COMMENTARY

Paving the way for electrosynthesized acetate: Self-pressurizing nanocatalytic capsules via CO_2 electroreduction

Yongjun Kwon,[1] Binhong Wu,[1] Fiona N. Okech,[1] Siwei Li,[2] and Qiaowan Chang[1,*]

[1]Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

[2]Institute of Industrial Catalysis, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

*Correspondence: qiaowan.chang@wsu.edu

Received: April 30, 2024; Accepted: September 29, 2024; Published Online: November 1, 2024; https://doi.org/10.59717/j.xinn-mater.2024.100098

Citation: Kwon Y., Wu B., Okech F., et al., (2024). Paving the way for electrosynthesized acetate: Self-pressurizing nanocatalytic capsules via CO_2 electroreduction. The Innovation Materials **2(4)**: 100098.

Climate change is one of the most pressing challenges, primarily driven by increasing levels of atmospheric carbon dioxide (CO_2). The electrochemical CO_2 reduction reaction (CO_2RR) offers a promising solution by transforming CO_2 into valuable chemical products, enhancing both environmental sustainability and commercial viability. However, achieving high production rates of valuable products, such as acetate and propanol, is currently hindered by low activity (current density below -30 mA/cm^2) and selectivity (Faradaic efficiency (FE) below 10%) in the CO_2RR processes.

An effective strategy to address these limitations is shifting the reactant from CO_2 to carbon monoxide (CO), due to the higher activity of the electrochemical CO reduction (CORR). Jiao et al.[1] demonstrated the potential of this approach using a flow electrolyzer that converted CO into acetate on micrometer-scale copper, achieving a FE of acetate to ~20% with a total current density of -300 mA/cm^2. Further optimization was realized in a CO electrolyzer designed to include a selective alcohol partial oxidation anode and an alcohol-permeable anion exchange membrane.[2] This setup, using a copper (Cu) cathode catalyst and a nickel-iron (Ni-Fe) anode catalyst separated by an anion exchange membrane (AEM), facilitated the production of concentrated high-purity acetate. An acetate product stream with a concentration of 7.6 M and a purity of over 97% was obtained. The high purity of the acetate was attributed to the rapid crossover of ethanol products from the cathode and their partial oxidation at the anode. While significant progress has been made in CORR to acetate, further exploration is needed to optimize CO_2RR to acetate.

Zhu and Lin et al. reported a novel strategy for enhancing CO_2RR to acetate by designing self-pressurizing nanocatalytic capsules that increased CO intermediate pressure to facilitate a new CO-CO_2 coupling reaction pathway (Figure 1A).[3] This approach significantly outperformed current benchmarks in CO_2RR with an acetate FE of 38.5±2.2% and an acetate partial current density of -328±19 mA/cm^2. Prior research indicated the critical role of CO partial pressure in controlling the formation of C_{2+} products, where lower pressures favored ethylene[4] while higher pressures favor ethanol production.[5] Building on this, Zhu and Lin et al. hypothesized that a sufficient increase in CO pressure would be crucial for optimizing acetate and propanol production. This was confirmed through theoretical calculations. Density functional theory (DFT) studies demonstrated distinct CO_2RR pathways on Cu(111) that ethylene, ethanol, and propanol formed via a CO-CO coupling pathway (COCO*), while acetate formed through a CO-CO_2 coupling pathway ($COCO_2$*). Increasing the CO coverage from 0 to 0.56 monolayers (MLs) showed that the $COCO_2$ pathway became dominant around a CO partial pressure of 0.17 bar.

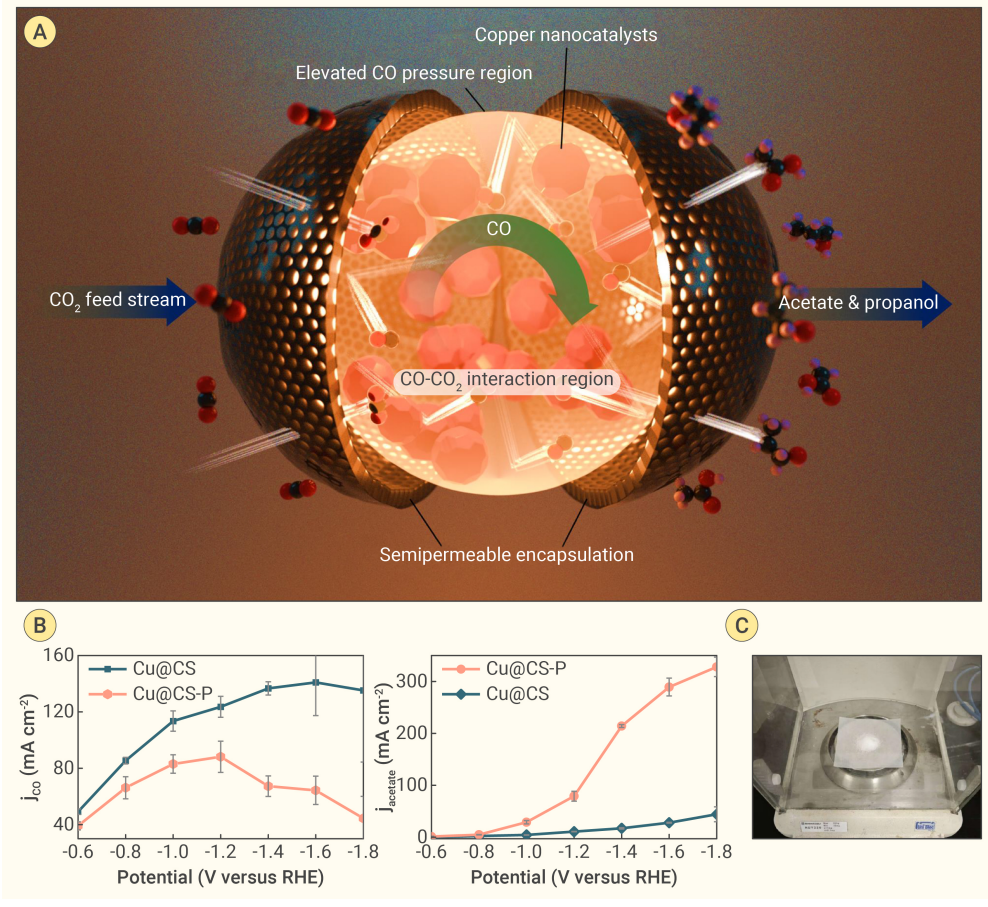

Figure 1. Sketch of self-pressurizing nanocatalytic capsules for CO_2 electroreduction to acetate (A) Schematic diagram of the designed self-pressurizing nanocatalytic capsules. (B) Partial current density for CO and acetate on the Cu@CS and the Cu@CS-P catalyst. (C) 1.92 g of potassium acetate generated in the catholyte during the stability test.

Microkinetic modeling indicated a rapid increase in acetate production once this pressure threshold was exceeded. A rate control analysis shed light on the kinetic mechanisms underlying this process: the rate constant for $COCO_2$* formation exhibited greater sensitivity to pressure changes compared to COCO*. Theoretical predictions suggested that elevating the CO pressure beyond a specific threshold on Cu(111) during CO_2RR should catalyze -$COCO_2$* pathway to favor acetate production. The prediction was validated by the experimental results from the external $^{13}CO_2/^{12}CO$ co-feeds on triangular Cu nanosheets with exposed (111) surfaces in a flow electrolyzer. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy confirmed the distinct reaction pathways for different reaction products, i.e., a CO-CO coupling pathway for ethanol and a CO-CO_2 coupling pathway for acetate, respectively. Importantly, once the CO pressure exceeded 0.2 bar, the CO-CO_2 pathway was activated for total acetate production.

Building on the experimental validation of

theoretical predictions, Zhu and Lin et al. further applied the "like dissolves like" principle to design self-pressurizing nanocatalytic capsules. These capsules selectively allowed polar CO_2 molecules and liquid products to pass through their polar enclosures while blocking the less polar CO, therefore increasing the CO intermediate pressure. They chose the permselective polymer Pebax as the capsule material because of its ability to selectively prevent CO diffusion out of the catalyst. To enhance the stability and functionality of these capsules, Zhu and Lin et al. developed a novel method using ethylenediaminetetraacetic acid (EDTA) tetrasodium salt as a key ingredient to initially encapsulate the unstable Cu nanoparticles in a hollow carbon shell to form Cu@CS. Subsequently, these microscopic apertures were sealed with Pebax to form Cu@CS-P. Using an energy-dispersive X-ray spectroscopy (EDS), Zhu and Lin et al. also illustrate the effective sealing of the pores on the carbon shell by Pebax, showcasing the successful implementation of their design. This approach not only reinforced the structural integrity of the nanocatalysts but also optimized the reaction environment for CO_2RR. At a potential of -1.6 volts versus reversible hydrogen electrode (V vs RHE), the FE of acetate on Cu@CS-P, after coating with Pebax, showed an eightfold increase compared to the uncoated Cu@CS, from 4.8±0.4% to 38.5±2.2% (Figure 1B). Additionally, the acetate partial current density of Cu@CS-P reached up to -328±19 mA/cm² (Figure 1B), surpassing nearly all other systems that utilized pure CO_2 for reduction. The stability of Cu@CS-P was tested in a flow cell system with a modified gas-liquid-catalyst interface. A stable current of ~-470 mA/cm² was maintained over 30 hours, and a total of 1.92 g of acetate was detected in the catholyte as shown in Figure 1C. This remarkable performance sets a new benchmark in the field, highlighting the effectiveness of the self-pressurizing nanocatalytic capsule design in enhancing CO_2RR to acetate.

The effectiveness of self-pressurizing nanocatalytic capsules was further examined by comparing the electrocatalytic performance of carbon-shell-Pebax (CS-P) catalysts and Cu/Ag@CS-P, which incorporated a silver layer on the Cu nanoparticles. The CS-P exhibited limited activity towards CO_2RR, indicating that its primary function was acting as a permselective layer rather than an active catalyst. When a silver layer was added to the Cu nanoparticles to change product preference towards CO, a significant number of Cu/Ag@CS-P capsules bursted due to excessive internal pressure. The selective blocking of CO by the capsule enclosure was also confirmed through the CORR performance of Cu@CS and Cu@CS-P. The presence of Pebax as an enclosure meant that non-polar CO could not cross the polar encapsule to reach the Cu active sites. Consequently, Cu@CS-P exhibited much lower CORR activity with 26.4% of FE for C_{2+} products compared to Cu@CS (FE of 82.2%), illustrating the significant impact of the permselective properties of Pebax on the catalytic CO_2RR performance.

Zhu and Lin et al. also investigated the reaction mechanism via an in-situ interruption experiment and in-situ Raman measurements. In the in-situ interruption experiment, where the normal operation of electrochemical measurement was paused to analyze internal conditions, they showed that the CO pressure inside the Cu@CS-P catalysts was around 8±3 Bar during the CO_2RR. The in-situ Raman measurements with an isotopic labeling method in the CO_2/CO co-feeds experiment showed that a possible reaction intermediate of CH_2COO* was formed in the CO-CO_2 coupling pathway. This strategy was further extended to other Cu-based electrocatalysts, such as CuI@CS-P, which demonstrated exceptional performance in propanol production. It achieved a Faradaic efficiency of 25.7±1.2% and a partial current density of -155±3 mA/cm² at -1.2 V, surpassing existing reports in CO_2RR. These results confirm the effectiveness of the strategy in producing other liquid C_{2+} chemicals.

The use of the "like dissolves like" principle to encapsulate nanoparticles to increase the local pressure of reaction intermediates presents an innovative approach, potentially applicable to other electrocatalytic reactions, such as nitric oxide (NO) reduction reaction and nitrogen (N_2) reduction reaction. It is also crucial to consider the evolution of the oxidation state of the Cu catalyst under these high-pressure conditions, as the chemical state of the active sites may change, influencing the reaction dynamics. When contemplating the commercial application of CO_2RR, it is important to evaluate the catalyst performance using impure CO_2 streams contaminated nitrogen oxides (NO_x) and sulphur oxide (SO_x) to realistically assess its industrial viability. Overall, the development of self-pressurizing nanocatalytic capsules offers promising new pathways for enhancing CO_2RR. This breakthrough signifies a potentially transformative step in catalysis research, bridging fundamental science and practical application to unlock the potential of using CO_2 as a feedstock to produce valuable products.

REFERENCES

1. Jouny, M., Luc, W., and Jiao, F. (2018). High-rate electroreduction of carbon monoxide to multi-carbon products. Nat. Catal. **1**: 748–755. DOI: 10.1038/s41929-018-0133-2.
2. Overa, S., Crandall, B.S., Shrimant, B., et al. (2022). Enhancing acetate selectivity by coupling anodic oxidation to carbon monoxide electroreduction. Nat. Catal. **5**: 738–745. DOI: 10.1038/s41929-022-00828-w.
3. Cai, Y., Yang, R., Fu, J., et al. (2024). Self-pressurizing nanoscale capsule catalysts for CO_2 electroreduction to acetate or propanol. Nat. Synth. DOI: 10.1038/s44160-024-00552-2.
4. Li, J., Wang, Z., McCallum, C., et al. (2019). Constraining CO coverage on copper promotes high-efficiency ethylene electroproduction. Nat. Catal. **2**: 1124–1131. DOI: 10.1038/s41929-019-0380-x.
5. Yang, P.-P., Zhang, X.-L., Gao, F.-Y., et al. (2020). Protecting copper oxidation state via intermediate confinement for selective CO_2 electroreduction to C_{2+} fuels. J. Am. Chem. Soc. **142**: 6400–6408. DOI: 10.1021/jacs.0c01699.

FUNDING AND ACKNOWLEDGMENTS

The authors acknowledge institutional funds from the Gene and Linda Voiland School of Chemical Engineering and Bioengineering at Washington State University. The funders had no role in study design, data collection and analysis, decision to publish or preparation of the manuscript.

AUTHOR CONTRIBUTIONS

Yongjun Kwon: writing - reviewing and editing. Binhong Wu: editing. Fiona N. Okech: editing. Siwei Li: editing. Qiaowan Chang: supervision, writing – original draft.

DECLARATION OF INTERESTS

The authors declare no competing interests.