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PERSPECTIVE

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Prospects of CO_2 Utilization via Direct Heterogeneous Electrochemical Reduction

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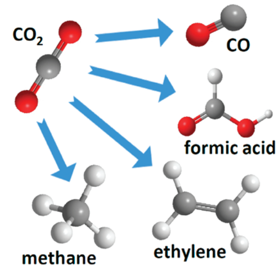
ABSTRACT This Perspective highlights recent efforts and opportunities in the heterogeneous electrochemical conversion of carbon dioxide to help address the global issues of climate change and sustainable energy production. Recent research has shown that the electrochemical reduction of CO_2 can produce a variety of organic compounds such as formic acid, carbon monoxide, methane, and ethylene with high current efficiency. These products can be used as feedstocks for chemical synthesis or converted into hydrocarbon fuels. This process is of interest (i) for the recycling of CO_2 as an energy carrier, thereby reducing its accumulation in the atmosphere, (ii) for the production of renewable hydrocarbon fuels from CO_2, water, and renewable electricity for use as transportation fuels, and (iii) as a convenient means of storing electrical energy in chemical form to level the electrical output from intermittent energy sources such as wind and solar. Accomplishments to date in this field of study have been encouraging, yet substantial advances in catalyst, electrolyte, and reactor design are needed for CO_2 utilization via electrochemical conversion to become a technology that can help address climate change and shift society to renewable energy sources.



Significant reductions in carbon dioxide (CO_2) emissions and the development of nonfossil fuel energy sources are critical to minimize the effects of CO_2 as a greenhouse gas in the atmosphere and reduce our dependence on imported nonrenewable energy sources, most notably crude oil. Studies by the Intergovernmental Panel on Climate Change (IPCC) show that to stabilize the atmospheric concentration of CO_2 at 350−400 ppm and limit the global mean temperature increase to 2.0−2.4 °C, global CO_2 emissions in 2050 would have to be reduced by 50−80% of the emission levels in the year 2000.[1] Carbon capture and sequestration (CCS) at large emission sources such as power plants has been proposed as a strategy to decrease the accumulation of CO_2 in the atmosphere. Proposed sequestration methods include geological or deep sea storage and mineralization. To reduce our dependence on imported petroleum, the development and expansion of natural gas to liquid (GTL) and coal to liquid (CTL) technology has been proposed. GTL and CTL yield syngas, a mixture of hydrogen and carbon monoxide, which is then converted into liquid fuels via the Fischer−Tropsch process,[2,3] and both are well-developed technologies.[4−7] While the implementation of CSS will decrease emissions and CTL and GTL would allow the use of relatively abundant coal and natural gas to decrease our dependence on imported oil for transportation fuels, such a solution does not address the nonrenewable nature of fossil fuels. Because of this issue, CCS and GTL/CTL will likely serve as bridging technologies to a more sustainable energy supply needed for the long-term.[7]

The electrochemical conversion of CO_2 has promise to help overcome several of the challenges facing the implementation of carbon-neutral energy sources because it provides a means of storing renewable electricity in a convenient, high-energy-density form.

Several other, potentially more sustainable alternatives to fossil fuels are being researched. For example, significant progress is being made in the production of biofuels from algae and woody biomass.[8,9] These are promising technologies that could potentially supply carbon neutral fuels while minimizing competition with the food supply. Wind, solar, and tidal power are also very popular and expanding rapidly along with increased interest in expanding nuclear energy.[10−12] Another attractive alternative to CO_2 sequestration is the use

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of captured carbon as a reagent for producing useful chemicals either through chemical or electrochemical means. Carbon dioxide is already used in the production of chemicals such as urea, salicylic acid, and polycarbonates;[13,14] however, the demand for these products is very small compared to the amount of CO_2 produced from the consumption of fossil fuels and thus unlikely to make a significant impact on emissions. Carbon dioxide can also be reacted with hydrogen to yield a mixture of water and carbon monoxide via the reverse water gas shift reaction (RWGS) (eq 1) or to directly produce water and methanol (eq 2).[15−19]

$$CO_2 + H_2 \leftrightarrows CO + H_2O \tag{1}$$

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \tag{2}$$

While the RWGS process (eq 1) is difficult to drive to completion, pilot plants producing methanol (eq 2) have already been built. Methanol production is particularly attractive if the hydrogen comes from renewable sources. We refer the reader to a number of good reviews for a more detailed account of the various options for carbon sequestration[20−22] and CO_2 utilization.[13,23,24] At this point, it is unclear which of these strategies are technologically feasible and make economic and practical sense, be it in distributed fashion or on a large scale. In this Perspective, we will focus on the benefits and prospects of CO_2 utilization via electrochemical reduction at electrodes, therefore, via heterogeneous catalysis. For a more detailed account on related research pertaining to the photochemical,[23,25−31] biochemical,[32−34] and mediated electrochemical[3,35−38] conversion of CO_2 using homogeneous catalysts, all areas in which significant progress is being made, we refer the reader to the references stated.

Research on the direct heterogeneous electrochemical reduction of CO_2 has already shown that several products can be produced, including formic acid,[39−44] carbon monoxide,[30,31,41,45,46] methane,[41,47,48] ethylene,[41,49] and methanol.[50−52] These products can be used as commodity chemicals as well as fuels, thus allowing CO_2 to be recycled into compounds that can act as energy carriers. The key requirement, of course, is that the electricity used to convert the CO_2 must be renewable, or at least from a carbon-neutral source such as nuclear; otherwise, more CO_2 would be emitted in producing the electricity than would be reduced in the process. Also, using renewable electricity to replace electricity produced by carbon-intensive energy sources, for example, coal, would likely result in a greater reduction in emissions than using that electricity to convert CO_2 into liquid fuels. Still, the electrochemical conversion of CO_2 has great potential to help overcome several of the challenges facing the implementation of carbon-neutral energy sources because it provides a means of storing renewable electricity in a convenient, high-energy-density form. Particularly exciting is the ability to produce methane and ethylene directly on copper catalysts and the possibility of producing even longer hydrocarbons from syngas.[46,48,49] The storage of electrical energy in chemical form is potentially useful in two key areas, (1) leveling the output from intermittent electricity sources such as wind and solar and (2) allowing the production of liquid fuels for the transportation sector with renewable electricity. In comparison, the electrolysis of water, which is a mature technology, also allows storage of electricity in chemical form (hydrogen); however, hydrogen does not fit into the existing infrastructure as well as liquid fuels, has a lower volumetric energy density, and requires compression or liquefaction for storage.[53−56]

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Potential Role of Electrochemical CO_2 Conversion in Our Shift to Renewable Energy Sources. Many studies have shown that drastic reductions in CO_2 emissions are needed to limit the potential effects of climate change.[1] The fact that fossil fuel consumption accounts for the majority of CO_2 emissions and the need to reduce dependence on imported fossil fuels indicate that significant reductions in fossil fuel use will be necessary in the future, even as energy demand continues to rise. Figure 1 highlights some of the challenges that such changes would present and the role that the electrochemical conversion of CO_2 could play by comparing our current energy consumption with a hypothetical situation in which fossil fuel use is significantly reduced as part of the efforts to reduce CO_2 emissions and dependence on imported energy.

The left-hand side of Figure 1 shows the primary energy consumption by source and sector in the U.S. for 2008,[57] which is also representative for the rest of the developed world, although the exact percentages vary (for example, the fraction of nuclear energy is 13% in Europe,[58] compared to 9% in the U.S.). This information points out several key aspects of our current energy use in relation to its sources. The most dramatic is the almost complete dependence of the transportation sector on petroleum-derived liquid fuels. Also noteworthy is that the vast majority of carbon-neutral energy (renewable and nuclear) produces electricity, effectively limiting utilization of these desirable energy sources to the electrical grid. Furthermore, many popular and fast-growing renewable sources, such as wind and solar, are intermittent and, to varying degrees, unpredictable. The fluctuating nature of these sources limits them to no more than 15−20% of the total electricity demand unless nontrivial large-scale electricity storage is used to level output and prevent instability in the system.[17]

The right side of Figure 1 shows a hypothetical, qualitative distribution of energy sources that accomplishes a reduction

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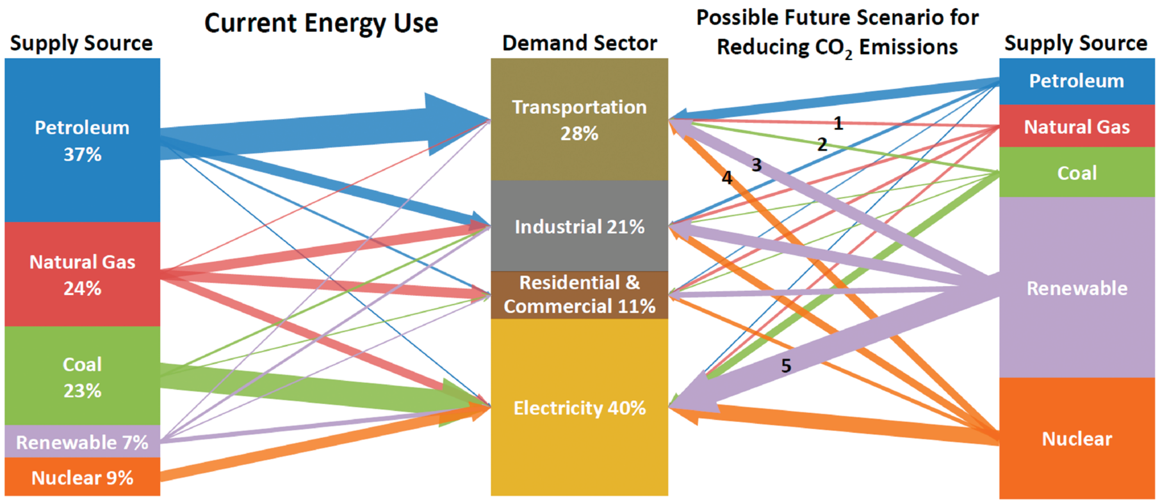

Figure 1. Primary U.S. energy consumption by source and sector for 2008[57] (left) compared to a hypothetical, qualitative scenario in which emissions are reduced by significantly reducing fossil fuel consumption (right). Key enabling technologies in the future scenario are (1) gas to liquid conversion, (2) coal to liquid conversion, (3) biofuels and electrochemical conversion of CO_2 to liquid fuels using renewable electricity, for example, wind and solar, (4) electrochemical conversion of CO_2 to liquid fuels using electricity from nuclear power, and (5) wind, solar, and tidal power with storage via electrochemical conversion of CO_2 or other methods such as pumped hydro, compressed air, and flow batteries.[59]

of CO_2 emissions through significant reduction of fossil fuel consumption while increasing carbon-neutral sources. While the total energy demand is expected to continue to increase substantially, the relative demand of each energy-consuming sector is not predicted to change significantly.[60] Thus, we used the same breakdown for the future scenario. This hypothetical scenario is not intended to be a quantitative prediction of the only or even the most probable conditions in the future. Certainly, these reductions could be achieved in several different ways, and which technologies are most feasible and end up being implemented at a meaningful scale will depend on factors such as local environment and political and economic conditions, factors that go well beyond the technical merit of each of these technologies. Similarly, given the immature technical status of the electrochemical conversion of CO_2 as well as the issues just mentioned, predicting the time frame or scale at which the electrochemical reduction of CO_2 could be implemented is impossible at this time. The purpose of the hypothetical scenario is to highlight some of the challenges that will be faced in meeting energy demand as concerns over climate change and a scarce supply of fossil fuels, particularly petroleum, cause a shift away from a fossil-fuel-dominated energy portfolio and the possible role that the electrochemical conversion of CO_2 could play (as one of many options being investigated) in overcoming these challenges.

While the exact makeup of future energy supply sources may not be certain, undoubtedly, we will face a number of challenges as we move away from fossil fuels. The first and foremost challenge will be to continue to supply energy to the transportation sector while fossil fuel use is being decreased. Unless a complete overhaul to hydrogen fuel cell or battery-powered vehicles is made, liquid fuels will continue to play a major role. Some of these liquid fuels could be supplied by GTL and CTL technology (arrows 1 and 2 in Figure 1), and still more could come from biofuels and fuels produced from the electrochemical reduction of CO_2 using electricity from renewable and nuclear sources (arrows 3 and 4 in Figure 1). A second key challenge will be to significantly increase the supply of electricity from carbon-neutral sources, that is, nuclear and renewables. For nuclear, this is fairly straightforward because we are already very familiar with this process and it provides a steady predictable supply. Increases in the use of renewable, but intermittent, sources such as wind and solar, however, would require leveling through an energy storage process, for example, through the electrochemical conversion of CO_2 (arrow 5). While many methods for massive electricity storage, such as pumped hydro, compressed air, and batteries,[59] are being proposed, storage in a chemical form via the electrochemical reduction of CO_2 gives added versatility as the products can be used as sources for electricity production, transportation fuels, or chemical feedstocks. These two challenges of the need to continue to provide energy to the transportation sector and the need to increase electricity production from carbon neutral sources highlight the value of a process that could convert and thus store electrical energy in a chemical form, particularly as a liquid, both for facilitating the penetration of renewable energy into sectors such as transportation and for storing excess electricity from intermittent sources.

Current Status of Electrochemical CO_2 Conversion. While the electrochemical conversion of CO_2 has great potential, significant technological advances are still needed for this process to become economically viable. Much of the early work in this area has focused on exploring different catalysts and the products that can be produced. Also, several investigations have elucidated how parameters such as electrolyte and temperature favor certain products over others.[48,61,62] More recently, several researchers have also proposed various reactor designs for the electrochemical reduction of CO_2 to either formic acid or syngas.[46,63−67] However, to be feasible, the electrochemical conversion of CO_2 needs to meet two

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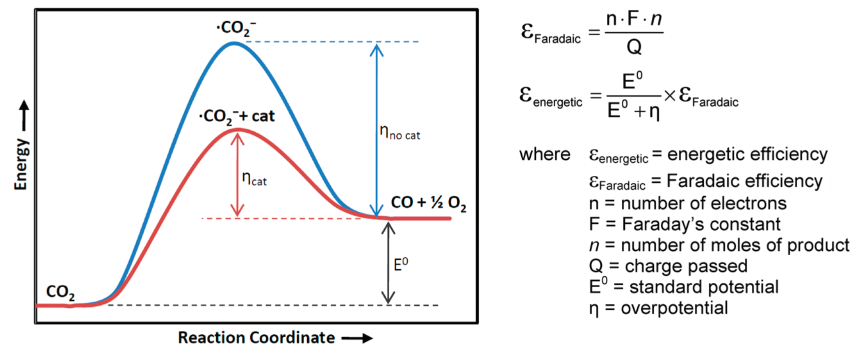

Figure 2. Qualitative reaction scheme for CO_2 conversion. Catalysts and electrolytes acting as cocatalysts can lower the energy of the intermediate and thus improve the energetic efficiency of the conversion. We use ε as the symbol for the Faradaic and energetic efficiencies to avoid confusion with the η symbol for the overpotential.

criteria, (i) high energy efficiency and (ii) high reaction rates. While it is not often discussed in the literature, the energetic efficiency is a critical parameter because it specifies the recoverable energy contained in the product; in other words, it defines the energy cost of producing the product. High energetic efficiency is achieved through a combination of high selectivity (Faradaic or current efficiency) and low overpotentials (Figure 2).

While researchers have reported high Faradaic efficiency for many products (typically $>90\,\%$ for formic acid and carbon monoxide, 65−70 % for methane and ethylene), high overpotentials are a major hindrance to improving energy efficiency. The reaction rate, as measured by the current density, is also an important parameter as it determines the reactor size and thus capital cost of the process. To date, researchers have reported moderate to high current densities (200−600 mA/cm^2) using gas diffusion electrodes (GDEs) similar to those used in fuel cells.

As mentioned above, despite the challenges of hydrogen storage and transport, water electrolysis is an attractive option for electricity storage, and thus, the efficiency and current density of a viable CO_2 reduction process should be close to those for water electrolyzers. Figure 3 shows the efficiencies and current densities for CO_2 reduction from data in the literature compared to the typical values for water electrolyzers. Typical efficiencies for commercial water electrolyzers are in the 56−73 % range, with alkaline electrolyzers running at 110−300 mA/cm^2 and PEM electrolyzers running at much higher current densities (800−1600 mA/cm^2).[56,68,69] These efficiencies for the electrolyzers are total system efficiencies (including losses from system peripherals), but because, no complete systems for CO_2 reduction are available at this time, the efficiencies plotted for CO_2 reduction only include losses on the cathode and ignore anode and system losses. The direct electrochemical reduction to hydrocarbons (methane and ethylene) is particularly interesting. However, this approach typically has the lowest energy efficiency due to exceptionally high overpotentials. In contrast, the electrochemical reduction to carbon monoxide has some of the highest energy efficiencies because the main side product, hydrogen, is included in the syngas product. However, because hydrogen evolution has a higher (less negative) theoretical reduction potential than carbon monoxide, it will likely be more efficient to optimize the electrolysis cell for CO production and supply

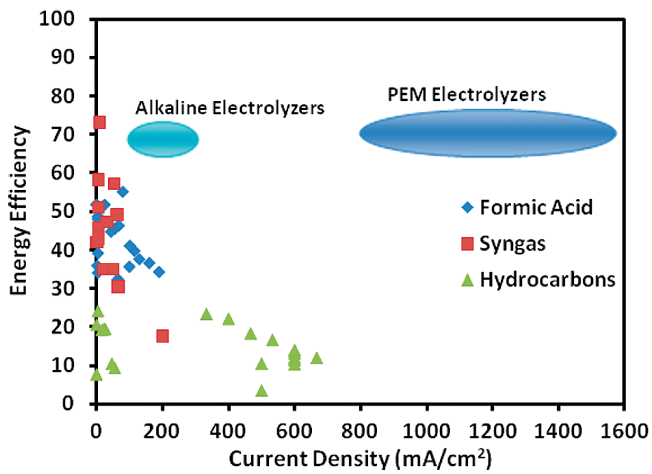

Figure 3. Comparison of the energy efficiencies and current densities for CO_2 reduction to formic acid,[40,41,43,45,65,70−73] syngas,[41,45,46,64,72,74] and hydrocarbons (methane and ethylene)[41,45,47−49,74] reported in the literature with those of water electrolyzers.[54−56,68,69,75] Efficiencies of electrolyzers are total system efficiencies, while the CO_2 conversion efficiencies only include cathode losses and neglect anode and system losses.

the hydrogen from a different renewable source such as electrolysis, biomass, or water gas shift.[56] A detailed system analysis for each of these options is required to identify the most effective method. In summary, Figure 3 shows that current research efforts in the electrochemical conversion of CO_2 have achieved moderate efficiencies and reasonably high current densities, although not at the same time. This, as well

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as the fact that additional losses have yet to be accounted for (system, anode), indicates that further work is needed to significantly improve the energetic efficiency and current densities for CO_2 reduction before it can become a technology that can help address climate change and shift society away from fossil fuels to renewable energy sources.

Remaining Challenges and Opportunities. The main challenge for advancing CO_2 reduction is increasing the energy efficiency, which is primarily hindered by high overpotentials for CO_2 reduction. The limiting step in the reduction of CO_2 is the formation of a ${}^{\bullet}CO_2^{-}$ radical anion intermediate. This step has a standard potential of −1.9 V versus SHE and is the reason for the high overpotentials.[76,77] This potential can be improved by stabilizing the intermediate, which is one of the main functions of catalysts. Research has shown that the potential to form this radical anion can be improved by 0.3 V by adsorbing it on a catalyst surface.[76] Further improvements could be possible through optimization of the catalyst. The Principle of Sabatier predicts that the best catalysts have intermediate adsorbate−surface bond strengths.[78] This principle leads to the volcano curves seen in Sachtler−Fahrenfort and Tanaka−Tamaru plots. However, in an electrochemical reaction, the presence of electrolyte, which can also act as a cocatalyst, adds complexity to the system. The added stabilizing effect of the electrolyte could result in shifting the volcano peak, thus opening the possibility to use other catalysts that may be more attractive for reasons such as cost, availability, or stability. The complexity of the catalyst, electrolyte (cocatalyst), and intermediate interactions makes understanding the transition state in the reaction particularly difficult and is an important area of further research. Furthermore, the main competing reaction to CO_2 reduction is hydrogen evolution. Consequently, metals with high hydrogen overpotentials typically give the highest Faradaic efficiencies. However, higher energy efficiency could potentially be achieved using catalysts with low hydrogen overpotentials in combination with electrolytes and reactor conditions that minimize hydrogen evolution. Thus, as research continues to improve our understanding of CO_2 reduction reaction intermediates, it will lead to more effective combinations of catalysts and electrolytes.

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As shown in Figure 3, efforts to increase the current densities for CO_2 reduction have been very successful, with current densities exceeding 600 mA/cm^2. These higher current densities have been achieved using catalysts deposited on GDEs, as is done in fuel cells.[47,49,79] While these results are very encouraging, significant improvements still need to be made. Improvements in the reactor design, particularly the electrode, and optimization of the reaction conditions will enable further increases in current densities. One of the key limiting factors in CO_2 conversion is mass transfer of CO_2 to the cathode surface, especially given the low solubility of CO_2 in many electrolytes. As mentioned earlier, this has largely been overcome using GDEs, which create a three-phase interface between the gaseous reactants, the solid catalyst, and the electrolyte. Thus, optimization of the electrode will be key to improving current densities. The extensive work on GDE optimization for fuel cells over the past decades will greatly accelerate progress in this area. Furthermore, as seen in fuel cell work, temperature is key to improving the performance of fuel cells, indicating that optimizing the reaction temperature will yield significant improvements for CO_2 reduction.[80,81] Also, work with solid oxide electrolyzers based on solid oxide fuel cells has already given promising results for high-temperature CO_2 reduction.[82]

In summary, recent work on the electrochemical reduction of CO_2 has shown the possibility of storing electricity as chemicals. The prospect of producing hydrocarbon fuels from CO_2 and renewable electricity is particularly interesting for addressing the several intertwined energy and climate change issues. Further work may lead to the advances in efficiency and current density that are necessary for heterogeneous CO_2 reduction to become an economically feasible process.

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REFERENCES

(1) Barker T. I. B., Bernstein, L.; Bogner, J. E.; Bosch, P. R.; Dave, R.; Davidson, O. R.; Fisher, B. S.; Gupta, S.; Halsnæs, K.; Heij, G. J.; Kahn Ribeiro, S.; Kobayashi, S.; Levine, M. D.; Martino, D. L.; Masera, O.; Metz, B.; Meyer, L. A.; Nabuurs, G.-J.; Najam, A.; Nakicenovic, N.; Rogner, H.-H.; Roy, J.; Sathaye, J.; Schock, R.; Shukla, P.; Sims, R. E. H.; Smith, P.; Tirpak,

D. A.; Urge-Vorsatz, D.; Zhou, D. *IPCC, 2007: Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Metz, B., Davidson, O. R., Bosch, P. R., Dave, R., Meyer, L. A., Eds.; Cambridge University Press: New York, **2007**.
(2) Oloman, C.; Li, H. Electrochemical Processing of Carbon Dioxide. *ChemSusChem* **2008,** *1*, 385–391.
(3) Sanchez-Sanchez, C. M.; Montiel, V.; Tryk, D. A.; Aldaz, A.; Fujishima, A. Electrochemical Approaches to Alleviation of the Problem of Carbon Dioxide Accumulation. *Pure Appl. Chem.* **2001,** *73*, 1917–1927.
(4) Choi, S.; Drese, J. H.; Jones, C. W. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. *ChemSusChem* **2009,** *2*, 796–854.
(5) Hao, X.; Djatmiko, M. E.; Xu, Y. Y.; Wang, Y. N.; Chang, J.; Li, Y. W. Simulation Analysis of a GTL Process Using ASPEN Plus. *Chem. Eng. Technol.* **2008,** *31*, 188–196.
(6) Sudiro, M.; Bertucco, A. Production of Synthetic Gasoline and Diesel Fuel by Alternative Processes Using Natural Gas and Coal: Process Simulation and Optimization. *Energy* **2009,** *34*, 2206–2214.
(7) Sudiro, M.; Bertucco, A.; Ruggeri, F.; Fontana, A. Improving Process Performances in Coal Gasification for Power and Synfuel Production. *Energy Fuels* **2008,** *22*, 3894–3901.
(8) Knocke, C.; Vogt, J. Biofuels — Challenges & Chances: How Biofuel Development Can Benefit from Advanced Process Technology. *Eng. Life Sci.* **2009,** *9*, 96–99.
(9) Williams, P. J. L.; Laurens, L. M. L. Microalgae as Biodiesel & Biomass Feedstocks: Review & Analysis of the Biochemistry, Energetics & Economics. *Energy Environ. Sci.* **2010,** *3*, 554–590.
(10) Abbott, D. Keeping the Energy Debate Clean: How Do We Supply the World's Energy Needs?. *Proc. IEEE* **2010,** *98*, 42–66.
(11) Langhamer, O.; Haikonen, K.; Sundberg, J. Wave Power-Sustainable Energy or Environmentally Costly? A Review with Special Emphasis on Linear Wave Energy Converters. *Renewable Sustainable Energy Rev.* **2010,** *14*, 1329–1335.
(12) Lenzen, M. Current State of Development of Electricity-Generating Technologies: A Literature Review. *Energies* **2010,** *3*, 462–591.
(13) Aresta, M.; Dibenedetto, A. *Carbon Dioxide Fixation into Organic Compounds*; Kluwer Academic Publishers: Boston, MA, 2003.
(14) Cohen, C. T.; Coates, G. W. Alternating Copolymerization of Propylene Oxide and Carbon Dioxide with Highly Efficient and Selective (Salen)Co(III) Catalysts: Effect of Ligand and Cocatalyst Variation. *J. Polym. Sci., Part A: Polym. Chem.* **2006,** *44*, 5182–5191.
(15) Centi, G.; Perathoner, S.; Wine, G.; Gangeri, M. Electrocatalytic Conversion of CO_2 to Long Carbon-Chain Hydrocarbons. *Green Chem.* **2007,** *9*, 671–678.
(16) Cifre, P. G.; Badr, O. Renewable Hydrogen Utilisation for the Production of Methanol. *Energy Convers. Manage.* **2007,** *48*, 519–527.
(17) Duthie, J. M.; Whittington, H. W. Securing Renewable Energy Supplies Through Carbon Dioxide Storage in Methanol. *Power Eng. Soc. Summer Meeting, 2002 IEEE* **2002,** *1*, 145–150.
(18) Mignard, D.; Pritchard, C. Processes for the Synthesis of Liquid Fuels from CO_2 and Marine Energy. *Chem. Eng. Res. Des.* **2006,** *84*, 828–836.
(19) Mignard, D.; Sahibzada, M.; Duthie, J. M.; Whittington, H. W. Methanol Synthesis from Flue-Gas CO_2 and Renewable Electricity: A Feasibility Study. *Int. J. Hydrogen Energy* **2003,** *28*, 455–464.
(20) Bachu, S. CO_2 Storage in Geological Media: Role, Means, Status and Barriers to Deployment. *Prog. Energy Combust. Sci.* **2008,** *34*, 254–273.
(21) Plasynski, S. I.; Litynski, J. T.; McIlvried, H. G.; Srivastava, R. D. Progress and New Developments in Carbon Capture and Storage. *Crit. Rev. Plant Sci.* **2009,** *28*, 123–138.
(22) van Alphen, K.; Noothout, P. M.; Hekkert, M. P.; Turkenburg, W. C. Evaluating the Development of Carbon Capture and Storage Technologies in the United States. *Renewable Sustainable Energy Rev.* **2010,** *14*, 971–986.
(23) Centi, G.; Perathoner, S. Opportunities and Prospects in the Chemical Recycling of Carbon Dioxide to Fuels. *Catal. Today* **2009,** *148*, 191–205.
(24) Song, C. S. Global Challenges and Strategies for Control, Conversion and Utilization of CO_2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing. *Catal. Today* **2006,** *115*, 2–32.
(25) Kalyanasundaram, K.; Graetzel, M. Artificial Photosynthesis: Biomimetic Approaches to Solar Energy Conversion and Storage. *Curr. Opin. Biotechnol.* **2010,** *21*, 298–310.
(26) Morris, A. J.; Meyer, G. J.; Fujita, E. Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels. *Acc. Chem. Res.* **2009,** *42*, 1983–1994.
(27) Grills, D. C.; Fujita, E. New Directions for the Photocatalytic Reduction of CO_2: Supramolecular, scCO_2 or Biphasic Ionic Liquid−scCO_2 Systems. *J. Phys. Chem. Lett* **2010,** *1*, 2709–2718.
(28) Licht, S.; Wang, B. H.; Ghosh, S.; Ayub, H.; Jiang, D. L.; Ganley, J. A New Solar Carbon Capture Process: Solar Thermal Electrochemical Photo (STEP) Carbon Capture. *J. Phys. Chem. Lett.* **2010,** *1*, 2363–2368.
(29) Wang, C. J.; Thompson, R. L.; Baltrus, J.; Matranga, C. Visible Light Photoreduction of CO_2 Using CdSe/Pt/TiO_2 Heterostructured Catalysts. *J. Phys. Chem. Lett.* **2010,** *1*, 48–53.
(30) Nielsen, I. M. B.; Leung, K. Cobalt−Porphyrin Catalyzed Electrochemical Reduction of Carbon Dioxide in Water. 1. A Density Functional Study of Intermediates. *J. Phys. Chem. A* **2010,** *114*, 10166–10173.
(31) Leung, K.; Nielsen, I. M. B.; Sai, N.; Medforth, C.; Shelnutt, J. A. Cobalt−Porphyrin Catalyzed Electrochemical Reduction of Carbon Dioxide in Water. 2. Mechanism from First Principles. *J. Phys. Chem. A* **2010,** *114*, 10174–10184.
(32) Lu, Y.; Jiang, Z. Y.; Xu, S. W.; Wu, H. Efficient Conversion of CO_2 to Formic Acid by Formate Dehydrogenase Immobilized in a Novel Alginate−Silica Hybrid Gel. *Catal. Today* **2006,** *115*, 263–268.
(33) Reda, T.; Plugge, C. M.; Abram, N. J.; Hirst, J. Reversible Interconversion of Carbon Dioxide and Formate by an Electroactive Enzyme. *Proc. Natl. Acad. Sci. U.S.A.* **2008,** *105*, 10654–10658.
(34) Xu, S. W.; Lu, Y.; Li, J.; Jiang, Z. Y.; Wu, H. Efficient Conversion of CO_2 to Methanol Catalyzed by Three Dehydrogenases Co-Encapsulated in an Alginate−Silica (ALG−SiO_2) Hybrid Gel. *Ind. Eng. Chem. Res.* **2006,** *45*, 4567–4573.
(35) Cole, E. B.; Lakkaraju, P. S.; Rampulla, D. M.; Morris, A. J.; Abelev, E.; Bocarsly, A. B. Using a One-Electron Shuttle for the Multielectron Reduction of CO_2 to Methanol: Kinetic, Mechanistic, and Structural Insights. *J. Am. Chem. Soc.* **2010,** *132*, 11539–11551.
(36) Ogura, K.; Migita, C. T.; Wadaka, K. Homogeneous Catalysis in the Mediated Electrochemical Reduction of Carbon-Dioxide. *J. Mol. Catal.* **1991,** *67*, 161–173.
(37) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. One-Electrocn and 2-Electron Pathways in the

Electrocatalytic Reduction of CO_2 by fac-Re(2,2′-bipyridine)-$(CO)_3$Cl. *J. Chem. Soc., Chem. Commun.* **1985,** 1414–1415.

(38) Jitaru, M. Electrochemical Carbon Dioxide Reduction — Fundamental and Applied Topics (Review). *J. Univ. Chem. Technol. Metall.* **2007,** *42*, 333–344.

(39) Azuma, M.; Hashimoto, K.; Hiramoto, M.; Watanabe, M.; Sakata, T. Electrochemical Reduction of Carbon-Dioxide on Various Metal-Electrodes in Low-Temperature Aqueous $KHCO_3$ Media. *J. Electrochem. Soc.* **1990,** *137*, 1772–1778.

(40) Furuya, N.; Yamazaki, T.; Shibata, M. High Performance Ru−Pd Catalysts for CO_2 Reduction at Gas-Diffusion Electrodes. *J. Electroanal. Chem.* **1997,** *431*, 39–41.

(41) Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. Electrocatalytic Process of CO Selectivity in Electrochemical Reduction of CO_2 at Metal-Electrodes in Aqueous-Media. *Electrochim. Acta* **1994,** *39*, 1833–1839.

(42) Ikeda, S.; Takagi, T.; Ito, K. Selective Formation of Formic-Acid, Oxalic-Acid, and Carbon-Monoxide by Electrochemical Reduction of Carbon-Dioxide. *Bull. Chem. Soc. Jpn.* **1987,** *60*, 2517–2522.

(43) Mahmood, M. N.; Masheder, D.; Harty, C. J. Use of Gas-Diffusion Electrodes for High-Rate Electrochemical Reduction of Carbon-Dioxide. 1. Reduction at Lead, Indium-Impregnated and Tin-Impregnated Electrodes. *J. Appl. Electrochem.* **1987,** *17*, 1159–1170.

(44) Udupa, K. S.; Subraman., Gs; Udupa, H. V. K. Electrolytic Reduction of Carbon Dioxide to Formic Acid. *Electrochim. Acta* **1971,** *16*, 1593.

(45) Furuya, N.; Koide, S. Electroreduction of Carbon-Dioxide by Metal Phthalocyanines. *Electrochim. Acta* **1991,** *36*, 1309–1313.

(46) Yamamoto, T.; Tryk, D. A.; Fujishima, A.; Ohata, H. Production of Syngas Plus Oxygen from CO_2 in a Gas-Diffusion Electrode-Based Electrolytic Cell. *Electrochim. Acta* **2002,** *47*, 3327–3334.

(47) Hara, K.; Sakata, T. Electrocatalytic Formation of CH_4 from CO_2 on a Pt Gas Diffusion Electrode. *J. Electrochem. Soc.* **1997,** *144*, 539–545.

(48) Kaneco, S.; Katsumata, H.; Suzuki, T.; Ohta, K. Electrochemical Reduction of CO_2 to Methane at the Cu Electrode in Methanol with Sodium Supporting Salts and its Comparison with Other Alkaline Salts. *Energy Fuels* **2006,** *20*, 409–414.

(49) Cook, R. L.; Macduff, R. C.; Sammells, A. F. High-Rate Gas-Phase CO_2 Reduction to Ethylene and Methane Using Gas-Diffusion Electrodes. *J. Electrochem. Soc.* **1990,** *137*, 607–608.

(50) Arai, G.; Harashina, T.; Yasumori, I. Selective Electrocatalytic Reduction of Carbon-Dioxide to Methanol on Ru-Modified Electrode. *Chem. Lett.* **1989,** 1215–1218.

(51) Qu, J. P.; Zhang, X. G.; Wang, Y. G.; Xie, C. X. Electrochemical Reduction of CO_2 on RuO_2/TiO_2 Nanotubes Composite Modified Pt Electrode. *Electrochim. Acta* **2005,** *50*, 3576–3580.

(52) Summers, D. P.; Leach, S.; Frese, K. W. The Electrochemical Reduction of Aqueous Carbon-Dioxide to Methanol at Molybdenum Electrodes with Low Overpotentials. *J. Electroanal. Chem.* **1986,** *205*, 219–232.

(53) Berry, G. D.; Cutler, J. C. *Encyclopedia of Energy*; Elsevier: New York, 2004; pp 253−265.

(54) Holladay, J. D.; Hu, J.; King, D. L.; Wang, Y. An Overview of Hydrogen Production Technologies. *Catal. Today* **2009,** *139*, 244–260.

(55) Summary of Electrolytic Hydrogen Production. *Milestone Completion Report NREL/MP-560−36734*; National Renewable Energy Laboratory: Golden, CO, **2004**.

(56) Turner, J.; Sverdrup, G.; Mann, M. K.; Maness, P. C.; Kroposki, B.; Ghirardi, M.; Evans, R. J.; Blake, D. Renewable Hydrogen Production. *Int. J. Energy Res.* **2008,** *32*, 379–407.

(57) *Annual Energy Review 2008*; U.S. Energy Information Agency: Washington, DC, **2009**.

(58) *Share of Total Energy Consumption by Fuel in 2007*. European Environment Agency; http://www.eea.europa.eu/data-and-maps/figures/share-of-total-energy-consumption (2010).

(59) Lee, B. S.; Gushee, D. E. Electricity Storage: The Achilles' Heel of Renewable Energy. *Chem. Eng. Prog.* **2008,** *104*, S29–S32.

(60) *Annual Energy Outlook 2010 with Projections to 2035*; U.S. Energy Information Agency: Washington, DC, **2010**.

(61) Hori, Y.; Murata, A.; Takahashi, R. Formation of Hydrocarbons in the Electrochemical Reduction of Carbon-Dioxide at a Copper Electrode in Aqueous-Solution. *J. Chem. Soc., Faraday Trans.* **1989,** *85*, 2309–2326.

(62) Li, H.; Oloman, C. Development of a Continuous Reactor for the Electro-Reduction of Carbon Dioxide to Formate — Part 1: Process Variables. *J. Appl. Electrochem.* **2006,** *36*, 1105–1115.

(63) Akahori, Y.; Iwanaga, N.; Kato, Y.; Hamamoto, O.; Ishii, M. New Electrochemical Process for CO_2 Reduction to Formic Acid from Combustion Flue Gases. *Electrochemistry* **2004,** *72*, 266–270.

(64) Delacourt, C.; Ridgway, P. L.; Kerr, J. B.; Newman, J. Design of an Electrochemical Cell Making Syngas ($CO+H_2$) from CO_2 and H_2O Reduction at Room Temperature. *J. Electrochem. Soc.* **2008,** *155*, B42–B49.

(65) Koleli, F.; Atilan, T.; Palamut, N.; Gizir, A. M.; Aydin, R.; Hamann, C. H. Electrochemical Reduction of CO_2 at Pb- and Sn-Electrodes in a Fixed-Bed Reactor in Aqueous K_2CO_3 and $KHCO_3$ Media. *J. Appl. Electrochem.* **2003,** *33*, 447–450.

(66) Li, H.; Oloman, C. The Electro-Reduction of Carbon Dioxide in a Continuous Reactor. *J. Appl. Electrochem.* **2005,** *35*, 955–965.

(67) Subramanian, K.; Asokan, K.; Jeevarathinam, D.; Chandrasekaran, M. Electrochemical Membrane Reactor for the Reduction of Carbon Dioxide to Formate. *J. Appl. Electrochem.* **2007,** *37*, 255–260.

(68) Gandia, L. M.; Oroz, R.; Ursua, A.; Sanchis, P.; Dieguez, P. M. Renewable Hydrogen Production: Performance of an Alkaline Water Electrolyzer Working Under Emulated Wind Conditions. *Energy Fuels* **2007,** *21*, 1699–1706.

(69) Millet, P.; Dragoe, D.; Grigoriev, S.; Fateev, V.; Etievant, C. GenHyPEM: A Research Program on PEM Water Electroysis Supported by the European Commission. *Int. J. Hydrogen Energy* **2009,** *34*, 4974–4982.

(70) Innocent, B.; Liaigre, D.; Pasquier, D.; Ropital, F.; Leger, J. M.; Kokoh, K. B. Electro-Reduction of Carbon Dioxide to Formate on Lead Electrode in Aqueous Medium. *J. Appl. Electrochem.* **2009,** *39*, 227–232.

(71) Kaneco, S.; Iwao, R.; Iiba, K.; Ohta, K.; Mizuno, T. Electrochemical Conversion of Carbon Dioxide to Formic Acid on Pb in KOH/Methanol Electrolyte at Ambient Temperature and Pressure. *Energy* **1998,** *23*, 1107–1112.

(72) Saeki, T.; Hashimoto, K.; Fujishima, A.; Kimura, N.; Omata, K. Electrochemical Reduction of CO_2 with High-Current Density in a CO_2−Methanol Medium. *J. Phys. Chem.* **1995,** *99*, 8440–8446.

(73) Whipple, D. T.; Finke, E. C.; Kenis, P. J. A. Microfluidic Reactor for the Electrochemical Reduction of Carbon Dioxide: The Effect of pH. *Electrochem. Solid-State Lett.* **2010,** *13*, D109–D111.

DOI: 10.1021/jz1012627 | *J. Phys. Chem. Lett.* **2010,** *1*, 3451–3458

(74) Frese, K. W.; Leach, S. Electrochemical Reduction of Carbon-Dioxide to Methane, Methanol, and CO on Ru Electrodes. *J. Electrochem. Soc.* **1985,** *132*, 259–260.
(75) Grigoriev, S. A.; Porembsky, V. I.; Fateev, V. N. Pure Hydrogen Production by PEM Electrolysis for Hydrogen Energy. *Int. J. Hydrogen Energy* **2006,** *31*, 171–175.
(76) Chaplin, R. P. S.; Wragg, A. A. Effects of Process Conditions and Electrode Material on Reaction Pathways for Carbon Dioxide Electroreduction with Particular Reference to Formate Formation. *J. Appl. Electrochem.* **2003,** *33*, 1107–1123.
(77) Tryk, D. A.; Fujishima, A. Global Warming Electrochemists Enlisted in War: The Carbon Dioxide Reduction Battle. *Electrochem. Soc. Interface* **2001,** 32–36.
(78) Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons, Inc.: New York, 1996.
(79) Hara, K.; Kudo, A.; Sakata, T.; Watanabe, M. High-Efficiency Electrochemical Reduction of Carbon-Dioxide Under High-Pressure on a Gas-Diffusion Electrode Containing Pt Catalysts. *J. Electrochem. Soc.* **1995,** *142*, L57–L59.
(80) Hollinger, A. S.; Maloney, R. J.; Jayashree, R. S.; Natarajan, D.; Markoski, L. J.; Kenis, P. J. A. Nanoporous Separator and Low Fuel Concentration to Minimize Crossover in Direct Methanol Laminar Flow Fuel Cells. *J. Power Sources* **2010,** *195*, 3523–3528.
(81) Nordlund, J.; Lindbergh, G. Temperature-Dependent Kinetics of the Anode in the DMFC. *J. Electrochem. Soc.* **2004,** *151*, A1357–A1362.
(82) Bidrawn, F.; Kim, G.; Corre, G.; Irvine, J. T. S.; Vohs, J. M.; Gorte, R. J. Efficient Reduction of CO_2 in a Solid Oxide Electrolyzer. *Electrochem. Solid-State Lett.* **2008,** *11*, B167–B170.

DOI: 10.1021/jz1012627 | *J. Phys. Chem. Lett.* **2010,** *1*, 3451–3458