Integrated Capture and Electrocatalytic Conversion of Carbon Dioxide to Alcohols

November 2019

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Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

The goal of this SEED LDRD project was to perform proof of concept studies that would provide proof of concept data that would demonstrate viability of an R&D approach to develop an innovative, scalable electrochemical technology for synthesis of liquid fuels and chemicals (e.g., ethanol) through coupling of H₂ produced from water splitting and CO₂ captured in solvents from industrial waste streams.
Acknowledgments

This research was supported by the Energy and Environment Directorate Mission Seed, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.
1.0 Research

The project team attempted electrochemical conversion of CO₂ in a capture solvent using a typical sandwich electrolysis cell. The cell uses an iridium oxide coated porous carbon electrode, anion exchange membrane (Fumatech FAA-3) and Ag/C catalyst as anode, electrolyte and cathode, respectively. In our electrolysis cell, the capture solvent with CO₂ loading and 0.2 M NaOH water solution are used as catholyte and anolyte, respectively. A peristaltic pump circulated the catholyte and anolyte to accomplish the electrode reaction at cathode and anode, respectively.

\[
\text{Anode: } 4\text{OH}^- - 1e^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad E^0 = 0.48 \text{ V} \quad (1)
\]

\[
\text{Cathode: } k\text{CO}_2 + a\text{H}_2\text{O} + be^- \rightarrow p + c\text{OH}^- \quad (2)
\]

Table 1. Main products of the CO₂ electrolysis process

<table>
<thead>
<tr>
<th>Product name (P)</th>
<th>k</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>E^0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>-0.1 V</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0 V</td>
</tr>
<tr>
<td>CH₄</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>8</td>
<td>-0.34 V</td>
</tr>
</tbody>
</table>

Initially, the feed gas of humidified CO₂ was flowed into cathode side, the voltage of 3V was maintained when the cell was held at a constant current density of 30 mA/cm², as shown in Fig.1a. The main reduction products of CO₂ electrolysis are hydrogen and CO (Table 2), indicating that Ag/C is a good catalyst for CO₂ reduction. When the feed changes to capture solvent with 2.5 wt% CO₂ loading, the results are shown in Fig. 1b, and the current density for our cell is approximately 75 mA/cm² when the cell was charged at 3V. However, only small amount of CH₄ could be observed through GC analysis, and the main reduction product is hydrogen. The voltage was then jumped up to 3.5 V as increasing the current density to 110 mA/cm². But again, the main reduction product is still hydrogen, and only small amount of CO and CH₄ could be detected through GC analysis on gas samples.
Figure 1. The cell's electrochemical testing with the feed gas of humidified CO₂ (a) and capture solvent with 2.5 wt% CO₂ loading (b) at various current densities at room temperature. Electrolyte flow rate: 20mL/min.

Table 2: The electrolysis cell test conditions and reduction products

<table>
<thead>
<tr>
<th>Condition</th>
<th>Applied voltage (V)</th>
<th>Current (mA/cm²)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidified CO₂ (CO₂ flow through water at RT) Flow rate (20 ml/min)</td>
<td>3</td>
<td>30</td>
<td>26.8% H₂, 5.1% CO and 66% CO₂</td>
</tr>
<tr>
<td>Liquid (2.5 CO₂ wt%) Flow rate (20 ml/min)</td>
<td>3</td>
<td>75</td>
<td>99.2% H₂, no detectable amount of CO, 0.1% CH₄ and 0.7% CO₂</td>
</tr>
<tr>
<td>Liquid (2.5 CO₂ wt%) Flow rate (20 ml/min)</td>
<td>3.5</td>
<td>110</td>
<td>59.5% H₂, &lt;0.1% CO, &lt;0.1% CH₄ and 0.4% CO₂</td>
</tr>
</tbody>
</table>
2.0 Summary

In summary, the CO₂ electrolysis test using capture solvent was performed and CH₄ is being produced, albeit at a very slow rate. This SEED project indicates that CO₂ could be electrochemically reduced in a carbon capture solvent, however, the electro-reduction rate of CO₂ is still quite low and the test conditions (CO₂ loading, operation temperature, and various catalyst, et. al) would need to be optimized to improve the electrochemical performance of CO₂ electrolysis in a working process. The project team will use these results in a proposal for CO₂ utilization to The Fossil Energy Office at DOE in FY20.
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