

Selective Solar-Driven Reduction of CO₂ to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell

Emily E. Barton, David M. Rampulla, and Andrew B. Bocarsly*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received October 3, 2007; E-mail: bocarsly@princeton.edu

One potential approach to reducing atmospheric CO₂ linked to global climate change is the trapping and subsequent photoinduced conversion to a value-added product without the use of additional CO₂ generating power sources.¹ This approach is referred to as “chemical carbon mitigation”, and a potentially useful product is methanol, an important bulk chemical. Although many electrochemical investigations of CO₂ reduction have been undertaken, to the best of our knowledge, there are no reports of CO₂ reduction selectively to methanol in an aqueous photoelectrochemical cell occurring at potentials where light energy is the only energy used to drive the reaction. Here, we report the aqueous reduction of CO₂ to methanol at a p-type semiconductor driven by radiation found in the solar spectrum.

While many attempts at the photoreduction of CO₂ to 2e⁻ reduced species such as CO and formic acid have been described in the literature, few attempts at the kinetically limited 6e⁻ aqueous photoreduction of CO₂ to methanol have been described, and all either do not produce methanol in useful yields or do not actually convert light to chemical energy. Homogenous photosensitizer systems with metal cocatalysts and semiconductor colloids have been observed to produce only CO and formic acid.^{2–6} Semiconductor powders have shown catalytic activity for the production of formic acid, formaldehyde, and methanol, but the reported data do not indicate either system stability or efficient light energy conversion.^{7–11} The use of semiconductor electrodes alone, that is, without cocatalysts, such as illuminated p-GaP^{12,13} and p-GaAs¹⁴ as well as n-type GaAs¹² (in the dark), has also been examined. These materials have shown the highest selectivity for the production of methanol but only at exceptionally high overpotentials. Though not directly related to the work presented here, good faradaic efficiencies for the photoelectrochemical conversion of CO₂ to CO have also been reported when nonaqueous electrolytes were employed, but again, high overpotentials were required to obtain these results.¹⁵ Good selectivity has also been observed at a catalyzed p-InP photoelectrochemical cell for the production of formic acid.¹⁶

We have previously reported on a system containing a soluble pyridinium component at hydrogenated Pd electrodes for the reduction of CO₂ to methanol.¹⁷ We have recently found that we can export this chemistry to a p-GaP semiconductor to reduce CO₂ to methanol with near 100% faradaic efficiency at underpotentials greater than 300 mV below the standard potential of -0.52 V vs SCE at our system pH of 5.2. Figure 1a shows the voltammetric response of an illuminated p-GaP electrode in the presence of 10 mM pyridine under argon or CO₂ at constant pH of 5.2. An enhancement in current^{18,19} is observed under CO₂, which is suggestive of a catalytic interaction between CO₂ and pyridinium.¹⁷ The flatband potential was determined to be 0.22 ± 0.01 V vs SCE in the presence and absence of pyridine from measurements of the open circuit photovoltage. All results reported here were obtained negative of this potential with the semiconductor band-bending in

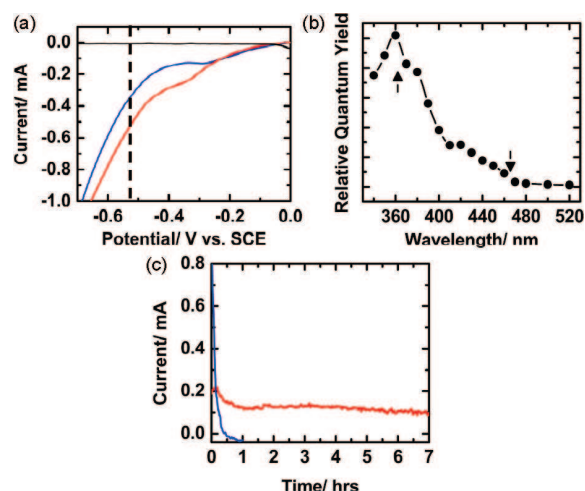


Figure 1. (a) *I*–*V* curves at illuminated p-GaP (Hg–Xe lamp 200 W), 0.1 M acetate buffer containing 10 mM pyridine maintained at pH 5.2 (black line) dark, (blue line) under Ar; (red line) under CO₂, dashed line shows the standard potential for CO₂ reduction to methanol at pH 5.2, radiant energy is solely used at potentials more positive than the line while electrical energy drives the reaction at potentials more negative than the line. (b) Photoaction spectrum of p-GaP in our system held at -0.4 V vs SCE showing the wavelengths chosen for quantum yield measurements. (c) Time response for potentiostatic reduction of CO₂ at -0.4 V vs SCE at pH 5.2 both (blue line) without pyridine and with (red line) pyridine.

depletion. Initial studies of the reduction of CO₂ using a p-GaP electrode illuminated by a 200 W Hg–Xe arc light source showed no production of methanol at the same pH without the presence of pyridinium. The photocurrent was also seen to drop off drastically in <10 min to a negligible value in the absence of pyridinium, as seen in Figure 1c. However, in the presence of pyridinium, CO₂ was observed by gas chromatographic and mass spectral analysis to be reduced to methanol at -0.4 V vs SCE with faradaic efficiencies ranging from 88 to 100%. Formaldehyde and formic acid were not detected (analyzed by the chromatropic acid method).²⁰ At greater than 100 mV below the standard potential, the reaction was driven by radiant light. The initial photocurrent was observed to stabilize within an hour and stay steady during experiments ranging from 6 to 30 h. A 7 h run is shown in Figure 1c. Similar studies utilizing a high pressure arc source with the p-GaP electrode held at a more negative potential (-0.5 V vs SCE) led to decreased faradaic efficiencies for the production of methanol of 22–25%. At the higher photocurrents observed at -0.5 V vs SCE, gas was seen to evolve at the electrode surface. Therefore, it appears that at potentials negative of the standard redox potential for CO₂ reduction this process competes in an unfavorable manner with the reduction of protons to H₂. At the operational pH of 5.2, however, our system did prove to be stable as methanol production was observed to be linear with charge passed ranging from 3 to 10

Table 1. Optical Conversion of CO₂ to Methanol

| <i>E</i> (V) ^a | under potential ^a (mV) | <i>J</i> (mA/cm ²) | faradaic eff. CH ₃ OH ξ (%) | quantum yield Φ _{e⁻} (%) | quantum eff. CH ₃ OH ^b Φ _{MeOH} (%) | OCE ^c η (%) |
|---------------------------|-----------------------------------|--------------------------------|--|--|--|------------------------|
| | | | 465 nm | | | |
| -0.70 | | 1.1 | 56 | (8.3) ^d | (4.6) ^d | (1.3) ^d |
| -0.60 | | 1.0 | 51 | (5.1) ^d | (2.6) ^d | (1.3) ^d |
| -0.50 | 20 | 0.46 | 78 | 3.4 | 2.6 ₅ | 1.0 ₅ |
| -0.40 | 120 | 0.33 | 83 | 2.3 | 1.9 | 1.0 ₃ |
| -0.30 | 220 | 0.27 | 90 | 1.6 | 1.3 ₅ | 0.84 |
| | | | 365 nm | | | |
| -0.50 | 20 | 0.92 | 62 | 71 | 44 | 10.9 |
| -0.40 | 120 | 0.48 | 89 | 38 | 34 | 8.9 |
| -0.30 | 220 | 0.28 | 92 | 16 | 15 | 5.8 |
| -0.25 | 270 | 0.21 | 96 | 12 | 11.5 | 4.6 ₅ |
| -0.20 | 320 | 0.21 | 96 | 13 | 12.5 | 4.8 |

^a All potentials referenced versus SCE. Underpotentials stated are versus the standard potential of -0.52 V for the reduction of CO₂ to methanol at pH 5.2. ^b As defined by eq 1 to be (mol methanol × 6)/mol photons. ^c As defined by eq 4 to be (chemical power out - electrical power in)/light power in. ^d These values were obtained at an overpotential, and thus external electrical power was also used.

C. The pyridine concentration was also observed to be invariant over the time of the experiments, indicating that it is not consumed by the methanol formation reaction.

Figure 1b shows the photoaction spectrum for p-GaP in our system held at -0.4 V vs SCE. With an indirect bandgap of 2.24 eV, the expected utilization of light should include wavelengths shorter than ~550 nm. A measurable photocurrent was observed at wavelengths lower than ~530 nm, which is consistent with the indirect bandgap. The sharp rise in photocurrent observed at 440 nm is indicative of the onset of the lowest energy direct band gap (2.8 eV). In order to examine the detailed photoresponse of the system, two accessible wavelengths were selected, 465 nm (indirect transition) and 365 nm (direct transition), for photoelectrochemical evaluation.

Table 1 lists the quantum yields for the photogeneration of electrons (Φ_{e⁻}) and the quantum efficiencies (Φ_{MeOH}) for production of methanol at the chosen wavelengths. Quantum efficiency¹⁰ as defined by the following equation

$$\text{quantum efficiency } (\Phi_{\text{MeOH}}) = \frac{(\text{mol MeOH} \times 6)/\text{mol incident photons}}{\quad} \quad (1)$$

measures the net yield of the six electron process associated with the reduction of one CO₂ molecule to methanol. The highest values of Φ_{e⁻} and Φ_{MeOH} were observed to be 71 and 44%, respectively at -0.5 V vs SCE and under 365 nm illumination. These values were observed at essentially zero overpotential, that is, at a potential approaching the short circuit potential for the iR compensated cell. To the best of our knowledge, this is the highest reported quantum efficiency for methanol production.

Optical conversion efficiency, η, defined as the ratio of power output to incident light power is a well-established parameter for the quantification of the optical response of a semiconductor junction.^{13,21,22} This parameter has traditionally been utilized as a measure of the efficacy with which semiconductor-electrolyte interfaces convert light energy to chemically stored energy using an adaptation initially suggested by Nozik:²¹

$$\eta = \frac{[\text{chemical power}] - [\text{parasitic losses}]}{\text{light intensity}} \times 100\% \quad (2)$$

where Nozik proposed that "chemical power" be defined as the per molecule enthalpy of combustion of the photogenerated fuel normalized to the stoichiometric number electrons (*n'*) associated

Table 2. Comparison to Literature: Conversion of CO₂ to Methanol at Various Electrode Materials

| ref | electrode | <i>E</i> (V vs SCE) | faradaic eff. ξ (%) | reported OCE ^a (%) |
|---------------------------------|------------------------------------|---------------------|---------------------|-------------------------------|
| <i>Semiconductor electrodes</i> | | | | |
| 13 | p-GaP | -1.4 | ~3 | 3.6 (<0) ^b |
| | | -1.4 | 60 | - (<0) ^b |
| 14 | p-GaAs | -1.3 | 55 | - ^c |
| | p-InP | -1.3 | 70 | - ^c |
| | n-GaAs | -1.3 | 100 | dark |
| <i>Metal electrodes</i> | | | | |
| 31 | Cu/Cd | -1.75 | 5 | |
| 26 | Cu | -1.1 | 40 | |
| 27 | Ru/Cu | -0.8 | 40 | |
| 25 | Ru | -0.54 | 42 | |
| 24 | RuO ₂ /TiO ₂ | -0.95 | 30 | |
| 29 | Cu/PdH | -1.6 | 15 | |
| 28 | RuO ₂ /TiO ₂ | -0.8 | 60 | |

^a Optical conversion efficiency values reported in the reference. ^b Values calculated based on information given in the reference. Earlier forms of eq 3 neglected to include ξ (faradaic efficiency for methanol) which is corrected for here. ^c Information on incident light intensity not given.

with the oxidation of the fuel × the rate of photoelectrochemical fuel formation expressed as a current.²³ The parasitic loss is supplied as the nonphotochemical current—voltage power utilized by the cell or, in other words, the product of the current and the overpotential represented as a bias voltage (*V_B*). Thus, eq 2 becomes

$$\eta = \frac{\left[i' \left(\frac{\Delta H}{n'} \right) - [i \times V_B] \right]}{I_{hv}} \times 100\% \quad (3)$$

where *I_{hv}* is the incident light intensity, Δ*H* is the enthalpy of fuel combustion expressed in units of eV/coulomb (7.259 eV in the case of methanol combustion), *n'* is the number of electrons required to oxidize the fuel completely to carbon dioxide and water (6 in the case of methanol), *V_B* is the bias or overpotential of the cell, *i* is the total current observed at potential *V_B*, and *i'* is the current at potential *V_B* that is associated with the formation of product (fuel) molecules. Note that in general *i* ≠ *i'*. These two currents are only equal when the faradaic efficiency for generating product is 1. Equation 3 can be rewritten as

$$\eta = \frac{i \left[\xi \left(\frac{\Delta H}{n'} \right) - V_B \right]}{I_{hv}} \times 100\% \quad (4)$$

where *i* is the total observed current, and ξ is the faradaic efficiency so that the product (*iξ*) is the fraction of current that produces the fuel of interest. Unfortunately, the need to apportion the current has often been ignored in the literature reporting on systems that are proposed to photoelectrochemically form methanol.¹³ Thus, as reported in Table 2, reports have directly equated *i* and *i'* while explicitly stating that ξ ≪ 1. In Table 2, a corrected η has been calculated for cases where this error has been made. With this correction, the data in Tables 1 and 2 demonstrate the unique response of the photoelectrochemical cell reported in this work. The incorporation of an electroactive pyridinium component produces for the first time a cell that converts CO₂ to methanol using light energy.

The analysis provided here is supported by the potentials reported in Table 2. Note, that prior studies indicate that it is possible to reductively produce methanol using metal electrodes at potentials well positive of those required for the prior reported photoelectrochemical production of methanol. Anytime a process can be carried out at a metal electrode employing an overpotential that is lower

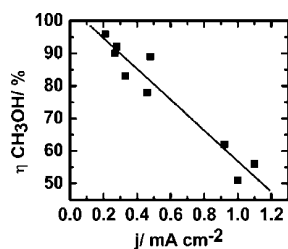


Figure 2. Relationship of increasing methanol yield with decreasing current density from data given in Table 1, indicating a kinetic limitation of methanol formation.

than needed at a photoelectrode, it can be unambiguously concluded that the photoelectrochemical process is not converting light energy to chemical energy.

A key feature of our system is the high faradaic efficiency (ξ) observed for methanol, indicating the selectivity of the process. Selectivity and efficiency for the reduction of CO₂ to methanol is extremely difficult due to similarity in reduction potentials for methanol, formic acid, formaldehyde, and hydrogen. Few metal electrode-based^{24–31} systems have shown selectivity for methanol and only n- and p-GaAs^{14,32} and p-InP¹⁴ semiconductor electrodes have yielded high faradaic efficiencies, though all these systems operated at extreme overpotentials as highlighted in Table 2. In contrast, here we operate at an underpotential to yield 100% faradaic efficiency, thus only using light energy and no external energy input. Table 1 and Figure 2 also show that faradaic efficiency (ξ) for methanol generally increased as the potential was lowered, indicating a reaction limited rate. Frese similarly observed that faradaic efficiency for methanol increased as the current density was reduced at a dark n-GaAs electrode due to competing H₂ evolution in conjunction with CO₂ reduction.³²

Here we presented the efficient and selective reduction of CO₂ to methanol by utilizing light energy at a p-type semiconductor electrode. Current efforts are focused on smaller bandgap semiconductors to effectively use more of the solar spectrum and methods to convert CO₂ to methanol with no external electrical energy. Mechanistic studies are underway to determine whether CO₂ reacts directly at the electrode surface via a pyridinium-mediated process or reacts in solution to reversibly form an electroactive carbamate that undergoes reduction. Preliminary results point to a carbamate as the catalytic species leading to reduction of CO₂ to methanol, with evidence of possible hydride transfer from the pyridinium ring to CO₂.

Early work on optimization of the cell has produced sustained cathodic currents as high as ~ 0.20 mA/cm² in our system at an illuminated p-GaP electrode with no applied bias. Estimates which assume that the electroactive species is a carbamate moiety show that the maximum limiting current density that can be achieved under no kinetic limitations is on the order of 5 mA/cm². Thus, we are encouraged by the current densities that we have observed under

no applied bias that highly efficient solar driven CO₂ to methanol conversion can be obtained.

Acknowledgment. E.E.B. gratefully acknowledges the National Science Foundation for support under a Graduate Research Fellowship. Financial support was provided by the National Science Foundation (Grant CHE-0616475). We thank Prof. Stefan Bernhard for help with quantum yield determinations.

Supporting Information Available: Experimental procedures, gas chromatographs, and NMR spectra of sample solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Ritter, S. K. *C&E News* **2007**, *85*, 11–17.
- Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. J. *Phys. Chem.* **1990**, *94*, 7957–7960.
- Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. J. *Chem. Soc., Dalton Trans.* **1987**, 2105–2109.
- Lehn, J. M.; Ziesel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701–704.
- Henglein, A.; Gutierrez, M.; Fischer, C. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 170–175.
- Inoue, H.; Torimoto, T.; Sakata, T.; Mori, H.; Yoneyama, H. *Chem. Lett.* **1990**, 1483–1486.
- Eggins, B. R.; Irvine, J. T. S.; Murphy, E. P.; Grimshaw, J. J. *Chem. Soc., Chem. Commun.* **1988**, 1123–1124.
- Halmann, M. *Energy resources through photochemistry and catalysis*; Academic Press: New York, 1983.
- Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, *277*, 637–638.
- Kuwabata, S.; Nishida, K.; Tsuda, R.; Inoue, H.; Yoneyama, H. *J. Electrochem. Soc.* **1994**, *141*, 1498–1503.
- Yamamura, S.; Kojima, H.; Iyoda, J.; Kawi, W. *J. Electroanal. Chem.* **1988**, *247*, 333–337.
- Aurian-Blajeni, B.; Halmann, M.; Manassen, J. *Sol. Energy Mater.* **1983**, *8*, 425–440.
- Halmann, M. *Nature* **1978**, *275*, 115–116.
- Canfield, D.; Frese, K. W. *J. Electrochem. Soc.* **1983**, *130*, 1772–1773.
- Hirota, K.; Tryk, D. A.; Yamamoto, T.; Hashimoto, K.; Okawa, M.; Fujishima, A. *J. Phys. Chem. B* **1998**, *102*, 9834–9843.
- Parkinson, B.; Weaver, P. *Nature* **1984**, *309*, 148–149.
- Seshadri, G.; Lin, C.; Bocarsly, A. B. *J. Electroanal. Chem.* **1994**, *372*, 145–150.
- Cheng, S. C.; Blaine, C. A.; Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1996**, *35*, 7704–7708.
- Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Bhadbhade, M. M.; Suresh, E.; Ramachandriah, G. *Inorg. Chem.* **1998**, *37*, 5733–5742.
- Grant, W. M. *Anal. Chem.* **1948**, *20*, 267–269.
- Nozik, A. *Nature* **1975**, *257*, 383–386.
- Tomkiewicz, M.; Woodall, J. *Science* **1977**, *196*, 990–991.
- This description of the power content of a fuel is physically unrealistic since it ignores the large entropic losses associated with the combustion, thereby inflating the η values. However, since this analysis has been generally applied, it is used here so that a comparison can be made with other methanol generating electrochemical cells.
- Bandi, A.; Kuhne, H. M. *J. Electrochem. Soc.* **1992**, *139*, 1605–1610.
- Frese, K. W.; Leach, S. *J. Electrochem. Soc.* **1985**, *132*, 259–260.
- Li, J. W.; Prentice, G. *J. Electrochem. Soc.* **1997**, *144*, 4284–4288.
- Popic, J. P.; Avramovic, M. L.; Vukovic, N. B. *J. Electroanal. Chem.* **1997**, *421*, 105–110.
- Qu, J. P.; Zhang, X. G.; Wang, Y. G.; Xie, C. X. *Electrochim. Acta* **2005**, *50*, 3576–3580.
- Ohkawa, K.; Noguchi, Y.; Nakayama, S.; Hashimoto, K.; Fujishima, A. *J. Electroanal. Chem.* **1994**, *367*, 165–173.
- Schwartz, M.; Cook, R.; Kehoe, V.; MacDuff, R.; Patel, J.; Sammells, A. *J. Electrochem. Soc.* **1993**, *140*, 614–618.
- Watanabe, M.; Shibata, M.; Kato, A.; Azuma, M.; Sakata, T. *J. Electrochem. Soc.* **1991**, *138*, 3382–3389.
- Frese, K. W.; Canfield, D. *J. Electrochem. Soc.* **1984**, *131*, 2518–2522.

JA0776327