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Addressing the “alkalinity problem” with catalyst design and translation empowers scalable and sustainable CO₂ electrolysis

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Introduction

In recent years, electrolysis of CO₂ and water has gained traction as an avenue towards directing renewable electricity to carbon-neutral high energy-density liquid fuels and valuable chemical precursors typically derived from fossil fuels. The development of a successful CO₂ electrolysis technology requires addressing multiple scientific and technical challenges in cell design, electrolyte selection, membrane optimization, and electrochemical operation parameters¹. Among these, the central obstacle for CO₂ electrocatalyst development lies in achieving high and stable production rates towards specific molecules at low overpotentials or activation energy. Notably, the electrochemical microenvironment over the catalyst surface, which directly influences catalytic performance, is largely determined by the cell design and electrolyte. Hence, progress in catalyst development must always be viewed in the context of the electrochemical system surrounding the catalyst.

Presently, three typical configurations of the electrochemical cell normally used by researchers are the H-cell, the flow cell with gas diffusion electrode (GDE) and the Membrane Electrode Assembly (MEA) (as shown in Figure 1). Whereas the cathode is fully immersed into aqueous electrolyte in an H-cell, the GDE configuration exposes one side of the cathode to the feeding gas, thus allowing the co-existence of liquid phase and gas phase within the catalyst layer. Recently, emerging GDE works have rapidly broadened the scope of CO₂RR and pushed current densities to a more practical level.²⁻³ This configuration not only dramatically mitigates the CO₂ mass transport limitation, but also allows experiments to be conducted in highly alkaline electrolyte. The MEA configuration leverages the GDE configuration of a flow cell while minimizing electrolyte usage by direct contact of the catalyst layer to the ion exchange membrane. This configuration can mitigate the full cell resistance and improve cell stability. In all configurations, the choice of electrolyte further determines the electrochemical environment around the catalyst. In particular, a recent popular development in the electrocatalytic community has been to employ highly alkaline

(e.g. 1M KOH or greater) electrolytes in a GDE environment to boost catalytic activity. However, the sustainability of this practice towards overall CO₂ reduction has recently been called to question⁴

In this commentary, we briefly overview the “alkalinity problem,” issues that ultimately discourage the use of alkaline electrolyte for CO₂ reduction. Then, we discuss catalyst design strategies as solutions to the “alkalinity problem,” by generating local microenvironments favorable for CO₂ reduction without requiring bulk alkalinity. Finally, we summarize cell-level design features, catalyst translation, and important metrics to report for CO₂ reduction, in the hopes of shifting the conversation towards more sustainable CO₂ reduction technologies.

The “alkalinity problem”

The sustainability problem with using highly alkaline electrolyte in CO₂ reduction at the cell level has previously been discussed.⁴ Here, we provide some background for why catalyst researchers have favored such electrolytes, by briefly discussing the molecular advantages of an alkaline environment. Cathodic surface pH during high current CO₂RR is much higher than that of the bulk solution due to the OH⁻ generated by cathodic reactions. As a direct result, CO₂RR selectivity is enhanced at high current due to the suppression of the hydrogen evolution reaction (HER). Furthermore, any elementary steps of CO₂RR that involve the H^{*} species (such as CH₄ production) will also be influenced⁵. Multicarbon products like C₂H₄ or C₂H₅OH generally exhibit less local pH dependence since the rate determining step (RDS) is the C-C coupling reaction.⁶ Interestingly, it has been found that under highly alkaline conditions (such as in >1 M KOH), OH⁻ ions play more diverse functions. OH⁻ influences Bader charge of catalyst surfaces², tunes the catalytic pathway by nucleophilic reaction with surface intermediates⁷, and may potentially influence H-bond network, near-surface electric field, *etc.* Thus, to benefit from these molecular advantages, or to further explore reaction mechanisms at a fundamental level, concentrated alkaline electrolyte has been employed in some GDE work.

Ultimately, however, the disadvantage of using high alkaline electrolyte under real operating conditions is too significant to ignore. The unavoidable reaction between OH⁻ and CO₂ results in the formation of carbonate/bicarbonate and irreversible acidification of the electrolyte. The resulting carbonate generation can increase whole cell resistance, block the gas diffusion channel, and accelerate electrolyte flooding, ultimately shutting down the cell. For comparison, although the locally generated OH⁻ at cathode in neutral electrolyte can also react with CO₂, the generated carbonate/bicarbonate is overall balanced with the anodic half reaction, in which the carbonate/bicarbonate can react with generated protons and release CO₂ back to the gas phase. While this results in the net transfer of CO₂ from cathode to anode, this is a more tenable problem than the irreversible acidification of KOH. Furthermore, the consumption of the feeding gas and alkaline electrolyte increases economic costs and significantly suppresses the CO₂ concentration near catalyst surface. As Rabinowitz, J. A. *et. al.* recently discussed, underestimating or ignoring energy consumption of recycling CO₂ and OH⁻ from CO₃²⁻ will lead to over-estimated CO₂RR energy efficiency and a misleading technoeconomic model.⁴ Recent techno-economic models have begun to take this into account and evaluate the future of CO₂RR from technology to market;⁸ additional comprehensive analyses of CO₂ transformation considering CO₂ and electrolyte regeneration and barriers towards commercialization would be intriguing additions to the literature.

Catalyst design strategies for generating CO₂RR favored local environments

Considering the molecular benefits and cell-level drawbacks of highly alkaline electrolyte (briefly listed in Table.1), we propose that one resolution to the “alkalinity problem” is through catalyst design that leverages the molecular advantages of local alkalinity in essence without relying on bulk KOH. By extension, we highlight two trends in recent catalyst development research that offer potential strategies to generate localized CO₂RR favored environments in a more sustainable KHCO₃ electrolyte: surface nanostructuring and molecular surface modification (as shown in Figure.2).

Catalyst surface nanostructuring has proven to be an efficient way to influence catalytic selectivity through delicately tuned surface pH and CO₂ concentration.⁹ Meanwhile, secondary structure in the catalyst layer induced by fabrication processes also result in significant, non-monotonic tunability of the catalytic performance by modulating local CO₂ availability.¹⁰ By optimizing the catalyst loading technique, CO₂ feeding rate and concentration, a 75.5% C₂₊ faradic efficiency (FE) with the majority products being C₂H₄ and C₂H₅OH can be achieved at 300 mA/cm² in 1M KHCO₃. Thus, by controllably nanostructuring the electrode surface, either through top-down methods or through well-controlled bottom-up synthesis, both H⁺ availability and CO₂ availability can be flexibly tuned, with substantial effects on catalytic selectivity – we consider this a fruitful future direction for catalyst design.

Another promising pathway to modulate local microenvironment is through surface interactions with molecular additives. As discussed above, an important role of OH⁻ over Cu surface is to tune the surface Bader charge and stabilize CO₂RR intermediates, which opens the door to other molecular adsorbates potentially playing similar roles, perhaps more effectively. For instance, coupling pyridinium-derived dimers to a Cu surface in GDE greatly boosts ethylene selectivity in neutral media.¹¹ A peak FE of 72% and partial current of 232 mA/cm² towards C₂H₄ was obtained at -0.83 V vs RHE in CO₂ saturated 1M KHCO₃. A different approach is to use molecular modification to change the interfacial microenvironment at the metal surface. This idea is inspired by the specific selectivity of enzymes in bacteria, which exhibit ultra high selectivity toward specific products during CO₂RR.¹² Along these lines, we have recently reported a nanoparticle ordered ligand interlayer strategy that creates a catalytic pocket to exclude water while enhancing CO₂ activation on a multitude of different metal nanoparticle surfaces through desolvated cation intercalation.¹³ Using this strategy, nearly unit CO selectivity can be achieved in the GDE configuration at 400 mA/cm² in 1M KHCO₃.

Ultimately, the catalyst strategies we highlight in this Commentary aim to decrease the energetic cost at the cathode to convert CO₂ to a given product by reducing overpotential and increasing faraday efficiency: this can be summarized as the cathodic energy efficiency (CEE). We conduct a rough estimation of the relative value of such catalyst design strategies weighed against an estimated energetic cost of using neutral vs. alkaline electrolyte. Using some simple assumptions supported by recent literature¹³ (~90% FE for industrially relevant production rates of CO at 0.8 V overpotential in pH 7 electrolyte or 0.4 V overpotential in pH 14), we estimate that the CEE increase owing to catalyst design strategies in neutral environment can effectively close the energetic gap from alkaline environment (Fig. 3C). While not a rigorous calculation, this back-of-the-envelope demonstration highlights the promise of using these microenvironment-driven catalyst design strategies instead of relying on alkaline electrolyte.

Additionally, we believe optimal catalysts for CO₂ electrolysis in neutral electrolyte will leverage multiple of the above-listed advantages in tandem, rather than rely on a single strategy. Thus, the interplay between these multiple effects, whether cooperative or competitive, should also be carefully investigated, as additional gains in CEE or other at-present unrealized catalytic benefits may arise at the interface of these strategies.

Effective catalyst translation to industrially relevant configurations

While the H-cell and GDE configurations are suitable for fundamental study and new catalyst development, the MEA configuration is highly attractive for industrial application, and research towards optimizing this particular configuration is a promising direction. For example, optimizing the critical membrane component can yield substantial gains in energy efficiency. Since the electrolyte usage is greatly reduced, current in the MEA is mostly transmitted through ionomers and membranes. Therefore, optimizing membrane conductivity can substantially reduce polarization losses over the full cell voltage, which are significant at high currents. More specifically, as discussed above, the generation of OH⁻ during cathodic electrolysis and the neutralization of the locally generated OH⁻ with CO₂ happens simultaneously. This results in a distribution of charge carrier species in the ion exchange membrane; therefore, correspondingly optimizing the ion exchange membranes for the major carriers with higher mobility can be a good strategy. Membrane technologies also offer advantages beyond reducing the full cell voltage. For example, bipolar membrane based MEAs can regenerate CO₂ from bicarbonate electrolyte, offering a relatively energy-efficient way to reuse the CO₂ consumed by KOH, compared with the traditional calcination cycle.¹⁴

To date, MEA development and catalyst development have been pursued separately and independently. Thus, new opportunities exist in the translation of catalytic strategies developed in the H-cell / flow cell regimes into MEA, towards enhancing full cell energy efficiency and prolonging system stability. One successful example is translating pyridinium-derived dimers treated Cu from flow cell to MEA, in which the catalyst could run continuously for 190 h with a ~60% C₂H₄ FE and 120 mA/cm² current density.¹¹ Further combining such catalysts with an ionomer-based gas diffusion channel strategy to enrich the local CO₂ concentration resulted in 208 mA/cm² C₂H₄ partial current density with 66% FE and 21% full cell energy efficiency under 3.9 V full cell bias in MEA. The device was shown to operate for 100 h with only slight whole cell voltage increase and C₂H₄ FE decrease.¹⁵

When considering the translation of catalysts into full cell configurations suitable for commercial application, additional important performance metrics should be reported. Catalytic stability tests are normally carried out for several hours, rather than the hundreds to thousands required for industrial application. Since many catalyst deactivation mechanisms, such as surface reconstruction, contamination, and mechanical failure are highly possible during long term electrolysis, these effects must be scrutinized carefully, especially for multi-component and nanostructured catalysts that aim to generate CO₂RR-favorable local environments. Moreover, for publishable device results, it is especially important to precisely quantify and report the energy efficiency; single pass CO₂ conversion and the relevant CO₂ conversion products (whether electrolytic product or bicarbonate). These parameters will help contribute to a more rigorous literature comparison and evaluation of CO₂RR industrialization progress.

Conclusion

In short, although useful fundamental insight about CO₂ transformation mechanisms and microenvironment over catalyst surface can be extracted from research in high alkaline flow cells, high-performing catalysts in neutral electrolyte will be necessary due to the “alkalinity problem”. To this end, we consider catalyst design strategies via nanostructuring and molecular modification at the interface to be two broad avenues of promise for further scientific study. Additionally, effective engineering efforts that facilitate the translation of effective CO₂RR catalysts from H-cell/flow cell towards MEA configurations is also an important step towards industrialization. Further advances in fundamental knowledge regarding the manipulation of catalyst microenvironments in neutral electrolyte, together with development in catalyst translation to effective electrolytic cell configurations, will provide the key necessary pieces to solve the “alkalinity problem” and enable CO₂ reduction as a sustainable technology.

AUTHOR CONTRIBUTIONS

All authors contributed equally.

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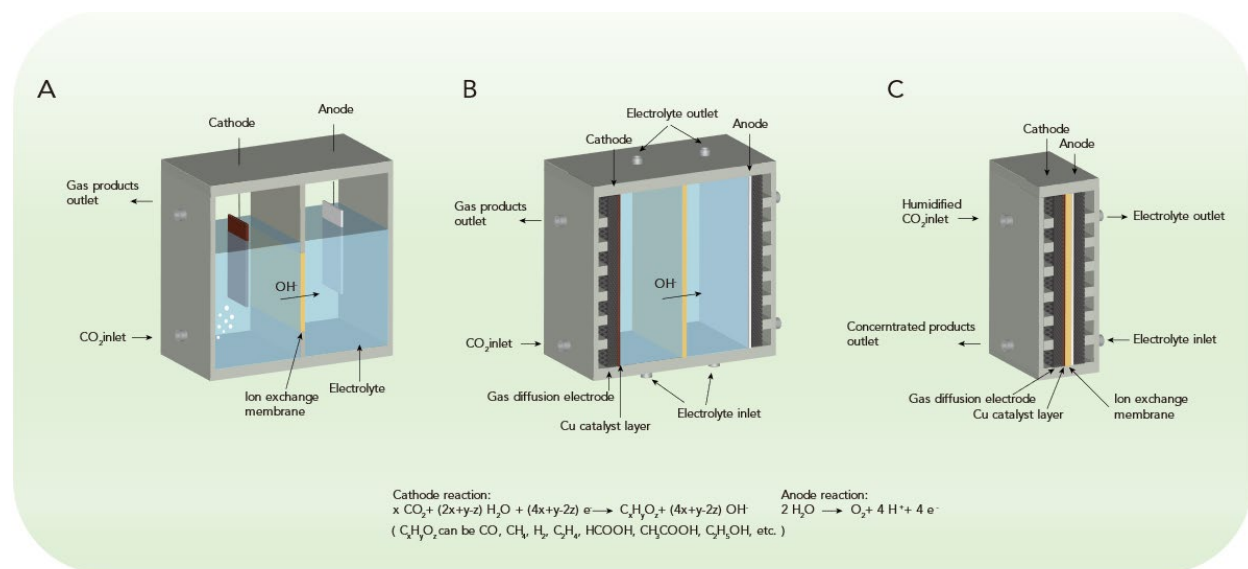


Figure 1. Schematic configurations of the (A) H-cell, (B) gas diffusion electrode-based flow cell and (C) membrane electrode assembly (MEA). In the H-cell, CO₂ first dissolves into the liquid electrolyte before diffusing to the cathode. In contrast, in the flow cell, CO₂ can directly diffuse into the catalyst layer with a gas diffusion electrode, generating three-phase interface with the catalysts and the electrolytes. In the MEA, contact with the electrolyte is further reduced via the ion exchange membrane being in direct contact with the cathode.

Table 1. Pros and cons of using high alkaline electrolyte

Influence of high alkaline electrolyte on electrolysis	
Pros:	Cons:
<ul style="list-style-type: none"> • Suppression of HER 	<ul style="list-style-type: none"> • Unavoidable CO₂ and electrolyte consumption
<ul style="list-style-type: none"> • Acceleration of multicarbon productivity 	<ul style="list-style-type: none"> • Higher near-surface CO₂ transport resistance
<ul style="list-style-type: none"> • New mechanistic pathways 	<ul style="list-style-type: none"> • Accelerated electrode flooding

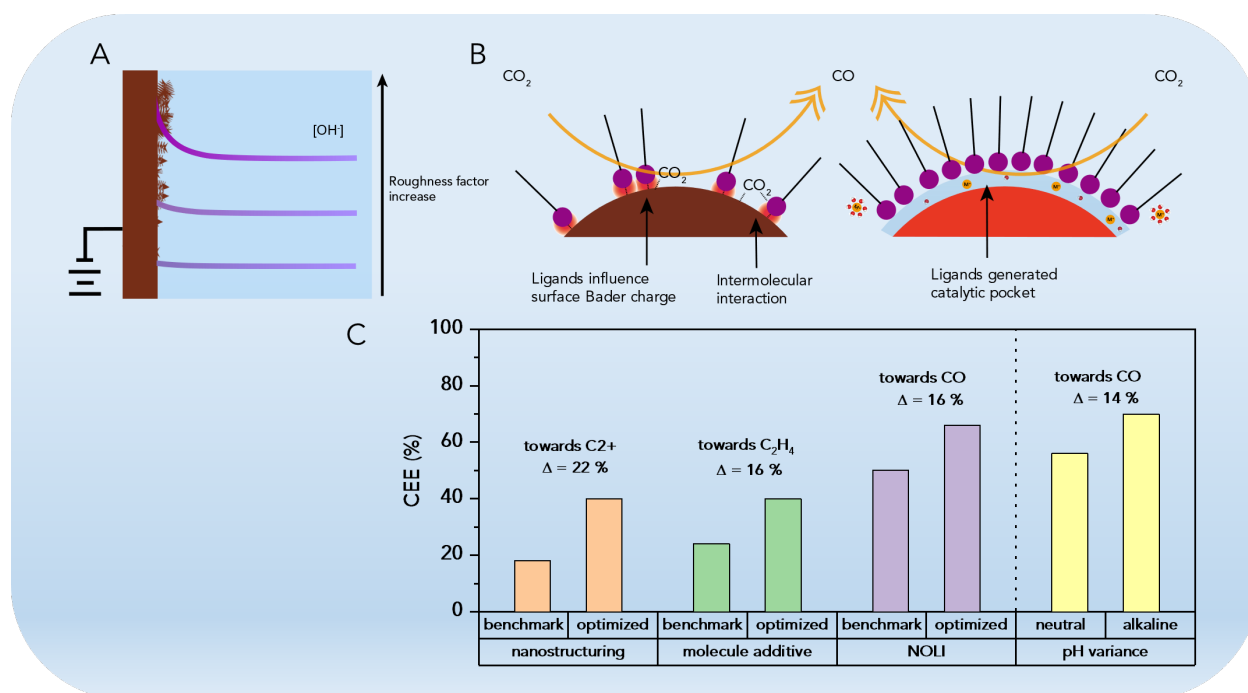


Figure 2. Catalyst design strategies for facilitating CO₂RR in neutral electrolyte through microenvironment chemistry. (A) Scheme of the relationship between surface nanostructure vs local pH. Designing and creating surfaces with larger roughness factors is beneficial for increasing local alkalinity. (B) Scheme of the potential interactions between molecular modifiers with the catalyst surface and CO₂ molecules. Left panel indicates the individual effect of the molecular modifiers, such as influences on the catalyst surface Bader charge and intermolecular interactions. Right panel exhibits the group effect of the ligands that can generate a chemically beneficial catalytic pocket. (C) Cathodic energy efficiency (CEE) enhancement of the different catalytic strategies

(nanostructuring¹⁰; molecule additive¹¹; NOLI¹³). For comparison, the electrolyte pH variation induced CEE change was also estimated. The CEEs were calculated with the equation: $CEE = \Sigma \left(\frac{1.23V - \text{thermodynamic potential of specific } CO_2RR \text{ product}}{1.23V - \text{actual working potential of } CO_2RR} \times \text{product } FE \right)$. For each strategy, the highlighted catalytic performance was compared with the corresponding internal benchmark under the same industrial relevant current density (200-400 mA/cm² depending on the data availability in the literature). To simplify the estimation of pH variance induced CEE change, only CO₂ conversion towards CO was considered. 90% CO FE, 0.8V overpotential for neutral and 0.4V overpotential for alkaline electrolysis are assumed parameters for estimation. The CEE difference between neutral and alkaline electrolyte is robust, which will not dramatically change when slightly varying the parameter value in the assumption.

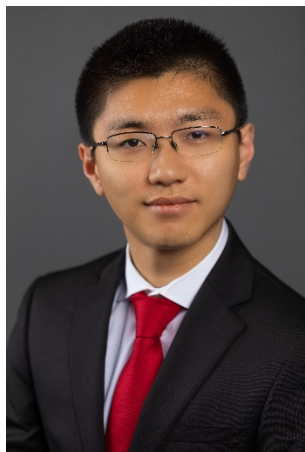
Personal Bio

Chubai Chen



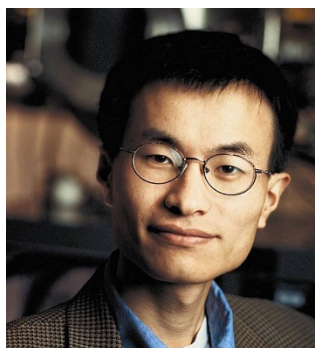
Chubai Chen joined the chemistry program at UC Berkeley in 2017 under the supervision of prof. Yang. Previously, he obtained his bachelor's degree in material chemistry from University of Science and Technology of China. Now, his research interests focus on small molecules electrochemical conversion and corresponding mechanism study.

Yifan Li



Yifan Li received his Ph.D in Chemistry from UC Berkeley in 2019 under Professor Peidong Yang, after receiving his A.B. in Chemistry from Princeton University in 2014. His graduate and post-graduate research has centered around identifying active sites on nanomaterial catalysts for the electrocatalytic transformation of CO₂, particularly to multi-carbon and multi-electron products. His continued research interests lie in the discovery and characterization of nanostructured materials for energy storage, generation, and conversion, with special interest in their behavior under operating conditions.

Peidong Yang



Peidong Yang is the S. K. and Angela Chan Distinguished Chair in Energy at UC Berkeley in the departments of chemistry and departments of materials science & engineering. He is also the senior faculty scientist at Lawrence Berkeley National Laboratory, the director of California Research Alliance by BASF and Kavli Energy Nanoscience Institute. Before being a professor at UC Berkeley, he conducted postdoc research at UCSB and received the Chemistry Ph.D. at Harvard University. He obtained his bachelor's degree in chemistry from University of Science and Technology of China. His research interests focus on nanoscience and renewable energy technology development.