

Scale up of reactors for carbon dioxide reduction

Andrew Nattestad (✉)^{1,2}, Klaudia Wagner¹, Gordon G. Wallace (✉)¹

¹ Intelligent Polymer Research Institute and ARC Centre of Excellence for Electromaterials Science,
University of Wollongong, Wollongong, NSW 2522, Australia

² School of Chemistry, Monash University, Clayton, VIC 3800, Australia

© The Author(s) 2022. This article is published with open access at link.springer.com and journal.hep.com.cn

Abstract In recent times there has been a great deal of interest in the conversion of carbon dioxide into more useful chemical compounds. On the other hand, the translation of these developments in electrochemical reduction of carbon dioxide from the laboratory bench to practical scale remains an underexplored topic. Here we examine some of the major challenges, demonstrating some promising strategies towards such scale-up, including increased electrode area and stacking of electrode pairs in different configurations. We observed that increasing the electrode area from 1 to 10 cm² led to only a 4% drop in current density, with similarly small penalties realised when stacking sub-cells together.

Keywords CO₂ reduction, electrochemical cell, electrosynthesis, upscaling

1 Introduction

A significant motivator in the conversion of carbon dioxide (CO₂) is the desire to address the problem of rising atmospheric CO₂ levels. Electrochemical reduction of CO₂ can not only remove it from the atmosphere, but also simultaneously provide us with valuable fuels and reagents, with what has been termed Power-to-X, when driven by renewable energy, particularly taking advantage of periods of ‘over supply’ [1]. As such, extraordinary effort has been devoted towards electrochemical reduction of CO₂ over recent years, resulting in impressive research achievements and discoveries of new catalysts [2–4]. Despite these great foundations laid down in the field of catalysis, this process has yet to be taken up by industry. The viability of this technology, competing with traditional chemical manufacturing processes,

directly relates to the economics of the products, in terms of the overall costs and demand [5]. A comprehensive assessment of profitability must take into account current state-of-the-art technology, which will heavily depend on catalysts and electrochemical reactor design, as highlighted by Tufa et al. [6]. Furthermore, integration of CO₂ electrolyzers into a larger systems, instead of as stand-alone units, will assist in the favourable scaling of this technology to a practical and impactful level [7].

The electrochemical reduction of CO₂ to carbon monoxide (CO), with molecular oxygen as a biproduct, (overall equation: $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$) requires only two electrons and is well developed with regards to the catalyst selectivity and faradaic efficiency (FE) [8]. Additionally, according to the techno-economic analysis, electro-synthesis of CO is considered one of the most profitable, and cost competitive, standing out as a strong candidate for further development from both economic and technical standpoints [5,9].

Large-scale implementation requires electrolyzers to operate with low overpotentials, high current densities and high FE, in order to facilitate high energy efficiency, conversion rate and selectivity [10]. One of the as-yet unsolved challenges, which hinders the mass adoption, is the productivity loss, due to decreased current density and FE, observed with scale-up [11]. Only a handful of examples of pilot systems have been reported to date. In each of these examples CO₂ is electrochemically converted into CO, on silver coated gas diffusion electrodes (GDEs) [8,12]. Silver (Ag) based electrocatalysts have been recognised as being promising for CO production, with excellent selectivity, activity and moderate cost [8]. The effectiveness of Ag as a catalyst is due to its relatively strong adsorption capability for key intermediates and low CO binding energy. To promote high selectivity towards CO₂ reduction while suppressing hydrogen evolution, a key competing reaction at the cathode-electrolyte interface, conditions such as solution pH, electrolyte composition, temperature, pressure, applied

Received January 28, 2022; accepted April 23, 2022

E-mails: gwallace@uow.edu.au (Wallace G. G.),
andrew.nattestad@monash.edu (Nattestad A.)

potential and concentration of CO_2 , as well as the chemical and morphological nature of the catalyst, play a significant role and have to be considered [13,14]. GDEs offer a less restricted mass transport of CO_2 to the catalyst [15,16], as it is delivered directly to the back of the porous electrode, making it a more effective approach than solution-side delivery, where the solubility of CO_2 is relatively low [17], as this typically limits the attainable current density.

In 2018, Jeanty et al. [11] demonstrated a reactor with a 100 cm^2 electrode area which could operate at a current density of $150\text{ mA}\cdot\text{cm}^{-2}$ over a couple of hundred hours with a FE for CO of 60%, while Kim et al. [12], in their continuous pilot scale electroreduction system, achieved a maximum CO partial current density of $51.14\text{ mA}\cdot\text{cm}^{-2}$, on a 50 cm^2 electrode size. More recently Endrodi et al. [18] demonstrated the first example of a multilayer, zero-gap, electrolyzer stack, with two configurations demonstrated for gas feed-in. In parallel operation, the electrolyzer stack was similar to the sum of single electrolyzers, while in series configuration, the CO_2 conversion rate increased up to 40% due to a preconcatenation of the gas products as the gas continue to flow through the consecutive cathodes. Both of these stack configurations were electrically connected in series.

In the present work we design and construct electrochemical cells for CO_2 reduction, showing possible configurations for scale-up, with focus towards practical considerations with what we believe to be the first literature report of such a system. In the first stage we demonstrated the electrolyser in stack configuration, which was tested in both parallel and series electrical configurations. Following this, we increase the electrode surface area from 1 to 10 cm^2 , with current collection managed by metal frames.

2 Experimental

2.1 Materials

Aqueous potassium hydroxide ($1.0\text{ mol}\cdot\text{L}^{-1}$, Sigma Aldrich) was used as an electrolyte. High purity, compressed CO_2 (Air Liquid) was used to feed the cathode gas compartment. Preveil polypropylene backed expanded polytetrafluoroethylene (ePTFE) membranes, with $0.2\text{ }\mu\text{m}$ pore size (General Electric Energy) were used as gas diffusion membranes for both the anode and cathode. The cathode was prepared by sputter coating (Edwards Auto 306) 250 nm of silver onto the ePTFE membrane. Ni mesh (200 lines per inch, Century Woven of Beijing, China) was laminated to the ePTFE and used for the anode. Two electrolyte compartments were divided by an anion exchange membrane (Sustainion, Fuel Cell).

2.2 Methods and characterisation

The experiments were performed in a series of flow cell configurations with different electrode areas of 1 and 10 cm^2 in order to examine the scalability of the CO_2 electrolysis. Plates were constructed of poly(methyl methacrylate) (PMMA, 6 mm, Cammthane, Australia) and gaskets (fluoroelastomer polymer, Viton A, 0.5 mm thickness, Reglin Rubber) and were cut with a laser cutter (ULS PLS6MW Laser Engraver, Universal Laser Systems). Detailed technical drawings can be found in the Electronic Supplementary Material (ESM). The flow reactors were operated under ambient conditions. Both catholyte and anolyte solutions were supplied through the cell continuously during operation at flow rates of $7\text{ mL}\cdot\text{min}^{-1}$ using a multi-channel peristaltic pump and silicon tubing (ATTO, Zaichi Universal Co.). Flow of CO_2 was set to $30\text{ mL}\cdot\text{min}^{-1}$ using a calibrated mass flow controller (Aalborg, Stanton Scientific, $100\text{ mL}\cdot\text{min}^{-1}$), however the precise gas flow rate was measured accurately with burette at the gas chromatograph (GC) outlet and used in the calculation of FE.

Electrochemical testing was carried out using a potentiostat (650D, CH Instruments). Electrochemical performances of the cells were characterised by cyclic voltammetry (CV), chronoamperometry (CA). Gas products were analysed by GC (GC-2030N, Shimadzu), operating with a thermal conductivity detection (TCD) and a flame ionization detector (FID) connected to a methanizer unit and Argon was employed as a gas carrier. The cell was connected directly to the GC in an in-line configuration so as to minimise any chance of contamination or loss of products.

3 Results and discussion

Performance of CO_2 reduction reactors based on GDEs are known to outperform conventional electrode configurations, with the reasons for this mostly attributed to limited solubility (hence mass transport) of CO_2 in water [15–17]. A number of 1 cm^2 GDE based reactors have previously been reported, including some which are available commercially [19]. These are typically used to evaluate catalyst materials and/or electrolyte conditions, with minimal attention paid to how these could be scaled. As a first step towards this scaling, we built a reactor, with 1 cm^2 electrodes, from a series of plates and sealing gaskets, as shown in Fig. 1. In the operation schematic in Fig. 1(a) gas and liquid supply and return ports can be seen to all be located on the front plate, as this configuration lends itself to easily create a stacked system with multiple pairs of electrodes. The use of plates and gaskets (Fig. 1(b)) is advantageous in terms of ease of manufacture (here produced using a laser cutter,

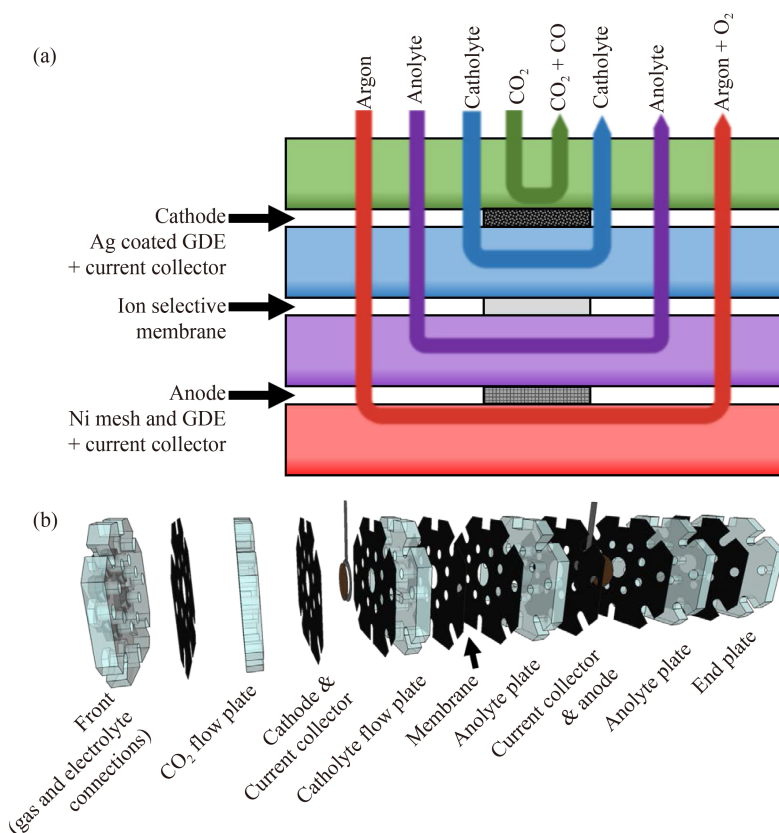


Fig. 1 (a) Schematic representation of CO_2 reactor, with connections for supply and return of gasses and electrolytes located at the front panel; (b) 3D rendering of the device with single pair of 1 cm^2 electrodes.

considered a 2.5D technique). Electrolyte and gas flow is directed across the electrode faces by virtue of channels etched into the plates (Fig. S1 (cf. ESM)), which helps to ensure the removal of products. A further advantage of the modularity afforded by the use of plates is that it allows us to readily examine reactor parameters, such as the interelectrode distance, where different thickness PMMA sheets may be easily exchanged.

Figure 2 shows the performance of the 1 cm^2 reactor (photograph in Fig. 2(a)), with a single pair of electrodes, namely a cathode fabricated by sputter coating of 250 nm of silver onto an ePTFE membrane and an anode comprising of nickel mesh and an ePTFE membrane. An anion exchange membrane was located between these, separating anolyte and catholyte. While materials other than the ones employed here have been demonstrated to give superior performances in terms of current density and conversion efficiency, we elected to use these as they are broadly representative, readily available, and relatively well understood, therefore ideal for reactor development. Reported current densities on Ag based catalysts are broad, between 2 and $312\text{ mA}\cdot\text{cm}^{-2}$ [8]. Current densities of slightly less than $60\text{ mA}\cdot\text{cm}^{-2}$ (at -3.0 V), were reported by Dufek et al. [19] on commercial silver GDE cathode (Silflon, Gaskatel), at ambient temperature and pressure.

The electrochemical and catalytic properties of the

device were characterised by cyclic voltammetry under argon and under CO_2 (Fig. 2(b)). The electrocatalytically activity of this cathode can be seen in early reduction onset and increased current in the presence of CO_2 , reaching $80\text{ mA}\cdot\text{cm}^{-2}$ at -3 V (Fig. 2(b), red line). Electrochemical CO_2 reduction was then performed under controlled 2-electrode voltages of -2.0 , -2.5 and -3.0 V . The maximum stable current density above $50\text{ mA}\cdot\text{cm}^{-2}$ at -3.0 V was achieved after initial cell stabilisation (Fig. 2(c)). The out-flowing gas mixture from cathodic chamber, was analysed GC and shows a high FE of over 80% for the CO_2 conversion to CO (Fig. 2(d)). The stability of the cell for electrochemical reduction of CO_2 was then investigated over 5 h at -3.0 V . The initial decay of the current density can be seen on chronoamperogram in Fig. 2(e), with the current stabilising above $50\text{ mA}\cdot\text{cm}^{-2}$ after 2–3 h. The increased uncompensated resistance (R_u) from 8 to $13\ \Omega$, (measured from the ohmic potential drop— iR) after 5 h electrocatalysis, could be due to the trapped gas bubbles [20] or increased resistance of the working electrode, if any delamination of silver occurred. Analysis of the gas products over the course of this electrolysis showed an excellent stability and selectivity (Fig. 2(f)).

As mentioned above, placing connectors for the feed and return lines on the front plate allows us to readily stack multiple pairs of electrodes in between a set of front

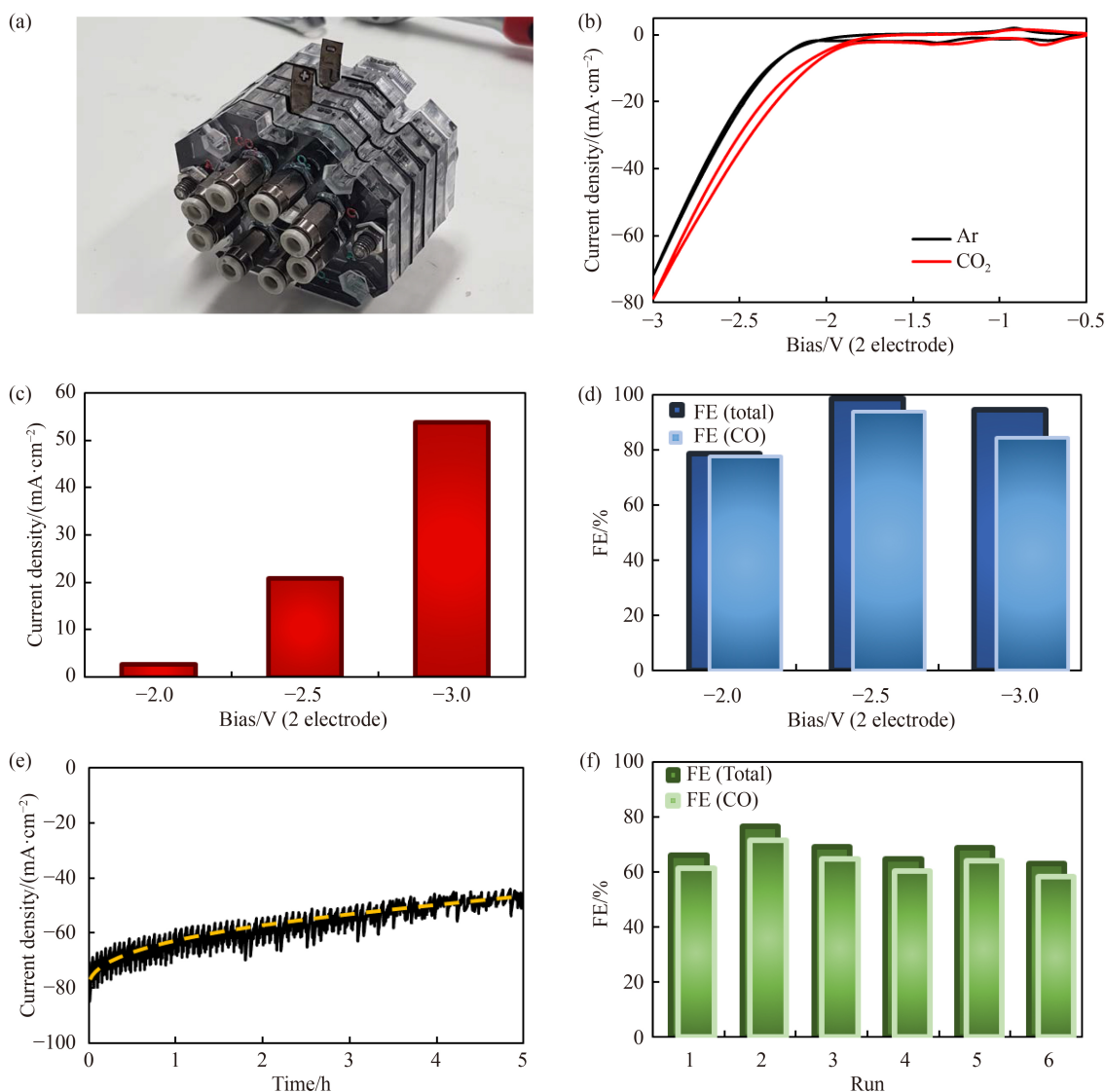


Fig. 2 CO₂ reduction reactor with 1 cm² electrode area. (a) Photograph of assembled reactor; (b) cyclic voltammograms with argon and with CO₂ flow; (c) stable current densities at -2.0, -2.5 and -3.0 V bias; (d) FE at biases shown in (c); (e) current density at -3.0 V over a 5 h period; (f) FEs from repeated sampling at -3.0 V over the course of several hours.

and end plates, as explored in Fig. 3. An example of such an assembly can be seen in Fig. 3(a), with two pairs of electrodes included. This de facto results in the electrolyte flowing in a parallel arrangement. Meanwhile, the electrodes themselves may be connected in either series or parallel. It is important to remember here that in a large-scale system, series connections are generally preferred as this minimises resistance based electrical losses. Figure 3(b) shows the current densities of single cells (averaged), as well as in both series and parallel (currents shown here are divided by two) stacked configurations, noting biases for the series configured system were double that of the individual and parallel connected. The series connected system provides a high current at a low applied bias -4.0 V (i.e., 2.0 V per pair of electrodes). Below we explore this in more detail and explain how this is unlikely to be a good response.

Cyclic voltammograms are compared for parallel (Fig. 3(c)) and series (Fig. 3(d)) electrical connections. In each case we look at the measured results in a stacked configuration against a prediction, based on the two pairs, measured independently, and Kirchoffs circuit laws. It can be seen that with the parallel electrical connection (and matching electrolyte flow path) the predicted and experimental results are in good agreement. Meanwhile, the response of the series connected stack is far from our initial prediction (purple and dotted traces respectively in Fig. 3(d)). To better understand this, we assembled each pair into stand along devices and connected these together, with the electrolyte being fed in either in series or parallel, but with a Y-connector at some distance from the cell (Figs. S2 and S3, cf. ESM). In both these disconnected cases, the device response was very similar to the prediction, based on individual cells, suggesting

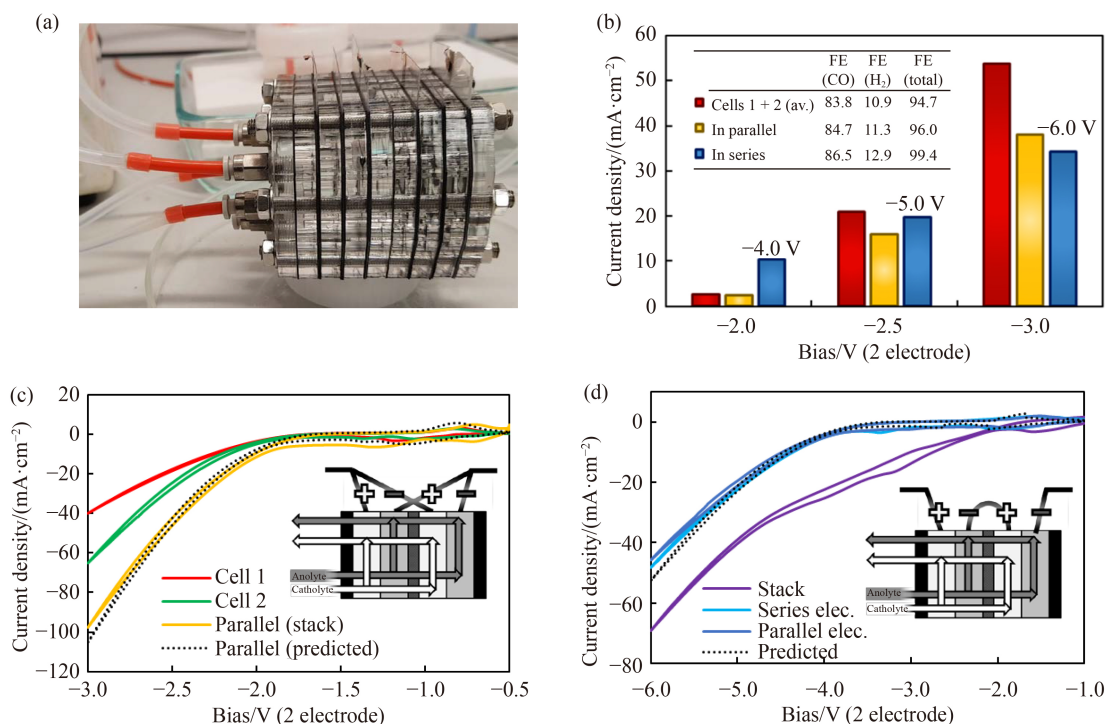


Fig. 3 Stacked reactors with multiple pairs of electrodes. (a) Photograph of a stacked device with two pairs of electrodes; (b) stable current density summary data for two pairs of electrodes; (c) stacked devices connected electrically in parallel; (d) stacked devices connected electrically in series, with electrolyte flow either in series or parallel.

that a parallel electrolyte circuit and series electrical connection can function effectively together, on the proviso that the flow path of the electrolyte is sufficiently long. In spite of this extra complexity, we believe it to be preferable to connect the electrolyte in parallel where possible as this will minimise concentration gradients of reactant and/or product in the electrolyte.

The high current at low voltages, seen for the stack (Figs. 3(b) and 3(d)) may be understood as resulting from the first cathode and second anode acting as a pair. It is important to remember that each electron passing through the series connected cells should be involved in reactions in each sub-cell. For the two-electron CO₂ to CO reaction, this means one mole of charge should provide one mole of product (assuming a FE of 100%). FE (Fig. S4, cf. ESM) greater than 100% for series connected systems is in line with expectations based on the idea that each charge passing through the system is involved in reactions in each component cell. While both the individual cell and parallel configurations have values in the range of 70%–100% for each applied voltage, the series connected stack has a FE of 100% at –4.0 V and up to ~200% at higher voltages. Current (and products) produced in the series stack at –4.0 V applied bias are not the result of voltage being dropped evenly across each component cell.

As well as the stacking of electrodes, it is important to address the issue of scaling the electrode area. In Fig. 4 we present data taking the first step, implementing 10 cm² electrodes. The system shown in Fig. 4(a) includes

metal fingers, spaced at 1 cm, to act as current collectors, as well as a serpentine electrolyte flow path, as per previous discussions on the issues related to stacking and series/parallel connections (Fig. S5, cf. ESM). The observed current densities and FE (Figs. 4(b) and 4(c)) show similar trends to the smaller area devices in Fig. 2. Importantly, Fig. 4(d) shows the partial current density (i.e., the current going towards the target reaction of CO₂ to CO + $\frac{1}{2}$ O₂) is nearly the same for the system with metal fingers as compared to the 1 cm² system, while the 10 cm² single tab gives a substantially worse performance.

Prior to implementing the metal finger current collector, different approaches were also examined (see Fig. S6), including a simple tabbed approach (onto silver coated ePTFE) for both 1 and 10 cm² (round electrodes ~11.3 and ~37 mm in diameter, respectively) and ring-shaped current collectors (either metal foil or metal mesh). In each case, the ring collector provided benefit compared to the tabbed connection (R_u recalculated for 1 cm², reduced from 20 to 16 Ω at 10 cm² round electrodes), however the fingers were again superior (the smallest R_u = 13 Ω). Based on the FE towards CO production for each case, the partial current density for CO can be compared. Figure 4(d) shows that the metal fingers provide the best performance towards CO production of the different 10 cm² electrode approaches, only marginally lower than for 1 cm².

We note that these steps towards the scale-up of CO₂ reduction reactors provide insight, while also

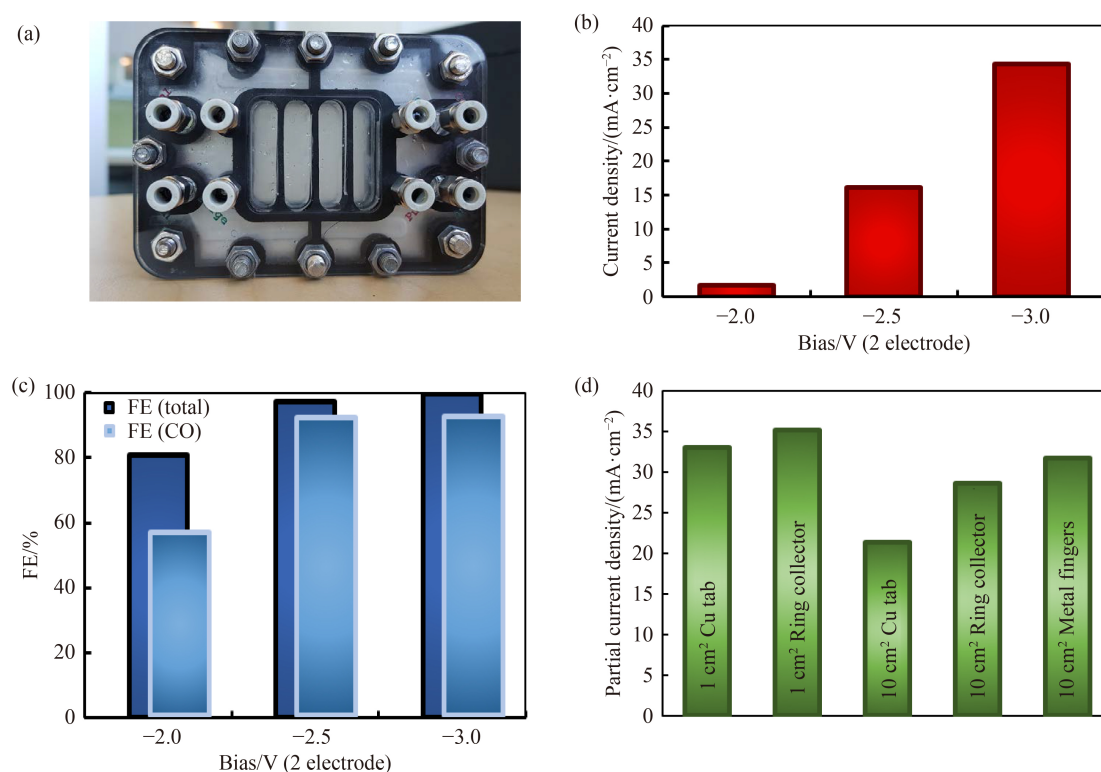


Fig. 4 CO₂ reduction reactor with 10 cm² electrode area. (a) Photograph of assembled reactor; (b) stable current densities at -2.0, -2.5 and -3.0 V (2 electrode potentials); (c) FE at the potentials listed in (b); (d) the partial current densities for CO generation for 1 and 10 cm² electrodes with various current collector options at -3 V.

acknowledging that further work is required. For one, active electrode areas must be further increased by several orders of magnitude. Other aspects, which seem to be less often considered, at least in the public scientific discourse, are the need for reactors to be supplied with realistic gas mixtures, rather than the highly purified CO₂ typically used. Related to this is the need to ensure that unreacted CO₂ can be separated from the product and recycled back into the reactor. Nevertheless, the steps towards scale-up reported in this paper reveal promise with regards to the viability of CO₂ reduction technology.

4 Conclusions

In this work we report several aspects related to the scale up of CO₂ reduction. This is done with a simple, modular, plate-based design. This design principle is conducive to further scale up as well as facilitating rapid prototyping and development. We show that a configuration, connected electrically in series, with electrolyte flow in a parallel configuration can provide close to ideal performance (double the output of a single cell), provided that the electrolyte flow is forked sufficiently far from the electrode. This arrangement is favourable as parallel electrolyte flow provides convenience in pumping and minimises reactant and product gradients, while the connection of electrodes in series minimises resistive

losses.

Further to the above, we see that scaling from 1 cm² to 10 cm² active area can result in similar partial current densities for CO production, provided that a current collector geometry is employed which ensures the distance from the current collector to the catalyst is in the range of several mm. Importantly, this current collector should not be in direct contact with the electrolyte as it is not gas fed which would lead to the production of undesired products (H₂).

Acknowledgements Funding from the Australian Research Council Centre of Excellence Scheme (Project Number CE 140100012) is gratefully acknowledged. The authors would like to thank Benjamin Filippi from Translational Research Initiative for Cell Engineering and Printing (TRICEP) for technical support, and the Australian National Nanofabrication Facility-Materials node for equipment use.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <https://dx.doi.org/10.1007/s11705-022-2178-7> and is accessible for authorized users.

Funding Note Open Access funding enabled and organized by CAUL and its Member Institutions.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are

included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Gong J, English N J, Pant D, Patzke G R, Protti S, Zhang T. Power-to-X: lighting the path to a net-zero-emission future. *ACS Sustainable Chemistry & Engineering*, 2021, 9(21): 7179–7181
- Zhang W, Mohamed A R, Ong W J. Z-scheme photocatalytic systems for carbon dioxide reduction: where are we now? *Angewandte Chemie International Edition*, 2020, 59(51): 22894–22915
- Prabhu P, Jose V, Lee J M. Heterostructured catalysts for electrocatalytic and photocatalytic carbon dioxide reduction. *Advanced Functional Materials*, 2020, 30(24): 1910768
- Wang J, Huang X, Xi S, Lee J M, Wang C, Du Y, Wang X. Linkage effect in the heterogenization of cobalt complexes by doped graphene for electrocatalytic CO₂ reduction. *Angewandte Chemie International Edition*, 2019, 58(38): 13532–13539
- Huang Z, Grim R G, Schaidle J A, Tao L. The economic outlook for converting CO₂ and electrons to molecules. *Energy & Environmental Science*, 2021, 14(7): 3664–3678
- Tufa R A, Chanda D, Ma M, Aili D, Demissie T B, Vaes J, Li Q, Liu S, Pant D. Towards highly efficient electrochemical CO₂ reduction: cell designs, membranes and electrocatalysts. *Applied Energy*, 2020, 277: 115557
- Smith W A, Burdyny T, Vermaas D A, Geerlings H. Pathways to industrial-scale fuel out of thin air from CO₂ electrolysis. *Joule*, 2019, 3(8): 1822–1834
- Nguyen D L T, Do H H, Nguyen M T, Vo D V N, Nguyen V H, Nguyen C C, Kim S Y, Le Q V. Electrochemical conversion of carbon dioxide over silver-based catalysts: recent progress in cathode structure and interface engineering. *Chemical Engineering Science*, 2021, 234: 116403
- Gao F Y, Bao R C, Gao M R, Yu S H. Electrochemical CO₂-to-CO conversion: electrocatalysts, electrolytes, and electrolyzers. *Journal of Materials Chemistry A*, 2020, 8(31): 15458–15478
- Park S, Wijaya D T, Na J, Lee C W. Towards the large-scale electrochemical reduction of carbon dioxide. *Catalysts*, 2021, 11(2): 253
- Jeanty P, Scherer C, Magori E, Wiesner-Fleischer K, Hinrichsen O, Fleischer M. Upscaling and continuous operation of electrochemical CO₂ to CO conversion in aqueous solutions on silver gas diffusion electrodes. *Journal of CO₂ Utilization*, 2018, 24: 454–462
- Kim K, Lee W H, Na J, Hwang Y, Oh H S, Lee U. Data-driven pilot optimization for electrochemical CO mass production. *Journal of Materials Chemistry A*, 2020, 8(33): 16943–16950
- Sun D, Xu X, Qin Y, Jiang S P, Shao Z. Rational design of Ag-based catalysts for the electrochemical CO₂ reduction to CO: a review. *ChemSusChem*, 2020, 13(1): 39–58
- Kas R, Yang K, Bohra D, Kortlever R, Burdyny T, Smith W A. Electrochemical CO₂ reduction on nanostructured metal electrodes: fact or defect? *Chemical Science (Cambridge)*, 2020, 11(7): 1738–1749
- Burdyny T, Smith W A. CO₂ reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy & Environmental Science*, 2019, 12(5): 1442–1453
- Higgins D, Hahn C, Xiang C, Jaramillo T F, Weber A Z. Gas-diffusion electrodes for carbon dioxide reduction: a new paradigm. *ACS Energy Letters*, 2019, 4(1): 317–324
- Dodds W S, Stutzman L F, Sollami B J. Carbon dioxide solubility in water. *Chemical & Engineering Data Series*, 1956, 1(1): 92–95
- Endrodi B, Kecsenovity E, Samu A, Darvas F, Jones R V, Torok V, Danyi A, Janaky C. Multilayer electrolyzer stack converts carbon dioxide to gas products at high pressure with high efficiency. *ACS Energy Letters*, 2019, 4(7): 1770–1777
- Dufek E J, Lister T E, McIlwain M E. Bench-scale electrochemical system for generation of CO and syn-gas. *Journal of Applied Electrochemistry*, 2011, 41(6): 623–631
- Kreysa G, Kuelpis H J. Experimental study of the gas bubble effects on the IR drop at inclined electrodes. *Journal of the Electrochemical Society*, 1981, 128(5): 979–984