have ups and downs but they are still working. I would consider this to be robust.

Deepak Pant asked: You also work on electrochemical reduction as well as MES – which approach has the most potential? Which one is at a higher TRL? What is the overall TRL for MES overall and in the lab? Would you say that a hybrid approach is optimal?

Eileen Yu answered: The electrochemical reduction of CO₂, although also at an early stage, has faster kinetics, higher conversion and good selectivity of products with the right catalysts. There has been progress in making this process more

commercially viable. However, the main challenge is the products, which are mainly C1. For MES, on the other hand, the kinetics are slow and the mechanisms are more complicated, particularly with mixed cultures. However, it can produce longer chain carbohydrates. Therefore, I consider the two systems to be complementary.

Both systems have passed the feasibility stage and we know that they both work, so they are probably TRL2-3 in the lab. The electrochemical process could reach a higher TRL quicker with all of the knowledge from fuel cells and electrolyzers.

Yes, I would consider a hybrid approach to probably be a better option with a bio-electrochemical process.

Deepak Pant asked: What did you use as a starter culture and was it enriched before use in MES? Was it from previously running system?

Eileen Yu responded: For the initial inoculum, it was from activated sludge from a wastewater treatment plant. For the work in the continuous mode, it was from the planktonic solution from a previous MES cell.

Moritz Schreiber said: How does the integrated electro-biochemical process compare to the combination of the separate processes (electrochemical CO₂ to CO or formate process as the first step and a separate biochemical CO or formate to bioproduct process in a second step) in terms of the energy efficiency (governing the operation expenditure) and typical reaction rates (which are an indicator for the capital expenditure)?

Eileen Yu answered: Thank you for your question Moritz. If you mean the integrated electro-biochemical process was the microbial electrosynthesis, then the kinetics of the microbial reaction are much lower, therefore the current density compared to the electrochemical reaction is two magnitudes lower. It makes more sense to combine electrochemical and microbial processes together. In theory, the products from the first electrochemical reaction would just be the same as the normal feedstock for the secondary bioreactor. In fact, our electrochemical reactions for formate and CO production are quite efficient, with more than 20% overall CO₂ conversion and a FE of more than 90% for CO and of more than 80% for formate over a wide range of potentials.

Some examples of C1 products from CO₂ can be found in ref. 1 and 2. We are still working on the combined process.

- 1 H. Xiang, H. A. Miller, M. Bellini, H. Christensen, K. Scott, S. Rasul and E. H. Yu, Production of formate by CO₂ electrochemical reduction and its application in energy storage, *Sustainable Energy Fuels*, 2020, **4**(1), 277–284.
- 2 H. Xiang, S. Rasul, B. Hou, J. Portoles, P. Cumpson and E. H. Yu, Copper–indium binary catalyst on a gas diffusion electrode for high-performance CO₂ electrochemical reduction with record CO production efficiency, *ACS Appl. Mater. Interfaces*, 2020, **12**(1), 601–608.

Xiangkun Elvis Cao asked: My question is on the scale-up and commercialisation potential of your microbial electrosynthesis (MES) system. One of the greatest challenges for using living organisms is that they will die. So, the first question I would ask is would the living requirements be very harsh for the

microbes involved in your study? Will the system perform differently under different scales? Would you be able to offer some insights into the challenges you would envision there being which would hinder the potential to commercialise your system?

Eileen Yu replied: Thank you for your question. Scaling-up is always something we like to think about as engineers.

Living organisms will die but they will also regenerate, given the right conditions for them to grow. We used a mixed culture from a wastewater treatment plant and applied conditions for the desired electroactive bacteria to be selected and enriched. Compared to a pure culture, a mixed culture would be more robust, although the efficiency might not be as high as that of a pure culture.

There are different approaches for scaling up microbial electrochemical systems. In terms of microbial fuel cells and microbial electrolysis cells, researchers are already working on 1 m³ reactors. For these reactors, the material conductivity, cost and reactor design in terms of the fluid dynamics (pressure drops *etc.*) would be more challenging with larger reactors.

Another approach is modular design, *i.e.* many small reactors connected together. These two approaches have different requirements and challenges.

Xiangkun Elvis Cao said: If impure CO₂ is used as the carbon source, what do you envision the effects of the different impurity species on the performance of the microbes to be?

Eileen Yu responded: Thanks for your question. So far, we have only used pure CO₂. For real flue gas or CO₂ from industrial processes, there would still need to be some purification process. Certainly, different impurities will have an impact on the microbes. This would be something for us to investigate further.

Jeffrey Poon commented: There is a significant focus in the paper (DOI: 10.1039/d0fd00132e) on HRT and pH maintenance. Does this essentially translate to the need for 'catalyst' stability (mechanically and biologically) instead of microbial 'activity'? If so, would it not make sense to incubate organisms that are known to form stable substrates (*e.g.* biofilms and EPS-forming organisms such as algae and cyanobacteria)? These types of media are known to buffer the organisms from environmental fluctuations and provide strong mechanical stability (so you could make utility out of 'biofouling').

Eileen Yu responded: Thanks for the question. This study focused on HRT and pH and was a continuation of our previous work. What it showed was that HRT and pH not only affected microbial activity but also dominated microbial communities in the system.

Algae and cyanobacteria produce oxygen during photosynthesis whereas acetobacteria are anaerobic. They have different functions. Acetobacteria also formed an electroactive biofilm where MES happened.

Dharmjeet Madhav remarked: You used one type of commercial CEM membrane, so the membrane parameter was constant. Would you please

elaborate on the effect of different kinds of membranes (different membrane parameters) and what would be an ideal membrane for this purpose?

Eileen Yu responded: Thank you for your question. Of course, there would be an ideal membrane. As the current density for MES is around 1–1.5 mA cm⁻², using different membranes does not have a big effect. Depending on the products, you could choose AEM or CEM. Low cost and stable membranes would be important for MES.

Jisiwei Luo asked: Have you ever integrated an intermittent electricity supply to your experiments?

Eileen Yu responded: Thank you for your question. We have not tested the system with an intermittent electricity supply yet, which is important considering the application of renewable energy. Deepak Pant's group has done some studies on that.¹

1 M. del Pilar Anzola Rojas, R. Mateos, A. Sotres, M. Zaiat, E. R. Gonzalez, A. Escapa, H. De Wever and D. Pant, Microbial electrosynthesis (MES) from CO₂ is resilient to fluctuations in renewable energy supply, *Energy Convers. Manage.*, 2018, **177**, 272–279.

Stephen McCord asked: The slides shown during your presentation showed a very high selectivity towards acetate as a product. Do you think that the product stream is pure enough to be used for a secondary biological/bio-chemical process as a feedstock? I was thinking in particular methanogenesis to allow for the production of methane given its importance and large market. Do you foresee a possibility in which this could be done on an industrial scale in the future?

Eileen Yu responded: Thank you for the question Stephen. We were able to produce a concentration of 8 g L⁻¹ of acetate from our reactor with a volume of 100 ml. That was sufficient for a secondary bioreactor to convert acetate to the target bioproduct. For this study, we particularly tried to avoid methane production as it would go through a different metabolic pathway without multi-carbon products. However, it could be possible by optimising the operational parameters, such as the pH (methanogens prefer a slightly alkaline environment) and applied potential, which could make methane production more selective.

Deepak Pant enquired: In Fig. 3 of your paper (DOI: 10.1039/d0fd00132e), you show several products being formed. How do you propose to improve the selectivity towards one product? What will be the approach for DSP?

Eileen Yu replied: Thank you Deepak. It is a very good question. Let us say that the target product is C4–C6 butanol, hexanol. There are different ways to improve the selectivity, such as the substrate, pH, HRT and adding extra electron donors, such as ethanol or methanol, as well as the *in situ* extraction of the product.

DSP, in the long term, definitely needs to be considered once the production and yield reach certain level.

Ali Reza Kamali asked: Thank you Eileen for your very nice work and presentation! I am wondering what would the survival rate of bacteria under the experimental conditions be like?

Eileen Yu responded: Thank you for your question. We are using a mixed culture with an inoculum from activated sludge which contains all kinds of different communities.

By applying -1.0 V/AgAgCl and using dissolved CO_2 , acetobacterium was enriched with more than 50% abundance and formed a biofilm covering the electrode. With these conditions maintained, the biofilm could be stable for quite a long time. These conditions were preferred by the acetobacterium.

If you are interested, our study our study on developing the active biofilm is in ref. 1.

1 P. Izadi, J.-M. Fontmorin, A. Godain, E. H. Yu and I. M. Head, Parameters influencing the development of highly conductive and efficient biofilm during microbial electrosynthesis: the importance of applied potential and inorganic carbon source, *npj Biofilms Microbiomes*, 2020, 6(1), 40.

Claudia Bizzarri commented: The use of microorganisms to manage the generation of value-added products from CO_2 is fascinating. Some bacteria are known to perform photosynthesis (*e.g.* Cyanobacteria, Prochlorytes). Nevertheless, microbial photoelectrosynthesis (MPES) combines microbial electrosynthesis with semiconductor photoelectrochemical hydrogen evolution. Do you think it might be possible to combine these processes and develop a MPES system from photosynthetic bacteria?

Eileen Yu replied: Thank you for your question. It is very interesting. Currently, MPES uses H_2 production from the photoelectrochemical process for microbial electrosynthesis. Photosynthetic bacteria mostly work in aerobic conditions, and often O_2 is produced during photosynthesis. Therefore, it could not currently be used for producing the products from MES. It is possible to use synthetic biology to design and modify microorganisms to produce targeted materials.

Peter Styring remarked: With regards to ILs, scaling with EMIM OTf is possible but hugely expensive unless there is no degradation/loss and there is good recycling. We used tetrabutyl ammonium acetate for our thermocatalytic studies and capture studies as the cost is similar to MEA. However, it does need to be used at elevated temperatures (<120 C) as it is a solid at RTP.

Walter Leitner said: CO_2/CO separation is technically done in the WGS process on scale.

Walter Leitner commented: For methanol from syngas, which is technically a mixture of $\text{CO}/\text{CO}_2/\text{H}_2$, it is now widely accepted that the hydrogenation over industrial ICI-type catalysts goes through the CO_2 pathway preferentially. CO_2 and CO are interconverted by the WGS equilibrium.

Michael North replied: Agreed, but I think that there is still a view that it is catalyst dependent.

Walter Leitner responded: Yes, you are right! My comment was for the CuZn-systems used industrially.

Deepak Pant said: Building further on the remark by Eileen Yu and that microbial electrosynthesis is a complementary approach to the electrocatalytic approach, as well as the example given by Vanesa Gil of the integrated approach in the 4AirCRAFT project,¹ I can confirm that it is indeed the case, and several recently approved projects in Horizon 2020 are following this line of electrochemical conversion of CO₂ followed by bioconversion of the C1 products to higher carbon molecules. One such example is the VIVALDI project starting on 1 June 2021,² where CO₂ is electrochemically converted to formate and methanol and these are then used in a biological system to produce C3–C4 organic acids.

1 Air Carbon Recycling for Aviation Fuel Technology, <https://cordis.europa.eu/project/id/101022633> (accessed June 2021).

2 innovative bio-based chains for CO₂ valorisation as added-value organic acids, <https://cordis.europa.eu/project/id/101000441> (accessed June 2021).

Vanesa Gil responded: 4AirCRAFT has been officially announced.¹ I will keep you informed. Maybe we can find synergies between our projects/activities.

1 EU and Japan jointly invest €10,7 million for breakthrough research on advanced biofuels and alternative renewable fuels, https://ec.europa.eu/info/news/eu-and-japan-jointly-invest-eu107-million-breakthrough-research-advanced-biofuels-and-alternative-renewable-fuels-2021-apr-14_en, (accessed April 2021).

Peter Styring addressed Walter Leitner and Michael North: There is a good discussion of the CO/CO₂ activation issue in the book by Maitlis and De Klerck.¹ This is an important issue as it will have significant impact on how processes are designed.

1 Maitlis and De Klerck, *Greener Fischer–Tropsch Processes for Fuels and Feedstocks*, Wiley-VCH, Hoboken, 2013.

Michael North answered: Yes, but the field has evolved a lot over the last 8 years. It is only recently that the debate over whether CO or CO₂ is the species being reduced has been shown to be dependent on the catalyst being used.

Peter Styring opened a general discussion of the paper by Max König: Why was acetonitrile used when it is not a very environmentally friendly solvent? Are there any other aprotic solvents that can be used?

Max König responded: Propylene carbonate (PC) is another promising solvent. It is not only much more environmentally friendly than acetonitrile (which is made with CO₂!), but is also less problematic in terms of health hazards. Typically, applied solvents in aprotic electrochemistry have to be highly polar, which PC is (its relative permittivity $\epsilon_R = 66$). This allows the supporting electrolyte to be readily dissolved and fully disassociated to achieve a suitable conductivity. The decision to work with acetonitrile was made based on an improved CO₂ mass transport and higher CO₂ solubility of 310 mmol L⁻¹ compared to a solubility of 130 mmol L⁻¹ at room temperature in PC.

Peter Styring remarked: What yield did you get with propylene carbonate?

Max König answered: In an experiment equivalent to the experimental setup described in the paper under “H-type cell experiments” (DOI: 10.1039/d0fd00141d) but employing propylene carbonate instead of acetonitrile, we could achieve a FE (oxalate) = 75% at a current density of 8 mA cm⁻². We are currently working on another publication exploring the role of the solvent on the selectivity between oxalate and CO/carbonate. At this point I would also like to refer to work done by Shi *et al.* (e.g. ref. 1) in propylene carbonate. They have been working on the reduction of CO₂ to CO, also exploiting the limited miscibility of propylene carbonate and water in a two-phase electrolysis.

1 Shi, *et al.*, *Electrochim. Acta*, 2017, **240**, 114–121, DOI: 10.1016/j.electacta.2017.04.065.

Michael North commented: Nucleophilic radical anions are known to react with MeCN. Is this an issue for the CO₂ radical anion?

Max König replied: There is a gap of about 20% in the charge balance of the reaction that we cannot account for with oxalate or CO. This could be accounted for by solvent reduction, but whether this is directly at the Pb cathode or due to a CO₂ radical anion we cannot say. Another possibility to account for the charge balance gap could be the re-oxidation of formed oxalate in solution at the anode due to the one-compartment configuration.

Elaine Moore asked: Lead is not environmentally friendly. Have you explored using a different metal?

Max König responded: I have tested Mo, Fe, Ti and achieved moderate selectivities between 40–60% for oxalate. There is a comprehensive publication by Ito *et al.* on the selectivity screening of metals in aprotic solvents.¹ Also, stainless steel electrodes are applied as it allows high selectivities and also has a high stability at largely negative potentials, so these could be particularly interesting for application in GDE.

1 S. Ikeda, T. Takagi and K. Ito, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2517–2522, DOI: 10.1246/bcsj.60.2517.

Michael North enquired: Which salt of the oxalate is initially formed?

Max König replied: As tetraalkylammonium salts are used as a supporting electrolyte the oxalate is initially present as a tetraalkylammonium oxalate. When employing a sacrificial anode (zinc was used in the study) the oxalate then precipitates as white zinc oxalate flakes.

Michael North asked: Can the CO₂ radical anion be trapped with other species to generate a broader range of products? Ben Buckley (and others) work on electrochemical CO₂ addition to alkenes and alkynes, so adding an alkene such as styrene to your reaction might result in carboxylic acid formation.

Max König answered: Electrocarboxylation with CO₂ is indeed quite an interesting reaction. We have not looked into it any further. There is a recent review including electrocarboxylation reactions in the literature.¹

1 R. Matthesen, J. Fransaer, K. Binnemans and D. E. De Vos, *Beilstein J. Org. Chem.*, 2014, **10**, 2484–2500.

Marcelino Maneiro asked: I would like to discuss the role of the supporting electrolyte in the electrochemical process. Everything seems to indicate that the chosen electrolyte, tetraethylammonium tetrafluoroborate, has a non-innocent effect since it causes some degradation of the cathodic electrode at very negative potentials. Also, a fluoride salt (PbF₂) is formed during the process by the reduction of the tetrafluoroborate anion. Thus, I wonder what are the reasons for choosing this electrolyte? Have you tried reducing the amount of electrolyte or using others?

Max König answered: Indeed, it does look like tetraethylammonium salts are involved in the deactivation of the electrode at highly negative potentials. I cannot comment on other R₄N⁺ such as butyl-, hexyl- *etc.* Preliminary experiments have not shown any effect of the size of the alkyl chain on the product distribution. Usually, tetraalkylammonium salts are applied precisely because they are innocent up to largely negative potentials, *e.g.* –2.4 to –2.6 V vs. Ag/Ag⁺ in acetonitrile. Ultimately, the optimization of the electrode has to go through the application at a maximum applicable potential to maximize the FE to oxalate as well as the current density while not deactivating the electrode. A different metal catalyst could also prove to be more stable under these conditions, for example applying stainless steel.

Jeffrey Poon said: In aqueous solutions, the evolution of the Pb/PbO catalysts' oxide layer has been known to significantly influence the catalytic performance.¹ How does this compare in an aprotic solvent environment? *Operando* spectroscopy using ATR-IR should be able to shine a light onto this issue and provide interesting mechanistic insights.

1 J. E. Pander, III, M. F. Baruch and A. B. Bocarsly, *ACS Catal.*, 2016, **6**, 7824–7833.

Max König responded: Thank you for this question. I have not done any *operando* spectroscopy therefore I cannot comment on the *in situ* state of the electrocatalyst. ATR-IR would certainly be a great method to further the understanding of the reaction at the active site.

Charles Cummings asked: What is the rationale for using a sacrificial Zn counter electrode and what are your thoughts for replacing this to decrease the consumables of the system?

Max König responded: The rationale for choosing the zinc electrode was the fact that it allowed us to avoid the aqueous oxygen evolution reaction to study only the effect of the local CO₂ concentration without introducing any water to the cathode chamber of the electrode (as small amounts of water already will shift the products towards formate and H₂). Other alternatives are halide oxidations (*e.g.* 2

Cl⁻ to Cl₂) employing tetraalkylammonium chlorides, but a sacrificial metal anode seemed like the easiest choice.

Michael North asked: Have you thought about changing the metal as Zn is not the most sustainable? We have used Al and Fe as sacrificial electrodes,¹ as both are more earth crust available and available as waste. Have you tried either?

1 K. J. Lamb, M. R. Dowset, K. Chatzipanagis, Z. W. Scullion, R. Kröger, J. D. Lee, P. M. Aguiar, M. North and A. Parkin, *ChemSusChem*, 2018, **11**, 137–148.

Max König responded: We have not tried other sacrificial anodes. Al and Fe sound like great alternatives. The target would be to combine the aprotic CO₂ reduction with an aqueous anode reaction forming protons. This could for example be achieved with a MEA which is stable in the aprotic solvent or an aqueous OER reaction employing an anion exchange membrane that allows the transport of oxalate to the aqueous anode solution. With this, oxalic acid can be directly produced as opposed to the metal oxalate and the water crossover to the cathode can be minimized.

Eileen Yu remarked: Thank you Max for a very interesting talk! Have you tried a porous Pb electrode in the solvent? Surface area seems to also have an effect on selectivity and current density?

Max König replied: The GDEs used in this study have a catalyst layer (CL) comprised of a commercial lead powder and PTFE binder, and in the cold rolling process a pore former was added to introduce pores into the CL. We have not tried a skeletal-type full lead GDE but we assume the PTFE to be inert in the reaction. Further work will focus on the tuning of this porous CL to increase the electrochemically active surface area of the GDE.

Ollie Thomas opened a general discussion of the paper by Samuel Perry: How stable is the thiol coating? Did you see any evidence of degradation or dimerization, for example, after operation? You cite a limited supply of protons at high current density as a limiting factor. Could an alternative solution to the addition of a hydrophilic layer be a reduction of the pH? Is high pH still needed to limit the competing water electrolysis as the coating is already limiting this. Presumably a reduction in the pH would also have a favourable impact upon the carbonate equilibrium? How stable do you imagine the thiol coating would be at reduced pH?

Samuel Perry replied: We can see by eye that the thiol coating is preserved at the end of the short term experiments, since the thiol coated electrodes do not exhibit the same black colour that is seen for oxidised copper on the bare copper GDEs after the cell is dismantled. More detailed post-reduction analysis of the thiol layer is planned in line with further developments to the thiol layer itself.

Regarding the solution pH, it is certainly interesting to see the impact of pH on CO₂ reduction at thiol coated electrodes. Reduction at neutral pH certainly seems feasible, which would hopefully give less hydrogen evolution thanks to the hydrophobic interface. The stability of the thiol coated electrodes in more acidic

media would likely be defined by the solubility of the Cu particles, rather than the stability of the thiol. It is not clear how the coating would affect the dissolution rate and how this would be affected by reductive potentials. These relationships merit further investigations.

Deepak Pant remarked: What is the impact of the pore size in the gas diffusion electrode? Is this impact seen on one side or both sides for CO₂ entering the reaction and ethylene going away (Fig. 2 of the paper (DOI: 10.1039/d0fd00133c) shows the product ethylene going out of the GDE)? For the hydrophobic layer with pores, I am wondering about the size of these pores in the thiol layer?

Samuel Perry replied: The CO₂ is able to permeate the thiol layer, so coating the copper nanoparticles with thiol should not impact the mass transport within the GDE itself. The pore size is defined by the copper nanoparticles in the catalyst layer, and the carbon paper in the GDE.

Deepak Pant said: By adding thiol to the pores do you improve the selectivity to ethylene, and if so, by how much?

Samuel Perry answered: The impact of the thiol depends on the applied current density. At low current densities there is a sizeable increase in the faradaic efficiency towards ethylene (at 50 mA cm⁻², 18% for the bare electrode and 32% for the thiol coated electrode), but at high current densities thiol appears to have little or no impact. This comparison can be seen in Fig. 4 of the article (DOI: 10.1039/d0fd00133c).

Alexander J. Cowan asked: In the paper (DOI: 10.1039/d0fd00133c) you use the Tafel slope to examine a possible change in the mechanism. The analysis of Tafel slopes when you are generating a complex mixture of products is difficult. How did you disentangle the contributions from the different pathways here?

Samuel Perry responded: During the linear sweep voltammetry (LSV) we took regular gas chromatography measurements, so that we know the faradaic efficiency (FE) at a range of given points along the LSV wave. We can then use the following expression to extract the current that was specifically used to generate ethylene ($j_{C_2H_4}$):

$$j_{C_2H_4} = j_{total} \times (FE/100\%).$$

The Tafel slope was plotted using the calculated values of $j_{C_2H_4}$, which allows us to extract the mechanistic information regarding ethylene formation that would otherwise be obscured within j_{total} .

Alexander J. Cowan said: There is a need to consider the carbon balance of the system. At high and even near neutral bulk pH values, CO₂ capture into the electrolyte will be occurring and this needs to be considered. An excellent discussion of the issue is in a recent paper from the Kanan group.¹

1 J. A. Rabinowicz and M. W. Kanan, *Nat. Commun.*, 2020, **11**, 5231.

Samuel Perry answered: Carbon capture by high pH electrolytes will certainly be occurring. We attempted to minimise the error this creates by keeping the experiments on a short time scale. We also calculated the faradaic efficiencies based on the gas volume out of the cell, rather than the flow rate in, so we do not overestimate the conversion rate due to dissolved CO₂ entering the carbonate equilibrium.

George Dowson remarked: Since the main function of the thiol layer is to provide hydrophobicity, C18 thiols might represent overkill, and their viscosity and wetting abilities may be the cause of some of the issues identified in your paper (DOI: 10.1039/d0fd00133c). Could a shorter chain thiol work? C8–C12 should still be hydrophobic and mixtures of specific chain lengths/branch structures may allow you to “dial into” an optimised compromise between hydrophobicity, CO₂ access and product formation.

Samuel Perry answered: The motivation for using C₁₈ was simply to build on an existing published work for a hydrophobic Cu surface for CO₂ reduction.¹ In this case, the Cu surface was a Cu foil that was fully submerged in the electrolyte, which is likely why the longer C₁₈ was favoured. The concept of a mixed-length thiol deposition to tune the degree of hydrophobicity is currently being investigated. The idea of branched thiols as an additional means of modulating this would be very interesting to look at as well.

1 D. Wakerley, S. Lamaison, F. Ozanam, N. Menguy, D. Mercier, P. Marcus, M. Fontecave and V. Mougel, *Nat. Mater.*, 2019, **18**, 1222–1227.

George Dowson said: In your paper (DOI: 10.1039/d0fd00133c), Fig. 4 shows a remarkable increase in the production of C₂H₄ but an even bigger increase (proportionally) in CH₄ production when the thiol is used. Given that methane production will require more hydrogen proportionally than C₂H₄ production, does this not suggest that there is some limitation in the C–C bond formation rate, rather than proton availability at the reaction surface?

You suggest that the thiols could be causing preferential formation of the C1 route (making methane), but could it instead be that you have improved the rate of CO₂ reduction to the point that the catalyst sites for C–C bond formation are overwhelmed and the methane is essentially where the “excess” reduction is happening?

A plot of the product gas proportions over time may shed light on this – if this mixture of methane and ethylene is always produced, it might indicate that the thiol is changing the reaction mechanism, while if the ethylene forms in the majority at first and methane appears in larger amounts over time, it may suggest site saturation. Would this be possible?

Samuel Perry responded: This is a very interesting interpretation of that data that we had not considered. For site saturation to occur there would need to be a commonly formed CO₂RR intermediate that is relatively long lived and not involved in the dimerisation step. Looking at the mechanism for methane/

ethylene formation from CO₂RR, there are a number of opportunities to form the C–C bond; *CO + *CO, *CO + *CHO and *CH₂ + *CH₂ have all been proposed from computational studies. All of these species have been proposed to be in both the ethylene and methane mechanistic pathway. For this reason, it is hard to see the accelerated CO₂RR causing a decrease in C–C bond formation, since there should be copious amounts of reactants for multiple dimerisation pathways. Decreases in C–C bond formation are usually caused by parasitic side reactions blocking surface sites (hydrogen evolution is a common culprit for this) or lower CO₂ partial pressures (CO₂/N₂ mixtures can increase the methane yield). This makes tracking changes in product mixtures over time challenging, since a failing ethylene will often produce more methane before it fails completely and flooded GDEs will produce hydrogen bubbles that block sites to hinder dimerisation and increase methane production. We are interested in the increase in methane production with these coatings as well. We are currently looking into modifications to the thiol and working with gas mixtures to see if this concept could be tweaked to give efficient methane production.

Waqas Tanveer commented: A paper by the DTU energy group¹ showed the overestimation of faradaic efficiencies due to the non-correct mass flow rate evaluation separation downstream of the electrolysis. There seems to be some overestimation of the faradaic efficiencies. How were you able to calculate the exact faradaic efficiencies without separating the flow rates of individual species in a continuous flow electrolyser?

Also, did you have any flooding issues and did the time help this? The diffusion layer may start to flood. Were there any flooding problems in 5 minutes?

1 M. Ma, E. L. Clark, K. T. Therkildsen, S. Dalsgaard, I. Chorkendorff and B. Seger, *Energy Environ. Sci.*, 2020, **13**, 977–985.

Samuel Perry answered: Overestimation of faradaic efficiencies tends to come from the value being calculated based on the flow of CO₂ into the reactor. The error comes about because some of the CO₂ dissolves into basic electrolytes as part of the bicarbonate equilibrium. Our faradaic efficiencies were instead calculated based on the gas volume flow out of the reactor. The concentration of ethylene in the known gas volume out of the cell should therefore not be affected by the upstream dissolution of CO₂ into the electrolyte. To help minimise any error, we also conducted experiments on a short (5 minute) time scale to minimise any changes. As the question insinuates, we found minimal evidence of electrolyte flooding thanks to this short time scale as well. Of course before any similar electrode designs are up-scaled, a thorough investigation of electrode flooding over long time experiments would be essential.

Jeffrey Poon said: If the thiol layer is indeed blocking H⁺ diffusion, leading to the carbon dioxide electroreduction behaviour seen, would it not make sense to try a hydrophobic layer deposition that is partially covering the Cu particles (such as a hydrophobic layer that would sinter if heated)? How much difference would you expect that to make? In addition, the paper (DOI: 10.1039/d0fd00133c) asserts that a 'single monolayer' of 1-octadecanethiol has been formed on the copper catalyst layer. The SEM images are not sufficient in proving this assertion other

than the significant roughening (which is a good indicator that multi-layers have been formed). What other more suitable data is available (e.g. neutron scattering, which would be sensitive) to reinforce the assertion made?

Samuel Perry responded: A partial hydrophobic layer would certainly be interesting. In this case, we would have to check to see if the partial layer does give an improved behaviour – it may be that anything less than a complete layer shows little or no impact on the overall reduction due to hydrogen evolution or competing CO₂ reduction to alternative products. Sintering thiol-coated particles would be challenging since it is not clear how stable the thiol would be to high temperatures. Additionally, oxidation of the Cu may lead to the stripping of the thiol layer – we remove Cu oxides with acetic acid prior to the thiol deposition for this reason. The assertion of a single monolayer is based on a literature recipe that we have taken, where the authors investigated varying deposition conditions to achieve a complete monolayer. The original study is given in ref. 25 of our article (DOI: 10.1039/d0fd00133c), given here as ref. 1.

1 M. Jalal Uddin, M. Khalid Hossain, M. I. Hossain, W. Qarony, S. Tayyaba, M. N. H. Mia, M. F. Pervez and S. Hossen, *Results Phys.*, 2017, 7, 2289–2295.

Jeffrey Poon remarked: Indeed, sintering the layer may expose the underlying copper to further oxidation. However, there is plenty of literature that oxidised copper may be beneficial to carbon dioxide electroreduction activity and selectivity (e.g. ref. 1). So it may be well worth trying killing two birds with one stone!

1 T.-C. Chou, C.-C. Chang, H.-L. Yu, W.-Y. Yu, C.-L. Dong, J.-J. Velasco-Vélez, C.-H. Chuang, L.-C. Chen, J.-F. Lee, J.-M. Chen and H.-L. Wu, *J. Am. Chem. Soc.*, 2020, 142(6), 2857–2867.

Samuel Perry answered: Oxidised copper has certainly been indicated as an excellent CO₂ reduction catalyst, particularly with regards to C₂₊ product production. In this case, we will need to revisit the experimental design to make sure that we can assign any impacts we see to changes in the Cu oxidation *versus* changes in the thiol layer.

Katarina Gugujonovic said: How do you know that you actually applied a monolayer? Is it an assumption or could you prove it somehow? Did the layer change after electrolysis?

Samuel Perry replied: We took the deposition technique from a previously published example, where they showed that deposition under these conditions would produce one monolayer. We can get some information about the state of the thiol layer after electrolysis from the colour of the electrode. A bare copper electrode will turn black after electrolysis due to the oxidation of the copper surface. After electrolysis, the thiol coated electrodes did not show a significant colour change, so we believe the thiol is still there. Of course, this is not proof that the thiol layer is still perfect, and the extent of degradation after use is still the subject of our ongoing research.

Katarina Gugujonovic asked: How can it be that the production of ethylene is higher at low current densities, when the reaction requires more electrons compared to the other reactions that can occur (referring to the reaction equations)?

Samuel Perry replied: The higher production of ethylene at low current density refers to the faradaic efficiency, which is the percentage of the total charge that went towards making the product you actually want. In other words, we know that a certain number of electrons are transferred, and when we have the thiol, more of those electrons are used to make ethylene.

Sourav Ghosh remarked: Copper sulfide is also a good electrocatalyst for CO₂ reduction. What is your thought about the formation of copper sulfide under the reaction operating conditions?

Samuel Perry answered: It is unlikely that we see copper sulfide formed under these operating conditions since we are under reducing conditions and the electrochemical production of copper sulfide from metallic copper is an anodic process. It would be interesting to look at copper sulfide with the thiol coating, since the potential for disulfide bonding may impact the stability of the thiol layer.

Peter Styring said: Have you tried CO₂ streams diluted in nitrogen in the system? We have looked at low temperature plasma chemistry (I know that it is not analogous) where the presence of nitrogen actually enhances CO₂ conversion to CO.¹

1 M. Moss, D. G. Reed, R. W. K. Allen and P. Styring, *Front. Energy. Res.*, 2017, 5, 20.

Samuel Perry replied: We have not tried diluting streams with nitrogen since this tends to favour C₁ rather than C₂ products – lower CO₂ partial pressures disfavour dimerisation, which increases methane or CO yields depending on the catalyst.

Charles Cummings remarked: The hydrophobicity of the thiol layer is limiting the diffusion of H⁺, so could you look at different thiol chain lengths as a longer or shorter chain length may affect the H⁺ availability?

Samuel Perry replied: This is a very nice suggestion and is currently planned as part of our future work in this area. It is likely that the full C₁₈ chain is excessive in terms of where the hydrophobic interface would be seen. A nice way to introduce the partially hydrophobic interface could be a co-deposition of, say, C₁₈ with C₂. This would likely improve the H⁺ diffusion, though it will need to be fine tuned to make sure the benefits of the hydrophobicity are not lost.

Michael North asked: Does the CO₂ react with the KOH electrolyte to form KHCO₃ and change the pH and other electrolyte properties during the reaction? What happens if KHCO₃ is used as the electrolyte?

Samuel Perry answered: CO₂ is certainly involved in the bicarbonate/carbonate equilibrium when it dissolves in KOH. We kept our experiments as short as possible (5 min per sample) and replaced the electrode and electrolyte after each one to minimise the change to the solution environment, though of course some change will still occur. We have not yet investigated neutral electrolytes with these catalysts and coatings though it is planned in currently ongoing work. Typically, we would see an increased rate of hydrogen evolution at lower pH, although our hope is that the thiol could somewhat offset this.

Stephen McCord asked: Fig. 2 in your paper (DOI: 10.1039/d0fd00133c) provides a schematic of your electrode cell in its current form. How scalable is this? Is this something that you consider to already be modular enough to scale, or do you foresee a need for a partial/total redesign to maximize product output? If the latter, is there anything that you identify as of now as the biggest challenge to overcome?

Samuel Perry answered: The cell design here is very much intended for small scale catalyst analysis. The Luggin capillary lowers the cell resistance, which could not be done in a larger scale set up. Instead, a scaled up reactor should bring the counter and working electrodes close together in a narrow or zero gap configuration. The biggest challenge in zero gap configurations tends to be providing sufficient proton transfer to the catalyst that is in contact with an ion conductive membrane. Narrow gap cells can address this by using a thin layer of electrolyte in a flow cell configuration in between the catalyst and the membrane. Fortunately, the catalyst/GDE design in this work is compatible with scale-up for such a narrow gap flow cell design. Work in this area would need to address (i) how to increase the faradaic efficiency at a high current density and (ii) how to provide high production rates over hundreds or thousands of hours.

Mzamo Shoji commented: I found this work so interesting because I have always associated CO₂ conversion with oxygenated products. Being able to also make ethylene is fantastic considering that it is an important monomer in the polymer industry and starting material for 1-hexene and 1-octene, which are also as important if not more so.

Samuel Perry responded: Thanks for your comment. It is interesting because from an electrochemical perspective oxygenated products like methanol and ethanol are often harder to make than the equivalent methane and ethylene. There is a lot of interesting work out there that looks into shifting the electrochemical method towards oxygenated products as well.

Peter Styring opened a general discussion of the paper by Walter Leitner: We have proposed a move to “defossilisation” to the UK Government repeatedly in recent months, but they are set on “decarbonisation”. How is this viewed in Germany at the scientific and policy level?

Walter Leitner responded: We are communicating on many channels, in particular within the framework of the Kopernikus Program “Power-To-X”. The

concept is increasingly understood and appreciated also in politics and society, but more efforts are still needed.

Veronica Del Angel Hernandez remarked: Would it be best to try and move away from metal catalysts and aim for carbon-based catalysts, particularly considering that some of the metals used in catalysis (Cu, Co, Ni, *etc.*) have limited availability¹ and we are aiming for a sustainable future?

¹ EuChemS Element Scarcity – EuChemS Periodic Table, <https://www.euchems.eu/euchems-periodic-table/>, (accessed April 2021).

Walter Leitner responded: Organo-catalysts are not necessarily preferred over metal catalysts. Metal-based catalysts in chemical processes are typically not dispersed or “lost”. After deactivation, they are recycled and regenerated. Of course, the environmental impact associated with their mining and recycling has to be considered in LCAs.

Xiangkun Elvis Cao said: A lot of the discussions in this online symposium were centered around the development of materials, and what is lacking is how to design scalable systems (*e.g.*, devices/reactors) if we were to push the technology to a commercial setting. Would you be able to comment on the pathways to design scalable systems for upscaling CO₂ reduction efforts?

Walter Leitner responded: There are two strategies: (1) To follow the “economy of scale” similar as in the petrochemical industry. The limiting factor is here more the generation of the required primary energy, rather than the chemical reactor; (2) consequently, decentralized, modular and highly integrated processing units may offer an interesting alternative, and such research efforts are going on also in the Kopernikus Project.

Claudia Bizzarri asked: Renewable energy sources are highly desirable for sustainable carbon dioxide utilization. Although in general discussions, light is always considered one of the appealing energy resources to be exploited, I found photocatalytic or photoinduced processes in this edition of carbon dioxide utilization surprisingly missing (besides a poster on photothermal CO₂ methanation by J. Ibanez *et al.* and a poster on photocatalytic CO₂ reduction by myself and coworkers). I would like to know what is the opinion of the CO₂ community about photochemical strategy? Can you please comment on this?

Walter Leitner responded: In principle, it seems very attractive to use photons directly – just as nature does in photosynthesis. There are, however, two major challenges to develop scalable technologies on this basis. Firstly, the low penetration of light into reactive media. Nature has the great advantage of using huge amounts of space. Second, photocatalysts operate in excited states and are hence often degrading very fast. In fact, Nature spends as much time on the repair of the catalyst as on its operation. Something we are simply not very good at with technical catalysts. Nevertheless, it is a fascinating area of research, and I agree that it would be interesting to hear more about it in future meetings.

Michael North said: Thanks for an excellent closing lecture and I would like to use the chair's privilege to make two points.

(1) In your lecture you mentioned the synthesis of organic carbonates from CO₂, including your own work with Bayer and Covestro. The synthesis of organic carbonates (cyclic, acyclic, polymeric) has been almost totally absent from this *Faraday Discussion*, though there were posters on the topic. I would just like to emphasise that this was a conscious decision of the organising committee as organic carbonate synthesis was a major feature of the first *Faraday Discussion* on Carbon dioxide utilisation (volume 183) and this time we wanted to highlight other areas of carbon dioxide chemistry. The synthesis of organic carbonates remains a large and very important area and I would encourage readers to look through both *Faraday Discussions* volumes to get a balanced view of the area.

(2) The 'CO₂Chemistry' mnemonic that you developed with Martyn Poliakoff and discussed throughout your lecture was also used by Martyn in his opening lecture to the first *Faraday Discussion* on Carbon dioxide utilisation (volume 183).¹ At that meeting, Peter Styring and I gave the closing lecture and, as we point out there, it is very important to consider all 12 terms in the mnemonic.² In particular, if you pick and choose as:

Catalysis is crucial.

Origin of the CO₂?

Sustainability is essential.

Thermodynamics cannot be beaten.

Large energy input (as opposed to reasonable).

Your enthusiasm is not enough.

Then the result could be very COSTLY!

1 M. Poliakoff, W. Leitner and E. S. Streng, *Faraday Discuss.*, 2015, **183**, 9–17.

2 M. North and P. Styring, *Faraday Discuss.*, 2015, **183**, 489–502.

Conflicts of interest

Max Konig declares that the gas diffusion electrodes prepared for this publication are based on patent applications EP20185780.2 and EP19213008.6 submitted by VITO in 2019 and 2020, respectively. There are no other conflicts to declare.