

Technology Development for Large Scale Electrochemical Conversion of CO₂ to Useful Products

Arun S. Agarwal, Yumei Zhai, Davion Hill, Shan Guan, Edward Rode and Narasi Sridhar
Det Norske Veritas (DNV), 5777 Frantz Road, Dublin OH 43017, USA

ABSTRACT

Electrochemical conversion of CO₂, a common green house gas, to value added products such as formic acid, methanol, ethylene and syngas is being increasingly pursued as a means for CO₂ remission. Although extensive research has been carried out on several electrochemical processes, there are very few attempts to develop a viable technology for large scale and continuous CO₂ treatment. Development of the ECFORM (electrochemical conversion of CO₂ to formate/ formic acid) technology focuses on evaluating and improving the various aspects of the process in order to make it economically feasible for commercial application. A multi-level approach has been undertaken to improve catalyst properties, optimize continuous operating conditions and maintain high product generation over long operating times.

Keywords: electrochemical, CO₂ reduction, cathode, formic acid, renewable energy

1 INTRODUCTION

The Electrochemical Conversion of CO₂ to Formate/Formic Acid is schematically shown in Fig. 1. It is a method of CO₂ utilization and recycling where electrical energy is used to convert dissolved CO₂ gas in solution at a catalyst surface to useful products. Such an electrochemical process can be customized to provide a preferred product by selecting suitable electrocatalyst, solutions and applied potential. CO₂ can be converted electrochemically to several products including carbon monoxide (CO), formic acid, oxalic acid, ethylene, methane, dimethyl ether, or methanol. We focus our research here on the production of formic acid for the following reasons:

- Less energy intensive: it requires 2-electrons as opposed to methane which requires 8-electrons, per converted molecule
- High selectivity and efficiency using relatively inexpensive catalysts
- Aqueous electrolytes (as opposed to DME, oxalic acid, etc.)
- Ease of storage with low likelihood of greenhouse gas emission (compared to methane, CO). Formic acid sold as end product or as storage medium for H₂ or CO.

Fig. 1 shows a simplistic configuration for continuous electrochemical reduction of CO₂. It consists of two electrodes, the cathode (negative electrode) and the anode (positive electrode), across which an electrical voltage is applied. The two electrodes are placed in chambers separated by an ion exchange membrane which disallows bulk mixing of the solutions flowing in each of the two chambers while allowing for ions to move across and maintain electrical contact in the solution. As shown, a suitable electrolyte along with CO₂ is introduced in the chamber where it comes into contact with the cathode and the dissolved CO₂ in solution is converted (electrochemically reduced) to the products. This reaction is completed by the complementary oxidation reaction occurring at the anode chamber. In ECFORM, tin or special alloys are used as the cathodes which convert CO₂ to formate salts. Some by-products (Hydrogen and CO) are also produced at the cathode. The oxygen evolution reaction takes place at the anode.

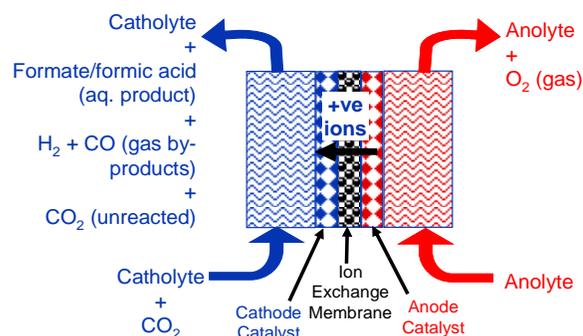


Figure 1: A schematic representation of the electrochemical process to convert CO₂ to formate/formic acid.

2 CATALYST STUDIES

Tin has been employed as a highly selective electrocatalyst for the conversion of aqueous CO₂ to formate salt/formic acid [1, 2]. In this work, novel alloy electrocatalysts are evaluated for performance metrics such as reactivity and equivalent selectivity to tin [3]. This leads to a decrease in overall cell potential required, thus making the process more economically feasible.

3 FULL CELL STUDIES

Size of an electrochemical reactor, and hence its associated costs depend drastically on the reactivity of the electrode. A highly reactive electrode is one that can convert large amount of CO_2 to desired product *per unit area*. For constant selectivity (dependent on catalyst material and electrolyte conditions) the electrode reactivity can be significantly improved by increasing its electrode active area per superficial area. High surface area cathode electrodes employed for CO_2 reduction are obtained by electrodeposition of tin on carbon fiber paper. As indicated in Fig. 4, the carbon fibers are uniformly coated with micron size tin particles, thereby increasing the active electrode area multiple times.

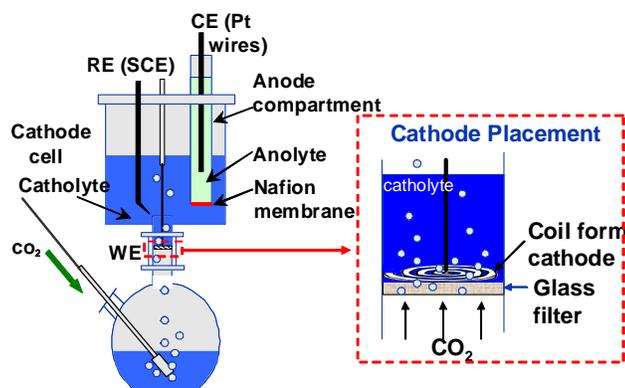


Figure 2: Schematics of the half cell experimental setup for catalyst studies.

A GLS half cell is used to evaluate the electrocatalytic performance of different alloys for CO_2 reduction to formate salts as depicted in Fig. 6. It illustrates the coil form cathode placed on top of a glass filter which acts as a gas distributor. The other side of the cathode was exposed to a suitable catholyte. Pure CO_2 gas was purged from the bottom of the cathode throughout the testing time while the catholyte remained the same (semi-continuous operation). One of the prominent features of this setup is to promote and measure the electrochemical CO_2 reduction at the three specie interface (CO_2 gas – liquid catholyte – solid electrode) where enhancement of mass transfer of dissolved CO_2 should increase the reactivity of the catalyst.

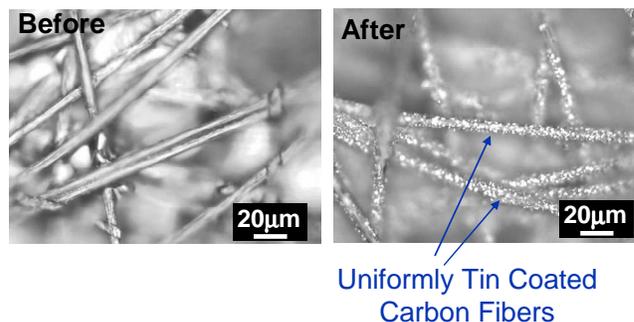


Figure 4: Electrode made by electrodeposition of tin on carbon fiber paper.

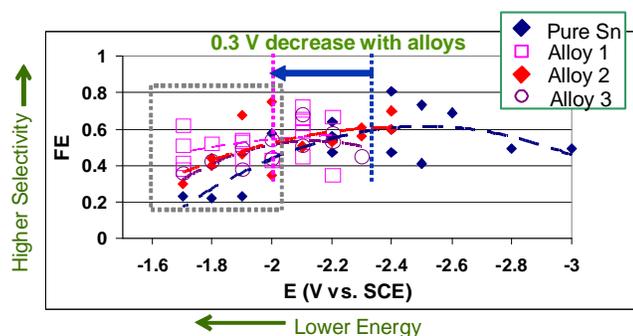


Figure 3: Novel catalyst alloys showed better energy efficiency for ECFORM.

As indicated in Fig. 3, special alloys exhibit the same high selectivity (FE) as pure tin at a lower applied voltage (by about 0.3 V) [3]. This signifies 10 – 20% savings in electrical energy required, thus decreasing operating costs for the process.

Degradation mechanisms of catalysts were evaluated. Pulse polarization techniques were developed to regain the selectivity of the catalyst to increase the operational lifetime without physical replacement of the electrode [3].

The cell and the setup used for testing these electrodes are illustrated in Fig. 5. CO_2 gas, catholyte, and anolyte were fed to the three-chamber cell from the bottom and withdrawn from the top of the reactor. The flow rates of CO_2 gas and liquid catholyte and anolyte in the cell were controlled. The pressures in the three chambers of the reactor were controlled using the back pressure regulators. The gas-liquid mixed outlet streams from catholyte and anolyte compartments were separated in a tank where the gasses are allowed to escape in the hood and the liquid spent electrolytes were collected. The CO_2 gas chamber pressure was always maintained higher than the catholyte flow chamber pressure, to force the gas across the porous electrode to the catholyte and thus decrease mass transfer limitations by maintaining high solubility of CO_2 in the catholyte. The anolyte, catholyte, and CO_2 gas were continuously flowed through the full cell and a constant total potential, V_{CELL} , was applied across the anode and cathode. The current density, which corresponds to the CO_2 electrochemical reduction reaction, was recorded. Periodic liquid catholyte samples were analyzed using Ion Chromatography to obtain formate salt generation.

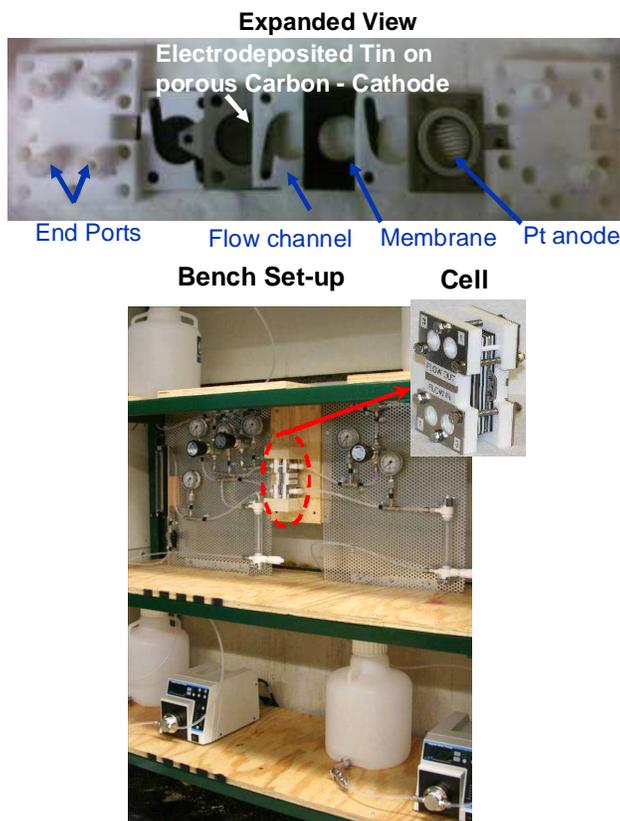


Figure 5: Expanded view of the three chamber cell and cell setup for high surface area electrode experimentation.

The performance of high surface area (HSA), tin electrodeposited electrodes was compared with solid or bulk tin electrodes in the continuous bench cell. While maintaining the same selectivity for formate production ($FE > 60\%$), the HSA electrodes displayed up to 7x increase in reactivity in terms of the rate of formate salt generation (Fig. 6). Efforts are currently underway to further increase electrode reactivity to make the process more economically feasible for commercialization.

Long term stable performance of HSA electrodes was determined by periodic measurement of reactivity (current density) and selectivity (%FE from formate product measurement in catholyte samples) under constant optimum operation. The results indicated stable performance over 4 days. There is also no appreciable damage or degradation of the tin electrodeposited carbon electrode. This is a significant improvement of about 20x over literature reported lifetime [2]. Currently efforts are underway to evaluate performance of ECFORM over longer periods (few months).

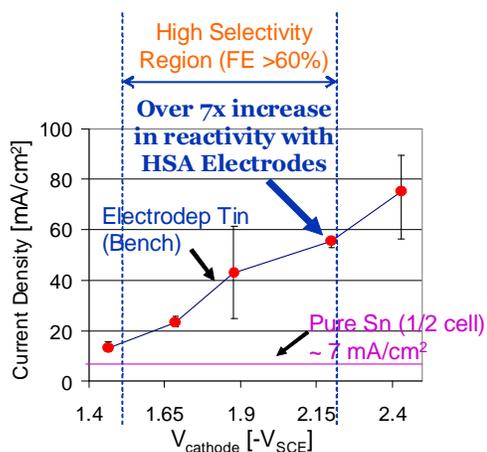


Figure 6: Multiple fold enhancement in reactivity with high surface area electrodes.

4 SOLAR POWERED REACTOR

Industrial electrochemical reactors of similar filter press type configuration have single cell electrode areas of the order of 1 to 2 m². For feasibility analysis, stable single cell operation with high selectivity and reactivity is essential. Favorable hydrodynamics associated with CO₂ gas – solid porous electrode – liquid catholyte, proper electrode fabrication for uniform voltage distribution on the electrode and negligible degradation, as well as stable performance over long periods of time are some of the important criteria for successful commercialization. A 600 cm² electrode size reactor is designed and evaluated in this work. ECFORM employing electrical energy from renewable or non-petroleum sources offers an attractive initiative to supplement its viability as an energy efficient method for CO₂ utilization. Hence, construction of a complete demonstration unit of ECFORM powered by solar trailer is undertaken, as indicated in Fig. 7. This would incorporate the advancements made in catalysis and continuous bench cell experimentation and support in progressing ECFORM technology development from lab scale research to pilot scale.



Figure 7: ECFORM reactor system housed and powered by solar trailer.

5 UTILITY OF PRODUCT/PROCESS

Formate salts are used in deicing of airport runways and in oil well completion fluids. Formate salts can be converted to formic acid by treatment with a strong acid. Formic acid is used in the leather tanning and animal feed markets. However, new uses in terms of hydrogen storage and fuel cells are being developed by BASF and others, providing opportunity for formic acid as a fuel. Formic acid represents a good storage medium for hydrogen gas (50 M ton demand in 2004) and stores as much hydrogen as 580 times the volume of hydrogen gas at STP [4]. The indirect production of hydrogen through CO₂ recycling is attractive because typical steam methane reforming for H₂ uses natural gas and produces twice the CO₂. Formic acid can also be selectively converted to synthesis gas (CO + H₂, in varying compositions) which is used to produce several bulk chemicals such as methanol (38 M ton demand in 2006) and acetic acid (5 M ton in 2005). Alternatively, the process described here can be tuned to produce other products directly, such as CO, syngas, or other fuels, however formic acid and CO command greater market prices with lower energy requirements than these fuels (Fig. 8).

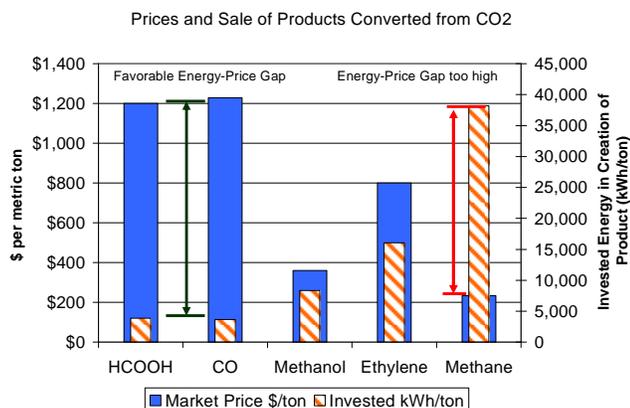


Figure 8: Formic acid and CO require less energy to produce and have higher value than other fuels and feedstock.

Arguments against the viability of CO₂ conversion identify the energy requirements as a barrier to economic viability. What has not been previously explored is viewing CO₂ conversion as an energy storage technology. Products created electrochemically from CO₂ have higher energy densities than modern battery technologies (Fig. 9). In this context, the process is open to electricity markets that are unavailable to conventional petrochemical processes, such as ancillary services, energy arbitrage, and renewables integration. These services can generate revenues as high as \$30/MWh in one- or two-way exchanges with the local transmission operator [5, 6]. Because the process is electrochemical, it marries electricity markets to chemical markets, benefiting from the opportunities offered by both. When integrated with waste heat capture technologies, the

process can be powered renewably with zero carbon output while simultaneously working with grid services. Finally, while more CO₂ would be avoided if renewable energy were directly used on the grid, the variability of renewable power does not lend to matching of supply with demand. Using CO₂ conversion as an energy storage medium for renewables produces up to 10x more value per ton of CO₂ avoided than competing processes such as CCS.

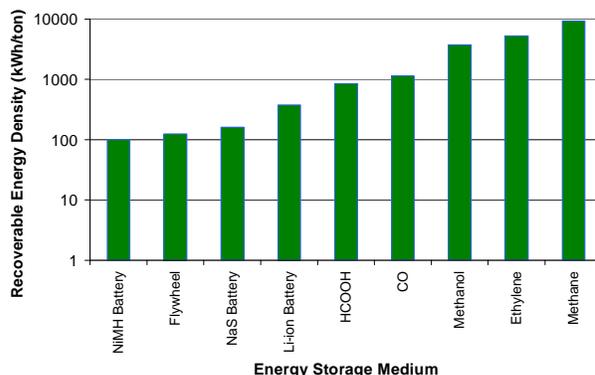


Figure 9: Products produced from CO₂ can have recoverable energy densities higher than traditional electrical energy storage technologies.

6 CONCLUSIONS

The process of electrochemical reduction of CO₂ to formate / formic acid product has been approached at different levels (catalyst development, continuous processing, semi-pilot reactor development) for a comprehensive development of this technology.

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