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Preview

Scale-up of CO₂ and CO electrolyzersThomas Burdyny^{1,*} and Fokko M. Mulder^{1,*}

Electrochemical CO₂ reduction aims to compete with Power-to-X alternatives but is well behind the scales of water electrolyzers and thermochemical reactors. In a recent issue of *Nature Chemical Engineering*, Crandall and co-workers demonstrate a 1000 cm² tandem CO₂/CO electrolyzer for acetate production. The work invites discussion on scientific and engineering scale-up challenges.

Our society depends on large quantities of fossil-derived carbon-based compounds due not only to their high energy value and utility but also their comparatively low cost. Shifting to a sustainable and low CO₂ emission society necessitates a substantial reduction in these compounds. Replacing the embedded carbon in our economy has varying levels of difficulty, however, with some easier to replace than others. Increasing the installed renewable electricity capacity, for example, can offset coal and natural gas power generation. Additionally increased electric mobility and battery storage can offset commuter emissions. Once the “easy” emissions have been abated, however, there remains a substantial amount of society’s carbon compounds (and their associated global emissions) that are particularly hard to abate; either because of their high versatility, energy density, or challenges to manufacture them renewably. Examples include aviation fuels and chemicals used for consumer goods (e.g., plastic precursors) and will likely be the emissions abated last. These realities have led to the rise of Power-to-X technologies that use CO₂, H₂O and renewable electricity as feedstocks to create carbon-based compounds with lower cradle-to-grave emissions than fossil fuel routes.

The most advanced Power-to-X technological route is through water electrolysis to produce H₂, with a series

of downstream thermochemical processes coupling H₂ and CO₂ to produce C_xH_yO_z compounds, which may be operated continuously using H₂ and CO₂ storage. An alternate approach for the direct conversion of water and CO₂ into base chemical feedstocks is CO₂ electrolysis, which can create building block molecules such as CO, C₂H₄, ethanol, and acetate. However, CO₂ electrolysis technology has predominantly been investigated in a laboratory environment on scales of ~5 cm² and powers of <10 W, far from the required scale. If CO₂ electrolyzers aim to offset meaningful global emissions, however, they will need to reach sizes like commercial water electrolyzers (~1 m² per cell and 100s of cells per stack) and collectively consume up to thousands of gigawatts (GW) of electricity.^{1,2} As the key CO₂ electrolyzer performance metrics such as selectivity, efficiency, and current densities linked to technoeconomics have improved, research and engineering is now needed to bridge the 10⁹ gap in system size and power between the lab and commercial scales.

A recent article in *Nature Chemical Engineering* by Crandall et al. takes a step in scaling electrochemical CO₂ reduction devices via a kW-scale tandem electrolyzer device.³ The demonstration pairs a 5-cell CO₂ electrolyzer (500 cm² total) producing predomi-

nantly CO, with a 5-cell CO electrolyzer (500 cm² total) connected downstream for the conversion of CO to primarily acetate. The tandem electrolysis system notably operates for 120 h with ~40% Faradaic efficiency for acetate, resulting in the production of a ~100 L of 1.2 M acetate and anolyte mixture. A clear deliberation of the matching flow rates and current density is also provided for the tandem system, showing relatively similar performance for the individual cells, and the small and large combined system. Lastly, the work is supported by a CO₂ feedstock contamination and technoeconomic analysis.

The 10 × 100 cm² system can also be compared to the few other scaled CO₂ and CO electrolyzer stacks reported in literature, which provides context about various means of cell stacking and operation. The latest system, for example, far surpasses the 3 × 20 cm² first demonstrated CO₂ electrolyzer stack⁴ reported in 2018, showing a positive scale-up trend in time. As shown in Figure 1, the 100 cm² cells are similar to a previous non-tandem CO₂ and CO electrolyzer demonstration⁵ (Figure 1A) but operate at a much lower current density and stack power (Figure 1B). Other reports of a 250 cm² single cell,⁶ and details of a 10 × 800 cm² cell-stack⁷ have also been published, but lack the detailed technical and engineering analysis present in the *Nature Chemical Engineering* article. The work then acts as an important piece that others can build off.

There is substantial value and necessity in large-scale demonstrations, motivating

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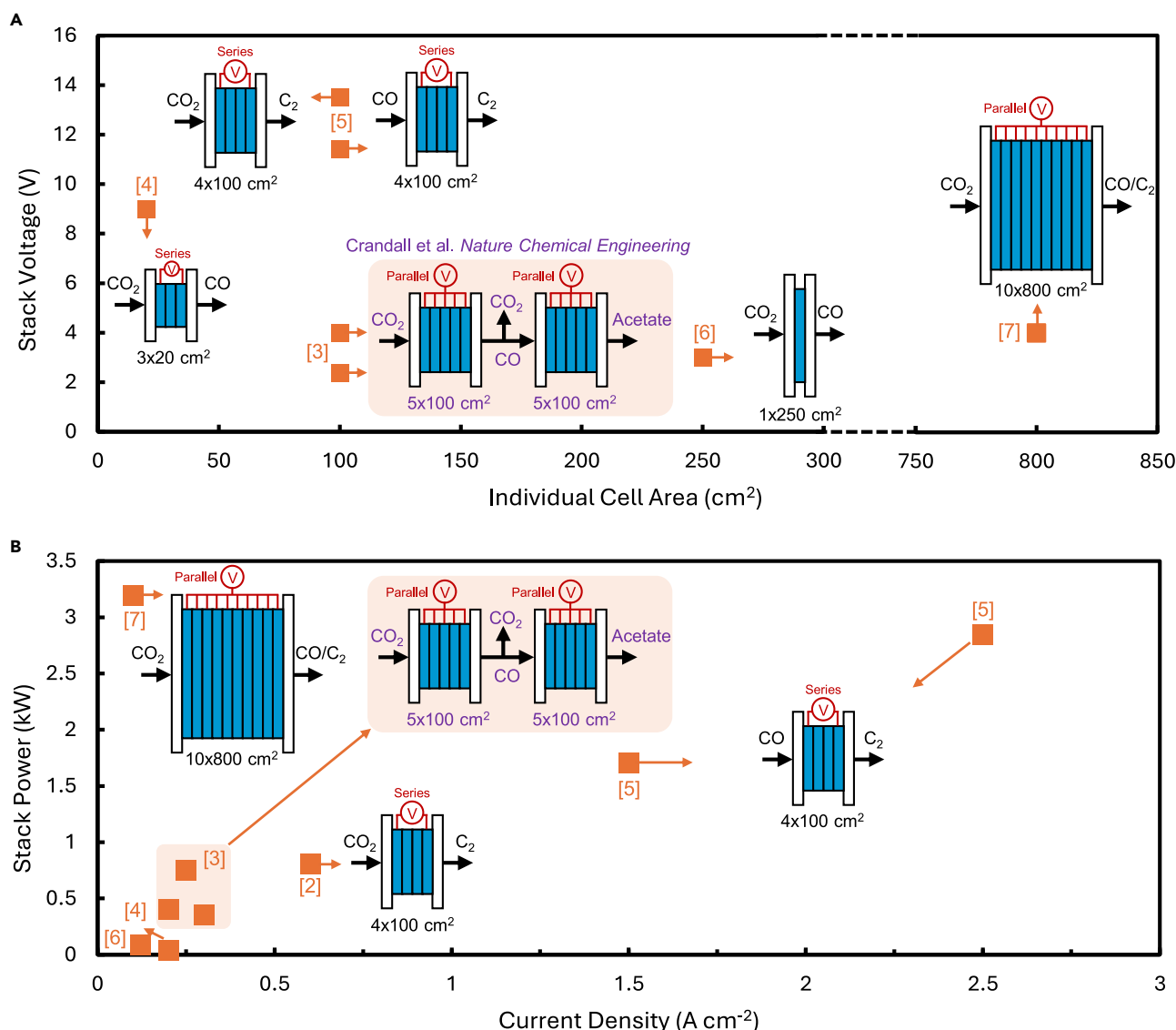


Figure 1. Overview of the largest reported gas-fed CO₂ and CO electrolyzers showing primary products, cell size, cells per stack, and power supply type

(A and B) These electrolyzers are compared by (A) cell area and supplied voltage, and (B) current density versus total stack power.

their continued open publication in literature instead of only in less-visible industrial research. Large platforms, for example, can elucidate aspects such as H₂/product crossover, safety,⁸ purification of product streams, and variable power operation linked to the use of renewables availability. Further research can be done on the potential sweeps as a result of product oxidation or variable power, which may cause catalyst phase transitions or dissolution and enhanced catalytic degradation over time.⁹ The concen-

trations of feeds and reactants may further influence the local (equilibrium) potentials. Lastly, larger cell areas are needed to observe the effects of pressure drops and imbalances because of increased flows, which pose engineering challenges for pressure equilibration and structural integrity.

The authors also directly discuss many challenges that they encountered in scaling up their Watt-scale system to the kilowatt scale. In principle, the

goal of scale-up is simple: increase active areas while maintaining the optimal performance metrics (selectivity, efficiency, rates) of the smaller cell. For many reasons, the authors show that this is easier said than done. Notable engineering considerations discussed by the authors include the need for multi-channel flow field design, powering multiple cells via series or parallel power connections, heat rejection from the electrolyzers, and repeatability of performance

between cells in a stack. Lessons can be learned from the authors' work and are worth discussing further, particularly the concepts of series/parallel power supply and electrolyzer cooling.

Powering multiple cells within an electrolyzer stack can be done by connecting cells in a series electrical circuit (bipolar plates) or in parallel (unipolar plates). When operated in series, a singular current flow through multiple cells leads to a cumulative stack voltage. From a power supply perspective, series operation leads to lower cost because it provides a larger voltage and lower total current. Alternatively, a parallel power supply leads to low voltage and high currents. In this work, each cell is powered in parallel with voltages of ~ 2.5 V, resulting in total stack currents of 300 A. Parallel operation was chosen by the authors to avoid stack failure if a singular cell in the series failed, and likely due to their imposition of cooling channels that would disrupt current transfer between cells via bipolar plates. Two challenges exist with parallel operation, however.

The primary challenge of parallel operation is higher ohmic losses and reaction inhomogeneity versus series operation. As individual cell areas increase, so too does the total current that needs to be distributed over a larger catalyst area. In parallel operation, current flows from a power connector through the side cross-sectional area of a current collector instead of perpendicular to the large current collector in series operation. Current distribution is then dependent on the thickness and conductivity of the current collector (e.g., Ni coated steel with $\sigma = 0.7e7$ S/m). However, thickness will ideally not increase with cell area, meaning that parallel operation will give relatively high ohmic drops when distributing currents throughout a cell. In addition the spatial voltage disparity will influence reaction homo-

geneity, creating challenges with temperature and current distribution and likely spatial product selectivity variations.¹⁰ A secondary challenge of the author's use of parallel channels and fixed current operation is that the current passing through each cell is uncontrolled. Figure 1A illustrates the comparative divide in series versus parallel cell powering in literature to date.

The authors also discuss an important aspect in stack heating due to the provided overpotential going beyond the thermoneutral voltage. Without the addition of cooling channels by the authors, they observed anolyte temperatures quickly rising from ambient temperature to $>50^\circ\text{C}$, which will degrade catalysts faster and potentially the anion exchange membrane. Such observations and data are welcome and further work in this area is highly valuable. Future work can hopefully analyze the energy cost of cooling, and create alternate approaches, such as cooling recirculating electrolyte reservoirs versus individual cells.

A final aspect of interest noted in this work, as well as other scaled CO_2/CO electrolyzer examples in Figure 1, is the apparent challenges of product quantification for larger systems. Many of the works fail to allocate near 100% of the imposed current. Reasons for this could include challenges in measuring the outlet flow rate of the reactor, oxidation of CO_2/CO products at the anode, crossover and reduction of O_2 at the cathode, high water contents and temperatures in the gas streams, or using less accurate analytical techniques due to the higher operating flow rates and pressures. As an important component of device performance metrics and techno-economics, however, it is crucial to know where electrons should be allocated in the system. As scale-up efforts become more common, further

instrumentation engineering is then encouraged.

In summary, the article by Crandall et al. provides a good balance of scale-up demonstrations and engineering discussions about the challenges that larger electrolyzers bring about. Such a different type of article will bring value to the broader electrochemical field and brings a more varied flavor of science and engineering discussion than previous CO_2/CO electrolyzer scale-up articles before it. Before novel Power-to-X technologies will bridge the technological valley of death from academia to industry, many more works like this article are necessary. We encourage the field to further embrace and report nuanced challenges of electrolyzer scale-up and draw on not just the collective experiences from CO_2 electrolyzers but all larger electrolysis systems.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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