Co-electrolysis of CO$_2$ and H$_2$O: From electrode reactions to cell-level development
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Abstract
The electroreduction of CO$_2$ into value-added products (e.g. CO) constitutes an excellent means of decreasing this greenhouse gas emissions, but limited efforts have been devoted to the implementation of this reaction within the so-called co-electrolysis cells operating at process-relevant currents $\gg$ 100 mA cm$^{-2}$. Reaching such performances shall require a combination of gas-fed reactants and the corresponding diffusion electrodes, along with ion-exchange membranes and ionomers that set the operative pH at the cells’ cathode and anode. The latter constitutes a key design parameter that must be combined with the need to minimize the crossover of reaction products and/or (bi)carbonate anions from the cathode to the anode, whereby their reoxidation to carbon dioxide leads to a decrease in the device’s net CO$_2$ consumption.

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Introduction
Attaining the global temperature increase target of $\leq$2 °C set by the Paris Climate Agreement requires a careful combination of decarbonization policies (e.g. carbon taxation) and sound business cases for novel, C-footprint reduction technologies [1]. The transformation of anthropogenic CO$_2$ emissions into value-added chemicals and fuels is increasingly regarded as a key technological enabler to reach this objective, and electrochemical CO$_2$-to-chemicals pathways are considered particularly promising to this end [2,3]. With this motivation, research on CO$_2$ electroreduction over the last $\approx$3 decades has preponderantly focused on understanding and improving the sluggish kinetics of this reaction on a large variety of catalytic systems (from model, extended metal surfaces to atomically dispersed sites) [4,5]. However, such studies are predominantly conducted in quasi-stagnant electrochemical cells filled with aqueous electrolytes with an intrinsically low conductivity and limited CO$_2$ solubility ($\approx 0.1$ S cm$^{-1}$ and $\approx 30$ mM, respectively), thus limiting the attainable currents to values of $\approx 1$ to $\approx 10$ mA cm$^{-2}$ that remain $\approx 1$--2 orders of magnitude below the $\geq200$ mA cm$^{-2}$ threshold for amenability within industrially relevant processes [6].

In an effort to bridge this gap, an unprecedentedly large number of studies published over the last $\approx$5 years have explored the implementation of CO$_2$ electroreduction catalysts in electrochemical setups in which currents in the hundreds of milliamps per centimeter square range can be drawn. Specifically, herein we focus on those works in which these current regimes have been attained by feeding gaseous CO$_2$ to a gas diffusion electrode combined with a membrane electrolyte, thus following the membrane electrode assembly approach well established for proton- and anion-exchange membrane (PEM, AEM) fuel cells and electrolyzers. As schematized in Figure 1a, the resulting, so-called co-electrolysis cell is constituted by a cathode and an anode generally fed with this CO$_2$(g) and H$_2$O, and on which the corresponding reduction and oxidation reactions lead to the evolution of value-added C-products (vide infra) and O$_2$, respectively.

Electrochemical reactions and acid–base equilibria in co-electrolysis cells
The extensive work devoted to the study of CO$_2$ electroreduction kinetics discussed previously has served to establish the large variety of C-products that can be derived from this reaction (e.g. CH$_4$, C$_2$H$_4$) [7,8], but recent technoeconomic analyses have concluded that the electrochemical production of CO has the greatest chance to become cost competitive with regard to current chemical routes (while the business case for
formate/formic acid production remains elusive owing to its small market size) [6,9–11]. As it will be discussed in the following section, the pH at which this and all other CO2 electroreduction reactions are undertaken plays a determining role on their selectivity and on the corresponding device’s features (from membrane choice to expected by-products), and thus, in Figure 2, we have plotted the effect of this key variable on the reversible potentials ($E_{\text{rev}}$) of this and all other co-electrolyzer reactions [12,13]. Notably, the $E_{\text{rev}}$ vs. pH line for CO2 reduction to CO (formulated in Eq. 1 of Figure 2) almost overlaps with that of the H2 oxidation/evolution equilibrium (cf. Eq. 2) and, as a result, hydrogen is a common co-electrolyzer cathode by-product. Chiefly, the cell’s cathode cannot be operated under acidic reaction conditions to minimize this H2 yield because the enhancement of the H2 evolution kinetics at low vs. high pHs on most metal surfaces [5] would lead to the exclusive evolution of H2, as opposed to the desired reduction of CO2 [13].

Alternatively, co-electrolyzer cathodes are operated at alkaline to quasi-neutral pHs at which the fed CO2 readily equilibrates with OH− to yield (bi)carbonate anions (see the discussion in the following sections and the chemical equilibria lines in Eqs. 6 and 7 of Figure 2). Moreover, the production of hydroxyl groups (OH−) associated with the cathodic reactions (see the alkaline medium formulations of Eqs. 1 and 2) implies an additional, current-driven increase in the local pH that can affect the interfacial concentration of CO2 and the corresponding reaction products’ distribution [14,15]. Complementarily, in alkaline and quasi-neutral media, the anodic O2 evolution reaction (OER) is associated with a consumption of OH− groups that causes a concomitant drop in the interfacial pH (see Eq. 3); nevertheless, if that pH remains sufficiently high to grant the presence of (bi)carbonate anions (i.e. ≥6.4 — see Eq. 6), the large OER overpotentials will likely cause the additional oxidation of these HCO3−/CO32− back to CO2 (cf. Eqs. 4 and 5) [13].

**Cell configurations as a function of the electrolyte/electrode pH**

To discuss the operational challenges faced by these gas-phase devices, we first discuss their architecture and design, which can generally be categorized into two types [16–19]: one in which the two electrodes are in direct contact with the polymer electrolyte membrane (sometimes referred to as ‘zero-gap’ configuration) [20] and a second one featuring an additional liquid electrolyte compartment between the cathode catalyst layer (CL) and the membrane [21]. In the latter, ‘flow cell’ configuration, a highly concentrated hydroxide or bicarbonate aqueous solution is typically pumped through this compartment, and this forced electrolyte
Convection helps to overcome mass transport limitations and favors high current density performance [22,23].

In the zero-gap case, the exclusive presence of a membrane solid electrolyte implies that the latter (along with the ionomers implemented in the cathodic and anodic CLs) determines the pH of the electrodes’ reaction environment. Because of the limitations in the choice of acidic reaction media discussed previously, numerous studies have instead implemented AEMs and anion-exchange ionomers used in alkaline fuel cells, whereby these operate in their OH−-exchange form. However, the latter state cannot be sustained upon contact with the gaseous CO2 feed in a co-electrolysis cell, which leads to a well-documented carbonation of the membrane that in terms causes a ~2- to ~10-fold decrease in its ionic conductivity with respect to its hydroxide form [24]. Despite this higher resistivity, AEM co-electrolysis cells display very appealing performances, especially when implementing imidazolium-based membranes and ionomers for which CO2-to-CO faradaic efficiencies >90% at a current density of 200 mA·cm−2 and an overall cell potential of 3 V have been reported [23−29]. However, as schematized in Figure 1b, the cathode-to-anode transport of HCO3/CO3 species across the membrane (i.e. ‘crossover’) has been identified as a major limitation of AEM-based devices [29−32]. More precisely, these anionic species have been claimed to be neutralized by protons [31] and/or (more likely) to be electrooxidized [30] back to CO2 upon reaching the cell’s anode, which leads to a low overall CO2 utilization of the device in which only less than half of all the fed carbon dioxide is actually devoted to the production of the desired C products. In addition, when such AEM-based devices are co-fed with concentrated KOH and/or potassium (bi)carbonate solutions, the high consumption of water at their cathodes upon high current density operation reportedly leads to an oversaturation with K2CO3 that precipitates and blocks the access of the reactants to the catalyst’s surface, thus leading to cell failure [20,33].

The crossover problem discussed previously can be overcome by substituting the AEM with a bipolar membrane (BPM), in which an anion-exchange layer (AEL) and a cation-exchange layer (CEL) are laminated against each other [34,35]. This configuration has mostly been implemented with the BPM operated in a so-called ‘reverse bias’ (RB) mode (i.e. the RB-BPM mode schematized in Figure 2c), in which the AEL and CEL are located at the cell’s anode and cathode, respectively [36]. With this orientation, the dissociation of water at the AEL−CEL interface leads to a sustained supply of H+ and OH− ions toward the cathode and anode CLs, which helps to maintain constant pHs at both electrodes [36−38] and to sustain 24 h of continuous operation at 100 mA·cm−2 and ≈3.5 V with a CO faradaic efficiency of ≈70% [37]. However, this configuration has systematically been implemented in flow cells including a supply of concentrated bicarbonate (or water) vs. hydroxide solutions to the cell’s cathode vs. anode, respectively, practically complicating

Pourbaix diagram displaying the effect of the electrolyte’s pH on the reversible potential ($E_{rev}$, at 298 K and assuming 1 M or 1 bar partial concentrations/pressures for liquid vs. gaseous species, respectively, and reported in volts vs. the reversible hydrogen electrode (VSHE)) of the cathodic and anodic electrochemical reactions (Eqs. 1−5, including their standard potentials ($E^0$) and, when applicable, formulated in the acid and base forms) and acid−base equilibria (Eqs. 6 and 7) at play in co-electrolysis cells [12,13].
the device’s operation [36–38]. Most importantly, we are not aware of any studies in which the possible cathode-to-anode crossover of CO\textsubscript{2}(g) and its carbonation and likely oxidation at the latter electrode (following Eqs. 4 and 5 in Figure. 2) have been quantified, and thus, this configuration’s net CO\textsubscript{2} consumption remains unclear.

Alternatively, (bi)carbonate crossover can be completely suppressed using the forward bias (FB) BPM configuration, schematized in Figure 1d and first implemented in the study by Patru et al [39], whereby HCO\textsubscript{3}/CO\textsubscript{3}\textsuperscript{2–}/CO\textsubscript{2} ions produced at the anode CL and transported across the membrane’s AEL react with the protons in the acidic CEL forming CO\textsubscript{2} and H\textsubscript{2}O. Chiefly, the same study [39] demonstrated that this FB-BPM setup also allows reaching significantly larger current densities than in the RB-BPM configuration because in the latter case this key operational parameter is limited by the splitting of H\textsubscript{2}O taking place at the interface between charge exchange layers. Moreover, the optimization of the AEL-CEL interface to avoid the layers’ delamination due to this evolution of H\textsubscript{2}O and CO\textsubscript{2} at their junction led to a CO Faradaic efficiency of \(\approx 10\%\) at 100 mA cm\textsuperscript{–2} and an overall cell potential of \(\approx 2.7\text{ V}\), with H\textsubscript{2} production becoming preponderant at larger current densities / cell potentials. Thus, even if this FB-BPM configuration constitutes the only cell layout for which the suppression of (bi)carbonate crossover and reoxidation have unambiguously been proven, further improvements of its operation are required to achieve a CO\textsubscript{2} reduction product selectivity on par to that reported with AEM and RB-BPM cells, as well as to improve the evacuation of produced water (and corresponding electrode flowing) reported in the study by Patru et al [39].

On the importance of OER electrocatalysis at quasi-neutral pHs

While the latter FB-BPM configuration implies the operation of the cell’s anode under strongly acidic conditions that limit the choice of OER catalyst materials to the scarce Ir oxides customarily implemented in PEM electrolyzers [5,40], the neutral to high pH at the cell’s...

Figure 3

Highlighted studies dealing with O\textsubscript{2}-evolution reaction (OER) electrocatalysts operating under quasi-neutral pH conditions. (a) Schematic illustration of the liquid cell used for in situ soft X-ray absorption spectroscopy (XAS) measurements in the study by Zheng et al [49], where UHV refers to ultra-high vacuum. (b) Potential dependent Ni\textsuperscript{4+}/Ni\textsuperscript{2+} ratios derived from those spectroscopic measurements for NiP, NiCoP, and NiCoFeP. (c) Corresponding OER polarization curve acquired at a scan rate of 1 mV.s\textsuperscript{–1} in 0.5 M KHCO\textsubscript{3}, with all potentials quoted in the reversible hydrogen electrode (RHE) scale [49]. (d) Crystal structure of Sr\textsubscript{2}GaCoO\textsubscript{5}, whereby cobalt, gallium, strontium, and oxygen are colored in blue, yellow, green, and red, respectively [50]. (e) Tafel plot of the same Sr\textsubscript{2}GaCoO\textsubscript{5} oxide and of a commercial IrO\textsubscript{2} benchmark, with the current densities normalized with respect to the surface area determined by N\textsubscript{2} sorption measurements (8 vs. 32 m\textsuperscript{2}.g\textsuperscript{–1} for Sr\textsubscript{2}GaCoO\textsubscript{5} vs. IrO\textsubscript{2}, respectively). (f) Corresponding comparison of the OER overpotentials for Sr\textsubscript{2}GaCoO\textsubscript{5} (SGC), Sr\textsubscript{2}AlCoO\textsubscript{5} (SAC), and IrO\textsubscript{2} at various current densities in electrolyte solutions of pH 7 or 13 [50]. Content in (a), (b), and (c) reprinted by permission from Springer Nature: Nature Chemistry, Zheng et al [49], Copyright 2017. Content in (d), (e), and (f) reprinted from the study by Zhou et al [50] and licensed under CC BY 4.0.
anode concomitant to the two other operational modes (AEM, RB-BPM) allows implementing inexpensive, oxide-based OER catalysts. Nevertheless, although highly active and relatively stable OER catalysts have been reported for the alkaline environments intrinsic to alkaline—and AEM—electrolyzers [5], significantly less is known concerning materials displaying a comparably high OER activity and stability under the quasi-neutral pHs concomitant to co-electrolyzers’ anodes.

In this regard, the relatively limited number of studies devoted to such OER catalysts in neutral media has focused on Co–phosphate [41–43], Co–borate [44, 45], and Ni based hydroxides [46], borates [47], or carbonates [48] that display a relatively promising OER activity compared with Ir-based catalysts. Moreover, a recent study dealing with NiCoFeP oxyhydroxides postulated that transition metals in the highest possible valence state should present the enhanced OER activities in the neutral environment [49]. Based on this, density functional theory calculations of Ni-based catalysts suggested that the formation energy of Ni⁴⁺ could be modulated by incorporating Co, Fe, and P to the material. This led to investigations of the oxidation state of NiP, NiCoP, and NiCoFeP oxyhydroxides by in situ soft X-ray absorption spectroscopy in neutral pH (cf. Figure 3a), whereby a correlation between the presence of Ni⁺⁺ under operative conditions and the corresponding materials’ OER activity was experimentally validated (see Figure 3b). As shown in Figure 3c, NiCoFeP featured the highest Ni⁺⁺:Ni²⁺ ratio and correspondingly highest OER activity among these catalysts in 0.5 M KHCO₃, outperforming an IrO₂ benchmark and retaining this activity over 100 h of operation [49].

Alternatively, Sr₂GaCoO₅ brownmillerite oxide (see Figure 3d for the crystallographic structure) has recently been reported to outperform NiCoFeP and IrO₂ as an OER catalyst at pH 7 (cf. Figure 3e) [50], and this catalytic performance appears to be insensitive to the electrolyte’s pH when compared with that of two other materials (Figure 3f). Differently, Kim et al. [51] have recently reported that perovskite oxides featuring the highest OER activities in alkaline environment (Ba₁₀.₅Sr₁₀.₅Co₁₃.₅Fe₅O₃₅, La₁₀₂Sr₁₄Co₁₃Fe₅O₃₅, and PrBaCo₂.₅Fe₅O₆.₃) display a first-order relation between OER performance and pH in the 12–14 range, whereas at quasi-neutral pHs, a zeroth-order relation is observed. This suggests that a different reaction mechanism is at play as a function of the electrolyte’s pH, and operando X-ray absorption spectroscopy measurements indicate that while in alkaline environment the oxidation of lattice oxygen [52] can take place in parallel to the conventional OER mechanism, the latter becomes predominant at quasi-neutral pHs.

Conclusions and outlook

In summary, the aforementioned discussed studies demonstrate the potential of co-electrolysis cells to reduce CO₂ into value-added products at application-relevant current densities, while highlighting the importance of numerous cell design aspects that were overlooked in previous electrolysis works but that are extremely relevant to the operation of such devices (e.g., membrane configuration, water management). Despite significant advancements, the optimum cell configuration for scale-up remains unclear and may be dictated by the preferred reaction product(s) and subsequent integration within industrially relevant processes. Notably, this ideal configuration should only be adopted after a rigorous assessment of its net CO₂ consumption, including a quantification of the possible evolution of carbon dioxide at the cell’s anode. Finally, more research efforts should be devoted to the latter electrode, whereby highly active and stable OER catalysts based on earth-abundant elements and capable of operating at quasi-neutral pHs are urgently needed to assure rapid co-electrolyzer development. We postulate that this OER catalyst design shall be greatly accelerated by combining synthetic efforts with fundamental studies including operando characterization, as to elucidate the parameters that determine these materials’ OER activity and stability in such quasi-neutral reaction environments.

Conflict of interest statement

Nothing declared.

Acknowledgements

The authors gratefully acknowledge the financial support of the Swiss Competence Center for Energy Research (SCCER) Heat and Electricity Storage. JH greatly acknowledges the Swiss National Science Foundation for financial support through the Ambizione Energy grant PZENP2_173632. TJS is thankful to Innosuisse.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

** of outstanding interest

1. World energy scenarios 2019: exploring innovation pathways to 2040. World Energy Council; 2019. https://www.worldenergy.org/publications/entry/world-energy-scenarios-2019-exploring-innovation-pathways-to-2040.

2. De Luna P, Hahn C, Higgins D, Jaffer SA, Jaramillo TF, Sargent EH: What would it take for renewably powered electrolysis to displace petrochemical processes? Science 2019, 364:eaav3506.

3. Bushuyev OS, De Luna P, Dinh CT, Tao L, Saur G, van de Lagemaat J, Kelley SO, Sargent EH: What should we make with CO₂ and how can we make it? Joule 2018, 2:825–832.

4. Arán-Ais RM, Gao D, Roldan Cuenya B: Structure- and electrolyte-sensitivity in CO₂ electrodeposition. Acc Chem Res 2018, 51:2906–2917.

5. Herranz J, Durst J, Fabbi E, Patru A, Cheng X, Pemmyakova AA, Schmidt TJ: Interfacial effects on the catalysis of the hydrogen
Electrocatalysis

6. Durst J, Rudnev A, Dutta A, Fu Y, Herranz J, Kaliginedi V, Kuzume A, Pernyakova AA, Paratcha Y, Broekmann P, Schmidt TJ: Electrochemical CO2 reduction – a critical view on fundamentals, materials and applications. *Chemia* 2015, 69: 769–776.

7. Hori Y, Wakebe H, Tsukamoto T, Koga O: Electrocatalytic processes of CO selectivity in electrochemical reduction of metal electrodes in aqueous media. *Electrochem Acta* 1994, 39:1833–1839.

8. Kuhl KP, Cave ER, Abram DN, Jaramillo TF: *Current Opinion in Electrochemistry* 2017, 15:366–376.

9. Jouny M, Luc W, Jiao F: General techno-economic analysis of CO2 electrolysis systems. *Ind Eng Chem Res* 2018, 57: 2165–2177.

10. Spurgeon JM, Kumar B: Comparative techno-economic analysis of pathways for commercial electrochemical CO2 reduction to liquid products. *Energy Environ Sci* 2018, 11: 1536–1551.

11. Verma S, Kim B, Jhong H-R, Ma S, Kenis PJA: A gross-margin model for defining techno-economic benchmarks in the electroreduction of CO2. *ChemSusChem* 2016, 9:1972–1979.

12. Van Muylder J, Pourbaix M. In Atlas of electrochemical equilibria in aqueous solutions. Edited by Pourbaix M, Oxford: Pergamon Press; 1966:449–457.

13. Delacourt C, Ridgway PL, Kerr JB, Newman J: Design of an electrochemical cell making syngas (CO + H2) from CO2 and H2O reduction at room temperature. *J Electrochem Soc* 2008, 155:E42–E48.

14. Gupta N, Gattrell M, MacDougall B: Calculation for the cathode surface concentrations in the electrochemical reduction of CO2 in KHCO3 solutions. *J Appl Electrochem* 2006, 36: 161–172.

15. Singh MR, Kwon Y, Lum Y, Ager JW, Bell AT: Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO2 over Ag and Cu. *J Am Chem Soc* 2016, 138: 13006–13012.

16. Weekes DM, Salvatore DA, Reyes A, Huang A, Berlinguette CP: Electrolytic CO2 reduction in a flow cell. *Acc Chem Res* 2018, 51:910–918.

17. Burdyny T, Smith WA: CO2 reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy Environ Sci* 2019, 12:1442–1453.

Perspective manuscript in which the authors discuss how crucial operative parameters (e.g., interfacial pH and CO2 concentration, resistance) are affected by high current density operation and largely overlooked in studies using cells incapable of reaching such large current regimes.

18. Liu K, Smith WA, Burdyny T: Introductory guide to assembling and operating gas diffusion electrodes for electrolychemical CO2 reduction. *ACS Energy Lett* 2019, 4:639–643.

19. Krause R, Reinisch D, Reller C, Eckert H, Hartmann D, Taroata D, Wiesner-Fleischer K, Bulan A, Luken E, Schmid G: Industrial application aspects of the electrochemical reduction of CO2 to CO in aqueous electrolyte. *Chem Ing Tech* 2020, 92:53–61.

20. Endrödi B, Kecsenovity E, Samu A, Darvas F, Jones RV, Török V, Danyi A, Janáky C: Multilayer electrolyzer stack converts carbon dioxide to gas products at high pressures with high efficiency. *ACS Energy Lett* 2019, 4:1770–1777.

21. Song JT, Song H, Kim B, Oh J: Towards higher rate electrochemical CO2 conversion: from liquid-phase to gas-phase systems. *Catalysts* 2019, 9:224.

22. Whipple DT, Finke EC, Kenis PJA: Microfluidic reactor for the electrochemical reduction of carbon dioxide: the Effect of pH. *Electrochem Solid-State Lett* 2010, 13:B109–B111.

23. Wu K, Biggersson E, Kim B, Kenis PJA, Karimi IA: Modeling and experimental validation of electrochemical reduction of CO2 to CO in a microfluidic cell. *J Electrochem Soc* 2014, 162: F23–F32.

24. Ziv N, Mustain WE, Dekel DR: The effect of ambient carbon dioxide on anion-exchange membrane fuel cells. *ChemSusChem* 2011, 11:136–1415.

25. Kutz RB, Chen Q, Yang H, Sajjad SD, Liu Z, Masel IR: Sustainim imidazolium-functionalized polymers for carbon dioxide electrolysis. *Energy Technol* 2017, 5:923–936.

26. Lee J, Lim J, Roh CW, Whang HS, Lee H: Electrochemical CO2 reduction using alkaline membrane electrode assembly on various metal electrodes. *J CO2 Util* 2019, 31:244–250.

27. Liu Z, Masel R, Chen Q, Kutz R, Yang H, Lewinski K, Kaplan M, Luopa S, Lutz DR: Electrochemical generation of syngas from water and carbon dioxide at industrially important rates. *J CO2 Util* 2016, 15:50–56.

28. Liu Z, Yang H, Kutz R, Masel R: CO2 electrolysis to CO and O2 at high selectivity, stability and efficiency using sustainin membranes. *J Electrochem Soc* 2018, 1653371–J3377.

29. Kaczur JJ, Yang H, Liu Z, Sajjad SD, Masel R: Carbon dioxide and water electrolysis using new alkaline stable anion membranes. *Frontiers Chem* 2018, 6:263.

30. A gross excellent overview of Dioxide Materials Inc.’s co-electrolyzer cell designs and best results (including upscale efforts) using imidazole-based anion exchange membranes.

31. Patru A, Binninger T, Pribyl B, Schmidt TJ: Co-electrolysis cell design for efficient CO2 reduction from gas phase at low temperature. Patent application number WO 2017/P15439 F5318, 1–4 (2016).

32. Larrazábal GO, Strom-Hansen P, Hei JP, Therkildsen KT, Cherkendorf I, Seger B: Analysis of mass flows and membrane cross-over in CO2 reduction at high current densities in an MEA-type electrolyzer. *ACS Appl Mater Interfaces* 2019, 11: 41281–41288.

33. Detailed study of the (bi)carbonate cross-over issues affecting AEM-co-electrolysis cells, including a rigorous assessment of the subsequent formation of CO2 at the cell’s anode.

34. Reinisch D, Schmid B, Martic N, Krause R, Landes H, Hanebuth M, Mayhtofer KJJ, Schmid G: Various CO2-to-CO electrolyzer cell and operation mode designs to avoid CO2-crossover from cathode to anode. *Z Phys Chem* 2019, https://doi.org/10.1515/zpch-2019-1480.

35. Weng L-C, Bell AT, Weber AZ: Towards membrane-electrode assembly systems for CO2 reduction: a modeling study. *Energy Environ Sci* 2020, 13:1950–1968.

36. Highly exhaustive modeling study that provides a comprehensive picture of the complex processes affecting AEM-co-electrolyzer operation, including the fine balance between dehydration and electrode flooding intrinsic to the cell’s operative conditions.

37. Vargas-Barbosa NM, Geise GM, Hickner MA, Mallouk TE: Assessing the utility of bipolar membranes for use in photoelectrochemical water-splitting cells. *ChemSusChem* 2014, 7:3017–3020.

38. Li YC, Yan Z, Hitt J, Wycisk R, Pintauro PN, Mallouk TE: Bipolar membranes inhibit product crossover in CO2 electrolysis cells. *Adv Sustain Syst* 2018, 2:1700187.

39. Straightforward and elegant demonstration of how reverse-bias BPMs suppress the cross-over of formate and alcohol products, as opposed to AEMs suffering from a significant cross-transport of these species.

40. Verma S, Kim B, Jhong H-R, Ma S, Kenis PJA: Microfluidic reactor for the electrochemical reduction of carbon dioxide: the Effect of pH. *Electrochem Solid-State Lett* 2010, 13:B109–B111. Manuscript featuring the best RB-BPM co-electrolysis performance reported to date, and showcasing the importance of membrane hydration (either through gas humidification or by co-feeding water / buffer solution) to attain stable cell operation.
**38.** Li YC, Zhou D, Yan Z, Goncalves RH, Salvatore DA, Berlinguette CP, Mallouk TE: Electrolysis of CO2 to syngas in bipolar membrane-based electrochemical cells. *ACS Energy Lett* 2016, 1:1149–1153.

**39.** Patru A, Binninger T, Pribyl B, Schmidt TJ: Design principles of bipolar electrochemical co-electrolysis cells for efficient reduction of carbon dioxide from gas phase at low temperature. *J Electrochem Soc* 2019, 166:F34–F45.

Only example in the literature of a co-electrolysis cell implementing a forward-bias BPM, and showcasing how this configuration allows operating at higher currents (vs. RB-BPMs) and leads to a full suppression of (bi)carbonate cross-over and concomitant anodic CO2 evolution.

**40.** Povia M, Abbott DF, Herranz J, Heinritz A, Lebedev D, Kim B-J, Fabbri E, Patru A, Kohlbrecher J, Schäublin R, Nachtegaal M, Copéret C, Schmidt TJ: Operando X-ray characterization of high surface area iridium oxides to decouple their activity losses for the oxygen evolution reaction. *Energy Environ Sci* 2019, 12:3038–3052.

**41.** Kim H, Park J, Park I, Jin K, Jerng SE, Kim SH, Nam KT, Kang K: Coordination tuning of cobalt phosphates towards efficient water oxidation catalyst. *Nat Commun* 2015, 6:8253.

**42.** Surendranath Y, Kanan MW, Nocera DG: Mechanistic studies of the oxygen evolution reaction by a cobalt-phosphate catalyst at neutral pH. *J Am Chem Soc* 2010, 132:16501–16509.

**43.** Costentin C, Porter TR, Savéant J-M: Conduction and reactivity in heterogeneous-molecular catalysis: new insights in water oxidation catalysis by phosphate cobalt oxide films. *J Am Chem Soc* 2016, 138:5615–5622.

**44.** Ma M, Qu F, Ji X, Liu D, Hao S, Du G, Asiri AM, Yao Y, Chen L, Sun X: Bimetallic nickel-substituted cobalt-borate nanowire array: an earth-abundant water oxidation electrocatalyst with superior activity and durability at near neutral pH. *Small* 2017, 13:1700394.

**45.** You C, Ji Y, Liu Z, Xiong X, Sun X: Ultrathin CoFe-borate layer coated CoFe-layered double hydroxide nanosheets array: a non-noble-metal 3D catalyst electrode for efficient and durable water oxidation in potassium borate. *ACS Sustainable Chem Eng* 2018, 6:1527–1531.

**46.** Dong Y, Komameni S, Wang N, Hu W, Huang W: An in situ anion exchange induced high-performance oxygen evolution reaction catalyst for the pH-near-neutral potassium borate electrolyte. *J Mater Chem A* 2019, 7:7699–7705.

**47.** Trzesniewski BJ, Diaz-Morales O, Vermaas DA, Longo A, Bras W, Koper MTM, Smith WA: In situ observation of active oxygen species in Fe-containing Ni-based oxygen evolution catalysts: the effect of pH on electrochemical activity. *J Am Chem Soc* 2015, 137:15112–15121.

**48.** Meng Y, Zhang X, Hung WH, He J, Tsai Y-S, Kuang Y, Kenney MJ, Shyue J-J, Liu Y, Stone KH, Zheng X, Suib SL, Lin M-C, Liang Y, Dai H: Highly active oxygen evolution integrated with efficient CO2 to CO electroreduction. *Proc Natl Acad Sci Unit States Am* 2019, 116:23915–23922.

**49.** Zheng X, Zhang B, De Luna P, Liang Y, Comin R, Voznyy O, Han L, García de Arquer FP, Liu M, Dinh CT, Regier T, Dynes JJ, He S, Xin HL, Peng H, Prendergast D, Du X, Sargent EH: Theory-driven design of high-valence metal sites for water oxidation confirmed using in situ soft X-ray absorption. *Nat Chem* 2018, 10:149–154.

In situ soft X-ray absorption spectroscopy (sxAS) was used to investigate the oxidation state of Ni-based catalysts under OER potentials and quasi-neutral pH values. The catalyst’s Ni-oxidation state was correlated with their OER activity, suggesting that incorporating Ni in the highest possible oxidation (as the case of NiCoFeP-oxyhydroxides) leads to the greatest OER-activity in this quasi-neutral environment.

**50.** Zhou LQ, Ling C, Zhou H, Wang X, Liao J, Reddy GK, Deng L, Peck TC, Zhang R, Whittingham MS, Wang C, Chu C-W, Yao Y, Jia H: A high-performance oxygen evolution catalyst in neutral-pH for sunlight-driven CO2 reduction. *Nat Commun* 2019, 10:4081.

Sr2GaCoO5 brownmillerite oxide presents a relatively high OER-activity at pH 7, exceeding that of an IrO2 benchmark catalyst tested under the same conditions. Interestingly, the OER-activity of the brownmillerite oxide also displays little dependency on the electrolyte’s pH.

**51.** Kim B-J, Fabbri E, Borial M, Castelli IE, Nachtegaal M, Graule T, Schmidt TJ: Oxygen evolution reaction activity and underlying mechanism of perovskite electrocatalysts at different pH. 2020. Submitted.

**52.** Fabbri E, Schmidt TJ: Oxygen evolution reaction – the enigma in water electrolysis. *ACS Catal* 2018, 8:9765–9774.