Scale-Up of a Gas Diffusion Electrode CO₂ Electrolyzer for Formate Production

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Highlights

- A successful development and construction of a 100 cm² CO₂ electrolyzer prototype
- Preliminary results show formate production of 96 g L⁻¹ at 30 mA cm⁻², with an 83 % of Faradaic Efficiency.
- The findings align with large-scale results, indicating the scalability of the technology

1. Introduction

Among various strategies to mitigate CO_2 emissions from industrial sources, electrochemical conversion and valorization of CO_2 into value-added products emerge as highly efficient and promising alternatives. This process enables the storage of excess energy from renewable sources in CO_2 -reduced products, such as formic acid or formate, methanol, or ethylene. The technology involves an electrochemical reactor where CO_2 is supplied to the cathode. Here, CO_2 molecules undergo transformation over a catalyst surface when an external voltage is applied. Simultaneously, an oxidation reaction occurs at the counter-electrode. Typically, both compartments are separated by an ion exchange membrane, facilitating the separation of reaction products and enhancing overall system efficiency [1].

While CO_2 electroreduction has been extensively studied at the lab scale, with research efforts focused on developing efficient reactor configurations, selective electrocatalysts, various electrode configurations, and evaluating different operating conditions [1], the Technological Readiness Level of the process currently ranges between 3 and 5, indicating a considerable gap from industrial scale-up. Therefore, it is imperative to consolidate prior knowledge to achieve an efficient design and construction of a CO_2 electrolyzer that enables the technology's successful scaling.

This work aims to develop an industrial demonstrator of a CO_2 electrolyzer as the initial step toward fully implementing CO_2 electroreduction to formate on an industrial scale. The prototype's design and testing have been collaboratively undertaken by the DePRO research group, actively involved in advancing CO_2 conversion technology in recent years [1-3], and APRIA Systems, a technology supplier company responsible for constructing the CO_2 electrolyzer.

2. Methods

The electrolyzer comprises various components, i) outer closure plates made of stainless steel, ii) the external reactor structure constructed from polypropylene, iii) internal spacers composed of Viton, and iv) titanium current collectors. In the anode compartment, an iridium mixed oxide plate acts as the counter electrode for the water oxidation reaction. As the cathode, a Gas Diffusion Electrode (GDE) is employed, with an active geometric area of 100 cm². This electrode is fabricated by automated spray pyrolysis, a process that has been previously optimized [2]. The catalytic ink consists of the catalyst (commercial Bi_2O_3) and Vulcan, with a mass ratio of 50:50, suspended in ethanol as a solvent and Nafion D-521 as a binder. This ink is applied over a Teflon-coated (50 %) carbon paper. Finally, a Nafion cation exchange membrane (CEM) separates the cathode and anode compartments.

The electrochemical reactor can operate in two different configurations, i) Liquid-Liquid (L-L), and ii) Liquid-Gas (L-G). In the case of L-L, two aqueous electrolytes are introduced into the reactor, with 1M KOH supplied to the anode, and a CO₂-saturated 0.5 M KCl + 0.45 M KHCO₃ provided to the cathode, both at a flowrate of 0.57 mL min⁻¹ cm⁻². On the other hand, for the L-G configuration, a humified CO₂ pure stream is fed to the cathode compartment with a flow rate of 10 mL min⁻¹ cm⁻². Preliminary tests were carried out in the L-G configuration, supplying a current density of 30 mA cm⁻² to the system.

3. Results and discussion

The final prototype, constructed by APRIA Systems (Figure 1), measures 180x180 mm in total dimensions and can be operated in both L-L and L-G configurations by adjusting the internal system configuration. However, the system has certain limitations related to the operating conditions, the temperature should not exceed 40 °C, and the pressure drop is limited to 1.5 bar. Nonetheless, since CO2 electroreduction is conducted at ambient temperature and pressure, these specifications do not impact the process.

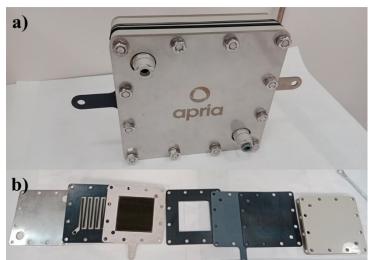


Figure 1. CO₂ electrolyzer prototype, a) L-G assembly, and b) L-G internal configuration

After construction, the prototype underwent testing to evaluate its performance. In this regard, the system operated continuously for 2 hours with a single pass of CO₂ and electrolyte through the system. The applied current density was 30 mA cm⁻², resulting in a cell voltage of 4 V. This led to a formate concentration of 96 g/L, with a Faradic Efficiency of 82.59 %, and an energy consumption of 259 kWh kmol⁻¹. These outcomes align with prior findings within the research group [3], therefore, the system is demonstrated to be scalable. Nevertheless, ongoing efforts are necessary to improve the stability and efficiency of the system, alongside

increasing the current density of operation up to 200 mA cm⁻², which is the targeted level for industrial implementation.

4. Conclusions

The efforts invested in designing and constructing an industrial demonstrator of a CO_2 electrolyzer have yielded a functional prototype with promising results in preliminary tests, showcasing the scalability of CO_2 electroreduction technology. Future work should be dedicated to maximizing the stability and efficiency of the system in long-term operations.

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Keywords

CO₂ electrolyzer, industrial demonstrator, reactor design, formate.