

was increased to 0.9 M, yielding the AORFB with the highest theoretical capacity (24.1 Ah/L) that has been reported for a ferrocyanide-based system so far (Figure 2). The battery has been cycled for 1,100 h and 1,000 cycles, proving an excellent cycling stability and no significant capacity loss. However, a slightly decreased power and current compared to the 0.5 M solution can be observed, which is ascribed to the increased viscosity as well as the electrolyte and membrane conductivity.

The high stability upon cycling, high initial capacity of the used electrolyte, and hardly any capacity decay even after 1,000 battery cycles make the reported battery system a fascinating and potent candidate for practical applications in energy storage.

## DECLARATION OF INTERESTS

U.S.S. and M.D.H. are cofounders of Jenabatteries GmbH. M.D.H. is a shareholder of Jenabatteries.

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## Preview

# Boosting the Single-Pass Conversion for Renewable Chemical Electrosynthesis

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**Efficient engineering design of CO<sub>2</sub> and CO electrolysis systems is key to achieving practical renewable energy conversion and storage via the upgrading of CO<sub>2</sub>. High selectivity, current density, and energy efficiency have been the focus of many research efforts. The single-pass conversion of the reactants is another crucial system parameter that has—until now—received too little attention. Recently in *Joule*, Ripatti et al. showcase an electrolyzer that achieves high single-pass conversion combined with high current density.**

The electrochemical reduction of carbon dioxide (CO<sub>2</sub>) to multi-carbon-based products provides a route to accelerate the deployment of renewable electricity and to realize low-carbon-footprint fuels and chemicals.<sup>1</sup>

The process can be performed in a single electrochemical reaction; or, alternatively, in a two-step process, such as CO<sub>2</sub> electroreduction to carbon monoxide (CO) followed by CO reduction to multi-carbon chemicals. CO electro-

reduction offers a route to generate multi-carbon chemicals with high selectivity because it avoids the formation of CO and formic acid, which are common single-carbon products in CO<sub>2</sub> reduction. In addition, CO has the benefit that it does not react with hydroxide ions presented in the electrolytes widely used in CO<sub>2</sub> and CO electrolysis.

Recently in *Joule*, Ripatti et al. demonstrate an electrolysis system that produces concentrated multi-carbon products with high single-pass conversion efficiency at high reaction rate and selectivity. They do so by carefully controlling the reactants and ion transport in a membrane electrode assembly system.<sup>2</sup>

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**Table 1. Comparison of Single-Pass Conversion in CO<sub>2</sub> and CO Reduction**

Electrolyzer Configuration	Feedstock	Main Products	J <sub>CO<sub>2</sub>/CO-Red</sub> (mA/cm <sup>2</sup> )	Operation Time	Single-Pass Conversion (%) <sup>a</sup>	References
Flow electrolyte	CO <sub>2</sub>	ethylene	61	6 days	0.3	Dinh et al. <sup>5</sup>
			473	2.5 min	2.2	Dinh et al. <sup>5</sup>
Flow electrolyte	CO <sub>2</sub>	ethylene, ethanol, CO	138	4 hr	11.3	Ma et al. <sup>8</sup>
			358	3 min	22.5	Ma et al. <sup>8</sup>
Flow electrolyte	CO	ethylene, ethanol, acetate	635	1 hr	27.3	Jouny et al. <sup>7</sup>
Flow electrolyte	CO	ethylene, acetate	107	4 hr	68	This work
Membrane electrode assembly			104	24 hr	43	This work

J<sub>CO<sub>2</sub>/CO-Red</sub>: CO<sub>2</sub>/CO reduction current density.

<sup>a</sup>Single-pass conversion (%) = 100 × (CO<sub>2</sub>(CO) consumed)/(CO<sub>2</sub>(CO) flowed in).

In CO<sub>2</sub> and CO electrochemical reduction, it is important to combine high energy efficiency, current density, selectivity, and single-pass conversion in order to reduce both capital and operational costs. Energy efficiency is the percentage of the energy stored in the desired products compared to the total input energy. High energy efficiency is important to reduce the cost of electricity required, for this is the dominant contribution to the cost of electrosynthetic chemicals.<sup>3</sup> The current density reflects the rate of the reaction and thus directly affects the contribution of capital cost in the production of chemicals. The selectivity (percentage of a specific product per total products) and single-pass conversion (percentage of reactant converted per total reactant input) are critical for minimizing the separation requirements, and these affect both capital and operational costs.

Achieving these figures of merit simultaneously in a single chemical electrosynthetic system is an unmet need. The single-pass conversion is a particularly underexplored area—in fact, the majority of reports have used high excess of CO<sub>2</sub> or CO to ensure the supply of reactants. This helps selectivity but works against single-pass conversion.

Electrochemical reduction of CO<sub>2</sub> or CO can be performed in either

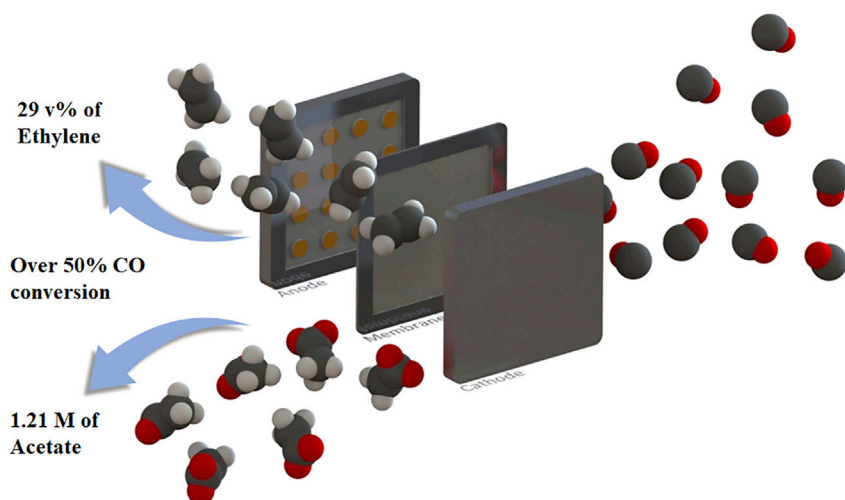
aqueous- or gas-phase systems. Aqueous electrolysis, wherein the gaseous reactants are dissolved in the electrolyte, offers a tool to achieve high selectivity and single-pass conversion.<sup>4</sup> However, due to the low solubility of the gas reactants in the aqueous electrolyte and the long diffusion distance, current densities remain below few tens of mA/cm<sup>2</sup>—far from the >100 mA/cm<sup>2</sup> regime needed to make CO<sub>2</sub> or CO electrolyzers economically viable.<sup>3</sup>

Gas-phase electrolysis of CO<sub>2</sub> and CO offers a path that overcomes the diffusion limitation of the aqueous system, thereby enabling a much higher current density. In gas-phase CO<sub>2</sub> and CO reduction systems, the catalyst is deposited onto a porous hydrophobic substrate (gas diffusion layer), reducing the diffusion length required and thus improving mass transport. Using a gas-phase electrolysis system, current densities in the hundreds of mA/cm<sup>2</sup> have been achieved with both liquid flow electrolyte and membrane electrode assembly configurations.<sup>5–8</sup> However, the separation of gaseous reactants and products, and the single-pass conversion efficiency, were issues yet to be resolved prior to Ripatti's advance (Table 1).

To achieve concentrated products, it is critical to optimize both the operating conditions and the system configura-

tion.<sup>9</sup> Using a gas diffusion electrolysis system coupled with a nafion membrane and an interdigitated flow field, Ripatti et al. optimize the operating conditions to achieve a single-pass CO conversion of 65% at a current density of 101 mA/cm<sup>2</sup> and a total CO reduction faradic efficiency of 65%–76%.<sup>2</sup> This high single-pass conversion allows a high ethylene concentration in the gaseous product stream, at 29 vol%, which is similar to the ethylene concentration in the product stream from an industrial naphtha cracking process.

As in water electrolysis, water oxidation at the anode side also plays a crucial role in CO electrolysis because it directly affects the energy efficiency of the system. In this reaction, alkaline media are more favorable compared to acidic ones because these help to reduce the reaction overpotential, leading to an improved overall energy efficiency.<sup>10</sup> In addition, basic reacting media allow the application of inexpensive and earth-abundant oxygen evolution catalysts, such as Ni-based ones. When Ripatti et al. replaced the IrO<sub>x</sub> catalyst in the anode side with a NiFe-based catalyst and switched the reaction electrolyte from neutral to basic, they observed a significant drop of 0.8 V in the cell potential.<sup>2</sup> The CO reduction faradic efficiency and CO single-pass conversion remain high at 65% and 56%, respectively, and a CO reduction current density of 168 mA/cm<sup>2</sup> is observed.



**Figure 1. Design of Electrochemical Cell for CO Electrochemical Reduction with High Single-Pass Conversion and High Product Concentration**

To reduce the resistance of the system and to increase the liquid product concentration, the authors further optimize the system by removing the cathode electrolyte to form a membrane electrode assembly structure (Figure 1). The authors used a nafion membrane to control the cation and water transport from the anode to the cathode. Because a limited amount of water is transported to the cathode during the reaction, a high liquid product concentration (acetate), as high as 1.21 M, is achieved. Interestingly, even without a catholyte flow layer, the total CO reduction faradic efficiency remains relatively high at 72%. Notably, the new cell configuration requires a cell voltage of only 2.32 V to reach 144 mA/cm<sup>2</sup> current density. When the CO pressure was optimized, the system can sustain its high CO reduction performance for 24 hr. To add on the advantages of this new configuration design, the authors demonstrated that the acetate products could be easily separated from the

liquid products with a yield of 85% using a simple crystallization process. This is a significant and exciting achievement that showcases a successful electrolyzer design for the efficient CO conversion into multi-carbon products.

The production of a highly concentrated product stream at a high current density exceeding 100 mA/cm<sup>2</sup> represents an impressive and significant advance for the field. Areas for future work include combining this with an increased energy efficiency for the main products (ethylene and acetate) to rise from the ~mid-20% values reported in this work to those that make water electrolyzers viable (60%–70%). Electrical energy cost is the main driver of the viability of electro-synthetic fuels and chemicals, so boosting the energy efficiency remains a crucial task for CO<sub>2</sub> and CO electrochemical reduction. Continued advancements in both system design, such as those demonstrated by Ripatti

et al., as well as ever-more-efficient catalyst design, are crucial on the path for commercial relevance for CO<sub>2</sub> and CO conversion technologies.

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