Best practices for electrochemical reduction of carbon dioxide

Brian Seger[1], Marc Robert[2,3], and Feng Jiao[4,*]

Affiliations:
[1] Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
[2] Université Paris Cité, CNRS, Laboratoire d'Electrochimie Moléculaire, F-75013 Paris, France
[3] Institut Universitaire de France (IUF), F-75005, Paris, France
[4] Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

*Corresponding author: jiao@udel.edu

Standfirst

Carbon capture, utilisation and storage, a fundamental process to a sustainable future, relies on a suite of technologies among which electrochemical reduction of carbon dioxide is essential. Here, we discuss the issues faced when reporting performance of this technology, and recommend how to move forward at both materials and device levels.

Main text

Electrochemical reduction of CO_2 into value-added chemicals has attracted much attention recently.[1-3] However, reporting the performance of a new CO_2 electrocatalyst or a new reactor design is not trivial because of the complex nature of CO_2 electroreduction reaction. Sometimes the results are presented in a confusing manner, which makes it difficult to assess the true performance of the catalyst/device. In this comment, we first discuss common problems in reporting the performance of a new electrocatalyst (including both heterogeneous and molecular catalysts) in the literature and then extend the discussion to how the products should be properly measured and quantified. Finally, we comment on the issues associated with full-cell level studies. Recommendations are given for best practices in electrochemical CO_2 reduction research.

Reporting electrocatalyst performance

Most research efforts in electrochemical CO_2 reduction are concentrated on searching for a novel electrocatalyst with improved properties.[4-6] The electrocatalytic evaluations are commonly conducted in a typical three-electrode batch cell (also called H-cell, see Fig. 1a). As the amount of CO_2 (reactant) accessible by the catalyst is limited by the solubility of CO_2 (approximately 34 mM at ambient conditions), the highest operating current density is limited to ~20 mA cm^{-2} before mass transport issues dominate. Additionally, the batch cell tests are usually performed at near neutral conditions to avoid side reactions (carbonate formation in alkaline electrolytes and hydrogen evolution in acidic electrolytes).[7] To ensure the reproducibility, all catalyst test conditions and procedures should be reported with sufficient details for others to reproduce the experiments.

Specifically, parameters such as catalyst material and company (if commercial), catalyst loading, electrode size, catalyst deposition technique, electrolyte salt purity, counter electrode type, pretreatment/preconditioning, and membrane material and company (if commercial), CO_2 flow rate and gas purity are the basic parameters for all tests, though additional parameters may also be needed for a specific experiment.

Fig. 1: Schematic illustration of basic configuration of an electrochemical cell for CO_2 reduction experiment. a, three-electrode H-type batch cell. b, gas-diffusion-electrode based flow cell.

The performance of a new catalyst is commonly reported using a matrix of four major figures of merit (i.e., product Faradaic efficiency, overpotential, current density, and stability). Because all figures of merit are strongly related, a single correlation between any of two figures is not sufficient to properly assess the catalyst properties. At minimum, the performance data set should include a current density vs. overpotential plot using conventional units together with Faradaic efficiencies for all detectable products across a wide potential window. Multiple tests should be conducted to show reproducibility with error bars on Faradaic efficiency. If the Faradaic efficiency does not reach 100% (or goes beyond 100%), the researcher should analyze this and provide a clear, reasonable justification. By doing so, this allows a more comprehensive understanding of the catalyst behavior under various operating conditions. Current densities should be normalized by electrochemical surface area for fundamental research purposes (geometric surface area for applied/device studies). Using unconventional units should be avoided because of potential confusions and difficulties in comparison to literature values. If a high operating current density is claimed, both overpotential and Faradaic efficiency should be specified at that current density. Simply reporting a maximum current density value obtained from a linear sweep voltammetry scan is unacceptable. Similarly, when claiming a high Faradaic efficiency, corresponding current density and overpotential must be reported together. Additionally, catalyst stability should be evaluated under relatively high current densities, which accelerate the exposure of any stability issues of the catalyst. Conducting stability test under less intense conditions may provide a misleading view of the stability of the catalyst. It should be noted that intrinsic catalytic activity is more complex to measure and analyse at higher current densities and mass transport effect should be taken into considerations especially in batch systems[8]. Beyond product stability measurements, post-test SEM and XPS of electrodes, as well as ICP of the electrolyte all are simple tests allowing for a more comprehensive stability analysis. As operando characterizations give the most optimal results to denote stability, they should be applied when available. However, given these techniques are often synchrotron based, it does restrict the availability of this approach.

Another issue often overlooked is the identification of the source of new products, especially C_{3+} chemicals. During catalyst synthesis and electrode preparation, the catalyst sample could be contaminated by carbon-containing species, causing a false claim of new products. Precautions should be paid to products that have never been reported in the literature or exceptionally higher Faradaic efficiencies than any previous reports. Control experiments and ^{13}C isotope labelling are mandatory to confirm the source of the product (similarly in the field of

electroreduction of N_2)[9], especially for carbon-containing catalysts and/or experiments at low current densities.

When using molecular catalysts, either in homogeneous conditions or with the complexes assembled in thin films at electrodes, specific attention should be paid to the nature of the active species and to the possible involvement of metal particles or aggregates caused by catalyst degradation. Careful analysis of the electrode surface after the reaction (if possible, during catalytic reaction) using spectroscopic and microscopic techniques should be conducted. Post-reaction characterizations are also helpful in the case of heterogeneous catalysts. In the case of homogeneous catalysis, rinse test of the electrode as well as analysis of the solution by dynamic light scattering and Hg poisoning test (that will amalgamate to metal particles) should be performed. Once converging elements have been gathered to assess the molecular nature of the catalysis, analysis of electrochemical responses such as cyclic voltammetric curves has proven very powerful to extract intrinsic rates (turnover frequency values)[10,11]. Benchmarking of catalysts by establishing relationship between these intrinsic rates and intrinsic thermodynamics is then possible. Similar as heterogeneous catalysts, stability metrics (turnover numbers) can only be estimated from long term electrolysis and should not be extrapolated from intrinsic activity rate.

Measuring CO$_2$ reduction products

While gaseous CO_2 reduction products only needs the cathode outlet to analyze products, analyzing the anode can give highly useful information. Furthermore, for any in-line gaseous analysis device, installing a simple pneumatic switch between outlet cathode and anode lines, allows testing of both sides with a single analyzer. As CO_2 crossover to the anode is a well-known issue,[12] measuring the $CO_2:O_2$ ratio and O_2 Faradaic efficiency can provide a wide degree of insights.

As gas chromatography and mass spectrometry are the two dominant techniques used to measure gaseous products, both only measure concentrations. To determine partial current density and Faradaic efficiency this must be multiplied by the volumetric flow rate. Positive displacement meters or mass flow meters calibrated for the average heat capacity of the outlet flow composition are two approaches to measure volumetric flow rate. While it is simple to use the inlet flow rate as an approximation of the outlet flow rate, this entails negligible conversion or loss of reactants. This could be a reasonable assumption for H-cells operating on the 1-10 mA cm^{-2} regime (but not always[12]); however, when the currents are an order of magnitude higher (100-1000 mA cm^{-2}), substantial conversion takes place and thus the outlet flow rate must be measured. This issue is further compounded in that flow cell devices allow non-equilibrated electrolytes (e.g., KOH) to be inserted into the catholyte. As CO_2 react with KOH to form carbonates[13], this homogeneous side reaction further scavenges CO_2 leading to a substantial loss in outlet flow rate, and, if not accounted for, an overestimation in results (a doubling of Faradic efficiency in extreme cases[14]). In general, the non-steady state nature of KOH in CO_2 saturated solvents entails it is highly challenging to accurately analyze results and make conclusions.

Liquid products also need careful analysis due to similar issues in that analysis techniques such as NMR and HPLC only provide concentrations whereas total volume is also needed to determine production rates. In catholyte based cells, ions will transfer across the membrane, and as these ions are hydrated, this entails the water content will naturally change during testing. If unaccounted for, this would lead to an overestimation when using anion exchange membranes,

and an underestimation when using cation exchange membranes[15]. As these errors scale with current density, catholyte reservoirs, and experiment duration, this will be an increasingly important issues as the field progresses. While water management engineering is quite complex[16], simply measuring the total water volume at the end of the experiment should be relatively simple and will allow for proper liquid product analysis.

Performance at the full-cell level

In a gas-diffusion-electrode (GDE) system (Fig. 1b), the fundamental science remains the same, though certain parameters (e.g., mass transfer, local pH) either diminish or become exacerbated. While a scalable high current density gas diffusion electrode electrolyser makes analysis more complex, the scientific rigor and integrity cannot be compromised. Currently, the field is not close to resolving whether the optimal CO_2 electrolysis design is a direct zero gap, MEA or a gapped (1-10 mm) catholyte based GDE (or even other designs).

The design in GDE based cells and the fact that many highly volatile and anionic species are produced entails products can reside at multiple areas. For a gapped cells, the catholyte is the most common place to find liquid products. However, for both zero-gap and gapped cells, having a cold trap in the outlet cathode gas line allows for trapping liquid species as their propensity to naturally condense makes quantifiable direct detection of their vapor content challenging. Anolytes should also be analyzed for liquid products, however anodic reoxidation of CO_2 electrolysis products can be a substantial issue with standards and blanks providing useful qualitative information about this extent of anodic oxidation.

As CO_2 electrolysis also consists of an oxidation reaction, authors need to ensure the same scientific rigor in experimental description of the anode and membrane as the cathode. While a simple task, this is often forgotten. When measuring energy efficiency or even device voltage all parameters should be included. This point is highly pertinent to ohmic resistance. During half-cell experiments removing ohmic resistance is essential as it allows catalytic activity to be isolated. However, with full-cell electrolysers the parameters of interest are related to the overall reaction, which includes cathode catalysis, anode catalysis, and all ohmic losses. While excluding any of these could help in breaking down losses, it would be non-relevant to exclude these when discussing performance.

CO_2 electrolysis's rapid ascension towards commercialization is also causing confusion with regards to stability. With commercial CO_2 electrolysers expected to need to operate between 3-20k hours for economic viability, it is impractical to determine whether a device is truly stable.[16] While there has been a proposed accelerated durability test[17], substantially more work is needed in this field before absolute stability statements can be made. A more practical way to denote stability is in relation to change in operating voltage, Faradaic efficiency, or partial current density on a per hour or per 100-hour basis. As stability breakdowns can be related to factors that increase non-linearly (e.g., exponentially), operating stability tests for at least 100 hours can catch many of these issues, and thus provide a more accurate analysis in terms of stability. As future works proceed beyond 100 hours, post testing of the electrolyte via ICP, the electrodes via SEM and XPS, and membranes via FTIR may give early insights into stability concerns for commercial devices expected to last beyond 10,000 hours.

Recommended practices

We highly recommend the following practices when conducting research in the field of electrochemical CO_2 reduction. First, the performance of any new catalyst should be evaluated and reported in a comprehensive way, i.e., using a matrix of figures of merits (Faradaic efficiency, overpotential, current density, and stability). This will allow the community to gain a comprehensive understanding of the catalyst performance under various experimental conditions. Secondly, as the test conditions could substantially influence the performance of the catalyst, it is crucial to report all the experimental details, including but not limited to source of materials, purity of chemicals, catalyst fabrication methods, pretreatments/preconditioning procedures, and electrochemical test conditions. The information should be detailed enough for others to reproduce all reported experiments. Finally, accurate methods should be adapted for product quantification. A careful analysis of products holds the key to an accurate assessment of the property of the catalyst or the electrolyser. This is particularly important in the case that products are not commonly reported in the literature, or a unique selectivity is observed.

Acknowledgement

Competing interests
The authors declare no competing interests.

References:

1. Appel, A. M. et al. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO_2 Fixation. *Chem. Rev.* **113**, 6621-6658 (2013).
2. Fan, L. et al. Strategies in catalysts and electrolyzer design for electrochemical CO_2 reduction toward C_{2+} products. *Sci. Adv.* **6**, eaay3111 (2020).
3. Overa, S., Ko, B. H., Zhao, Y. R. & Jiao, F. Electrochemical Approaches for CO_2 Conversion to Chemicals: A Journey toward Practical Applications. *Acc. Chem. Res.* **55**, 638-648 (2022).
4. Lu, Q. & Jiao, F. Electrochemical CO_2 reduction: Electrocatalyst, reaction mechanism, and process engineering. *Nano Energy* **29**, 439-456 (2016).
5. Nitopi, S. et al. Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **119**, 7610-7672 (2019).
6. Ross, M. B. et al. Designing materials for electrochemical carbon dioxide recycling. *Nat. Catal.* **2**, 648-658 (2019).
7. Lu, Q. et al. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat. Commun.* **5**, 3242 (2014).

8.   Clark, E. L. et al. Standards and protocols for data acquisition and reporting for studies of the electrochemical reduction of carbon dioxide. *ACS Catal*. **8**, 6560-6570 (2018).

9.   Chen, Y. F. et al. Revealing nitrogen-containing species in commercial catalysts used for ammonia electrosynthesis. *Nat. Catal.* **3**, 1055-1061 (2020).

10.   Costentin, C. Molecular Catalysis of Electrochemical Reactions. Overpotential and Turnover Frequency: Unidirectional and Bidirectional Systems. *ACS Catal.* **11**, 5678-5687 (2021).

11.   Costentin, C., Drouet, S., Robert, M. & Saveant, J. M. Turnover Numbers, Turnover Frequencies, and Overpotential in Molecular Catalysis of Electrochemical Reactions. Cyclic Voltammetry and Preparative-Scale Electrolysis. *J. Amer. Chem. Soc*. **134**, 11235-11242 (2012).

12.   Larrazabal, G. O., Ma, M. & Seger, B. A Comprehensive Approach to Investigate CO_2 Reduction Electrocatalysts at High Current Densities. *Acc. Mater. Res.* **2**, 220-229 (2021).

13.   Rabinowitz, J. A. & Kanan, M. W. The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem. *Nat. Commun.* **11**, 5231 (2020).

14.   Ma, M. et al. Insights into the carbon balance for CO_2 electroreduction on Cu using gas diffusion electrode reactor designs. *Energy Environ. Sci.* **13**, 977-985 (2020).

15.   Ma, M., Zheng, Z., Yan, W., Hu, C. & Seger, B. Rigorous Evaluation of Liquid Products in High-Rate CO_2/CO Electrolysis. *ACS Energy Lett*. DOI: 10.1021/acsenergylett.2c01288.

16.   Garg, S., Rodriguez, C. A. G., Rufford, T. E., Varcoe, J. R. & Seger, B. How membrane characteristics influence the performance of CO_2 and CO electrolysis. *Energy Environ. Sci.* DOI: 10.1039/d2ee01818g.

17.   Nwabara, U. O. et al. Towards accelerated durability testing protocols for CO_2 electrolysis. *J. Mater. Chem. A*, **8**, 22557-22571 (2020).