Electrochemical Conversion of CO₂ on Cu Electrodes

Kendra P. Kuhl, Jakob Kibsgaard, Etosha Cave, and Thomas F. Jaramillo

Department of Chemical Engineering, 283 Keck Sciences Building, Stanford University, Stanford CA 94305 USA

Introduction

The conversion of CO₂ to fuel using renewable power would be a convenient source of carbon neutral energy. Unfortunately, the reaction requires a high overpotential making it inefficient and a variety of products are formed including H₂.

In order to increase reaction efficiency and selectivity, new catalysts are needed. This requires a robust method for studying the products formed in the course of the reaction and the potentials necessary to form them on new materials.

We report here our progress towards such a method and a number of experimental factors that affect the results of the measurement.

Electrolysis

Assembly of Electrochemical Cell:
- Copper working electrode
- Platinum counter electrode
- Silver/silver chloride reference electrode
- 0.1 M potassium bicarbonate electrolyte
- CO₂ gas purge at known flow rate

Electrochemistry:
- Determination of cell resistance using impedance spectroscopy
- Application of constant current or potential

Effect of Surface Preparation

A different distribution of products occurs when using an electropolished Cu electrode versus an electrode that has only been polished with sand paper, demonstrating the effect of electrode surface morphology on the product distribution.

Mechanically Polished

Electropolished

Effect of CO₂ Flow Rate

Ineffective transfer of CO₂ to the electrode can constrain the amount of CO₂ reduced. To determine if mass transport of CO₂ was limiting the reaction, the flow rate through the electrolysis cell was varied and the products measured.

The results show that at a 5 SCCM flow rate, there is more hydrogen and fewer carbon containing products than at higher flow rates indicating mass transfer limitations at lower flow rate. However, the products are roughly the same at 20 and 50 SCCM suggesting that the reaction is limited kinetically in this regime.

Product Detection:
Effluent gas sampled every 15 mins and product concentrations determined by gas chromatography

Calculation of Current Efficiency:

\[ \text{Current Efficiency} = \frac{\text{mols/mL} \times \# \text{e's} \times 96485 \text{C/mol}}{\text{Amps} \times \text{sec/mL}} \]

Effect of CO₂ Flow Rate

Electrolysis experiments can be run in two ways: 1) by holding the potential constant or 2) by holding the current constant. Holding the potential constant allows for the current to change, making current efficiency calculation more difficult. Holding the current constant allows for the potential to fluctuate between higher and lower energy where different products may be formed.

Conclusion and Outlook

We are developing a method to quantify the reaction products of electrochemical CO₂ conversion with novel catalysts. Using the well studied copper electrode we have identified multiple factors which impact the reaction.

So far our efforts have focused on gaseous products. The next step will be to identify solution phase products which is complicated by their low concentration in the electrolyte and the inability of standard gas chromatograph detectors to detect some products, such as formic acid.

One day, electrochemical CO₂ conversion could be an important source of carbon neutral fuels. Further study is needed to find catalysts which produce products selectively and efficiently to allow for it's widespread use.

Acknowledgements and Funding

KPK acknowledges support through the GRFP of the NSF and GCEP. JK acknowledges support from the Villum Kann Rasmussen Foundation, Denmark. E.C. acknowledges support from the GRFP of the NSF. Thanks to David Abram for help with mass flow controller setup and to the rest of the Jaramillo Lab for helpful discussions.

References

Electrochemical Conversion of CO₂ on Cu Electrodes

Kendra P. Kuhl, Jakob Kibsgaard, Etosha Cave, and Thomas F. Jaramillo

Department of Chemical Engineering, 283 Keck Sciences Building, Stanford University, Stanford CA 94305 USA

Introduction

The conversion of CO₂ to fuel using renewable power would be a convenient source of carbon neutral energy. Unfortunately, the reaction requires a high overpotential making it inefficient and a variety of products are formed including H₂.

In order to increase reaction efficiency and selectivity, new catalysts are needed. This requires a robust method for studying the products formed in the course of the reaction and the potentials necessary to form them on new materials.

We report here our progress towards such a method and a number of experimental factors that affect the results of the measurement.

Electrolysis

Assembly of Electrochemical Cell:
- Copper working electrode
- Platinum counter electrode
- Silver/silver chloride reference electrode
- 0.1 M potassium bicarbonate electrolyte
- CO₂ gas purge at known flow rate

Application of constant current or potential

Electrochemistry:
- Determination of cell resistance using impedance spectroscopy

Effect of Surface Preparation

A different distribution of products occurs when using an electropolished Cu electrode versus an electrode that has only been polished with sand paper, demonstrating the effect of electrode surface morphology on the product distribution.

Effect of CO₂ Flow Rate

Ineffective transfer of CO₂ to the electrode can constrain the amount of CO₂ reduced. To determine if mass transport of CO₂ was limiting the reaction, the flow rate through the electrolysis cell was varied and the products measured.

Electrolysis experiments can be run in two ways: 1) by holding the potential constant or 2) by holding the current constant. Holding the potential constant allows for the current to change, making current efficiency more difficult. Holding the current constant allows for the potential to fluctuate between higher and lower energy where different products may be formed.

Conclusion and Outlook

We are developing a method to quantify the reaction products of electrochemical CO₂ conversion with novel catalysts. Using the well studied copper electrode we have identified multiple factors which impact the reaction.

So far our efforts have focused on gaseous products. The next step will be to identify solution phase products which is complicated by their low concentration in the electrolyte and the inability of standard gas chromatograph detectors to detect some products, such as formic acid.

One day, electrochemical CO₂ conversion could be an important source of carbon neutral fuels. Further study is needed to find catalysts which produce products selectively and efficiently to allow for its widespread use.

Acknowledgements and Funding

K.P.K. acknowledges support through the GRFP of the NSF and GCEP.
J.K. acknowledges support from the Villum Kann Rasmussen Foundation, Denmark.
E.C. acknowledges support from the GRFP of the NSF.
Thanks to David Abram for help with mass flow controller setup and to the rest of the Jaramillo Lab for helpful discussions.

References