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CO_2 Conversion to Formic Acid in a Three Compartment Cell with Sustainion™ Membranes

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Formic acid generated from CO_2 has been proposed both as a key intermediate renewable chemical feedstock as well as a potential energy storage chemical media for hydrogen. In this paper, we describe a novel three compartment electrochemical cell configuration with the capability of directly producing a pure formic acid product in the concentration range of 5 – 20 wt% at high current densities and Faradaic yields. The electrochemical cell employs a Dioxide Materials Sustainion™ anion membrane, allowing for the improved CO_2 electrochemical reduction performance. Stable electrochemical cell performance for more than 500 hours has been experimentally demonstrated.

Introduction

Developing technologies in reducing CO_2 emissions by converting it into selected economically sustainable chemical and fuel end-products is one key controlling environmental atmospheric CO_2 levels.

Formic acid and CO have been identified as two key chemical intermediate products that can be commercially viable if produced at:

- High commercial current densities (100 mA/cm^2 or greater)
- High Faradaic efficiencies (90%+)
- Low cell potential
- Long operating life (5 years or greater)
- Low CAPEX

Formic acid also has potential applications in energy storage and hydrogen generation as shown in Figure 1.

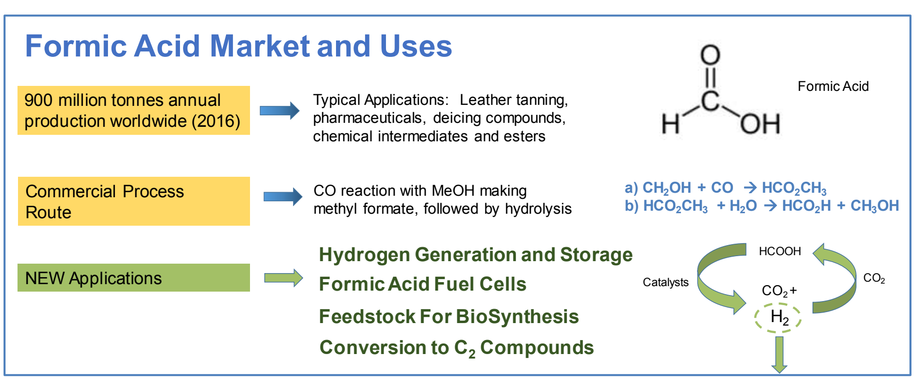

Figure 1. Formic acid market and current and new product applications.

Over the past 30 years, researchers have worked on numerous catalysts and conditions in electrochemically reducing CO_2 to formate/formic acid in the quest for obtaining high conversions to formate at current efficiencies (1-27). The utilization of GDEs helps solve the solubility limit of CO_2 in aqueous systems (33 mM) at ambient temperature and pressure, but their application and testing require these additional items:

- Utilizing GDEs to improve CO_2 mass transport into formate/formic acid
- Preventing GDEs from electrolyte flooding
- Identifying and evaluating best catalysts with the GDEs
- Determining optimum cell configurations in operating the system
- Conducting longer term experimental testing to confirm performance and stability of catalysts and operating system

Cell Design Development

Dioxide Materials has developed key technologies in solving these issues designing a novel 3-compartment cell design employing a recently developed anion membrane (28-36).

- Employing a membrane to prevent cathode GDE flooding
- Development of imidazole-based ionomers that reduce CO_2 reduction overpotentials
- Development of a highly conductive, alkaline stable anion membrane - Sustainion™ membrane
- Selection of GDE cathode electrocatalysts
- Cell design modifications to improve conductivity
- Membrane selection to reduce crossover
- Stability testing, preferably 100 hours and more

The Dioxide Materials 3-compartment cell design is shown in Figure 2. The cell design incorporates a center flow compartment bounded by a cation ion exchange membrane on the anode side and a Sustainion™ anion exchange membrane on the cathode side. The center compartment uses a cation ion exchange resin media to provide compartment electrolyte conductivity. Only DI water is used as the anolyte and flow into the center compartment. Pure formic acid is the product from this cell configuration.

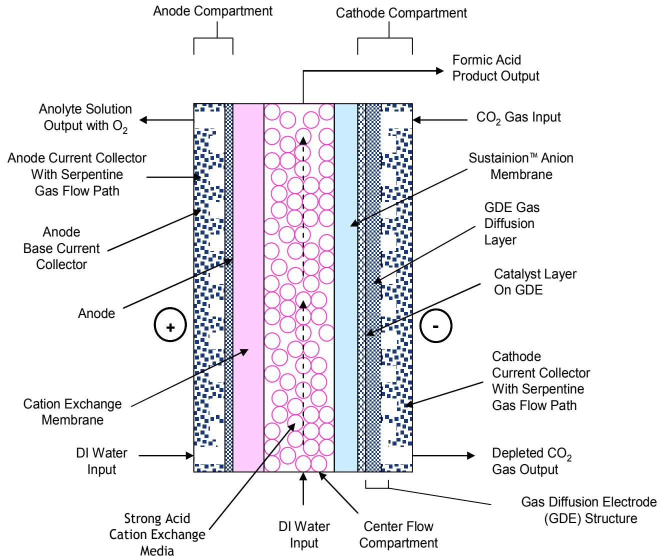

Figure 2. Dioxide Materials 3-compartment formic acid cell design.

Experimental Results

Figure 3 shows the current produced as a function of the cell voltage in a cell with a tin cathode, and IrO_2 anode, and deionized water in the middle compartment with no electrolyte added to the water. Notice that one can obtain up to 200 mA/cm² at reasonable cell voltages.

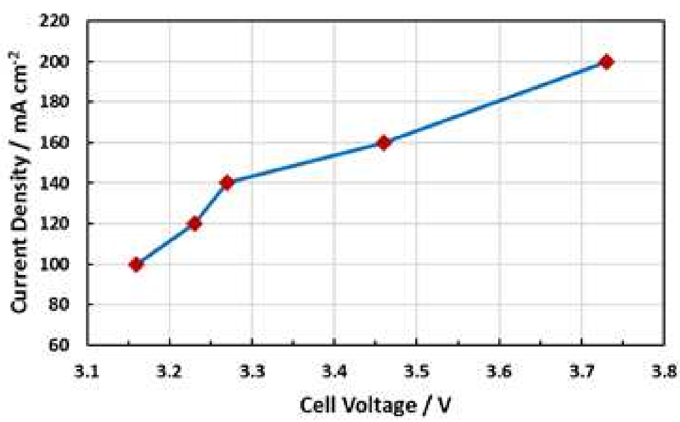

Figure 3. Formic acid cell voltage versus current density plot.

Figure 4 shows how the exit concentration and Faradaic efficiency varies with a single pass flowrate. Experimentally, as the Faradaic efficiency decreases as the formic acid concentration rises. Physically, some of the formic acid is transported to the anode, where it is oxidized leading to formic acid loss. The use of thicker and/or higher MW PSA cation membranes significantly reduces these formate losses.

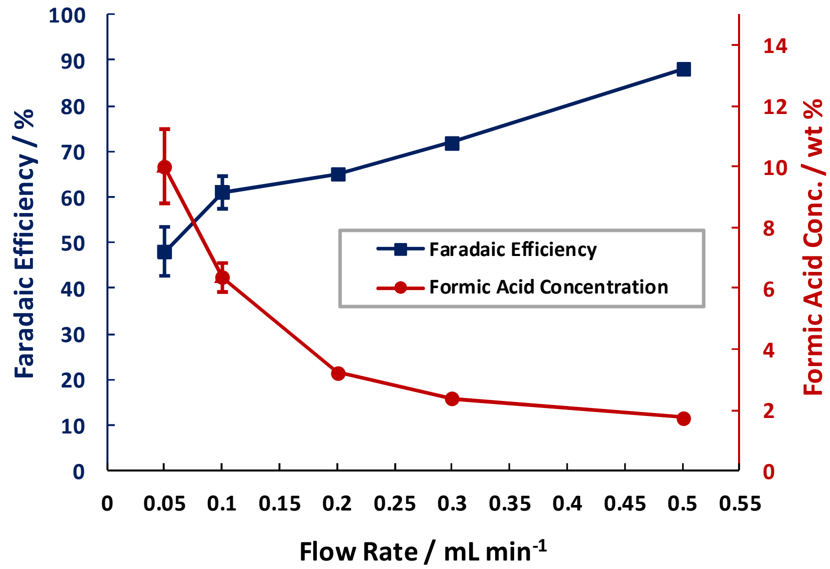

Figure 4. Cell formic acid FE vs formic acid product in wt%. A PSA cation membrane not optimized for minimizing formate ion transport was used in the test runs.

Figure 5 shows a steady state run. In this case, we were able to maintain an output concentration of about 15 wt% formic acid for more than 500 hours, with no significant change in cell voltage.

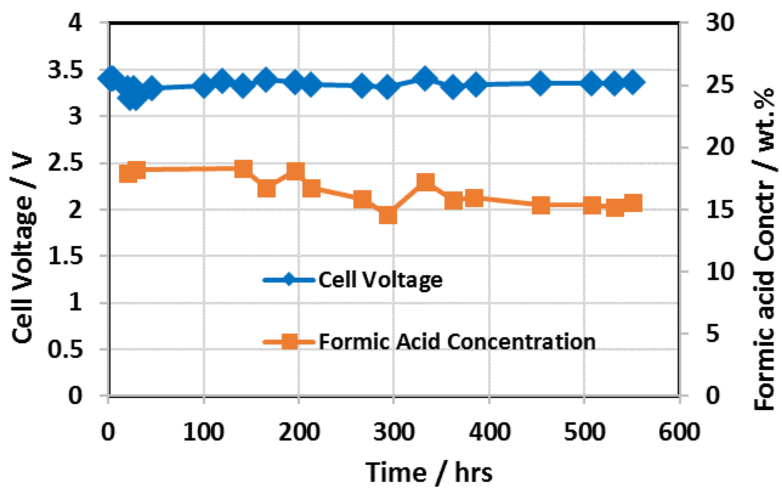

Figure 5. Cell performance during an extended 550 hour test run.

Formate ion crossover transport through the cation ion exchange membrane was found to be the major loss of Faradaic efficiency (FE) in the cell when operating at these high formic acid concentrations. Utilizing a Nafion® 324 membrane, the formate crossover through the membrane was substantially reduced. The formic acid cell FE performance increased dramatically to 94%, producing a 10 wt% formic acid product at a 140 mA/cm^2 current density.

Summary

A novel 3-compartment electrochemical cell design with the capability of generating a high concentration pure formic acid product from the reduction of CO_2 is detailed in this paper. The cell configuration consists of an anode compartment, a center flow compartment containing a cation exchange resin electrolyte bounded by a PFSA cation exchange membrane on the anode side and a proprietary Sustanion™ anion exchange membrane on the cathode side, and employing an imidazole-nanoparticle Sn catalyst-based GDE in the cathode compartment. The electrochemical cell operated at a current density of 140 mA cm^{-2} at a cell voltage of only 3.5 V with formic acid Faradaic efficiencies of up to 94%. High formic acid Faradaic efficiencies were found to be critically dependent on the selection of the cation membrane utilized in the anolyte compartment side of the cell. Nafion® 324 was found to provide the lowest formate/formic acid crossover into the anolyte compartment. The novel formic acid cell design shows a potential route for future commercial use of formic acid as a sustainable chemical feedstock in generating downstream chemicals, as well becoming a viable chemical-based energy storage medium in hydrogen storage/generation.

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