Solar-Driven Reduction of 1 atm of CO₂ to Formate at 10% Energy-Conversion Efficiency by Use of a TiO₂-Protected III–V Tandem Photoanode in Conjunction with a Bipolar Membrane and a Pd/C Cathode

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Supporting Information

ABSTRACT: A solar-driven CO₂ reduction (CO₂R) cell was constructed, consisting of a tandem GaAs/InGaP/TiO₂/Ni photoanode in 1.0 M KOH(aq) (pH = 13.7) to facilitate the oxygen-evolution reaction (OER), a Pd/C nanoparticle-coated Ti mesh cathode in 2.8 M KHCO₃(aq) (pH = 8.0) to perform the CO₂R reaction, and a bipolar membrane to allow for steady-state operation of the catholyte and anolyte at different bulk pH values. At the operational current density of 8.5 mA cm⁻², in 2.8 M KHCO₃(aq), the cathode exhibited <100 mV overpotential and >94% Faradaic efficiency for the reduction of 1 atm of CO₂(g) to formate. The anode exhibited a 320 ± 7 mV overpotential for the OER in 1.0 M KOH(aq), and the bipolar membrane exhibited ∼480 mV voltage loss with minimal product crossovers and >90 and >95% selectivity for protons and hydroxide ions, respectively. The bipolar membrane facilitated coupling between two electrodes and electrolytes, one for the CO₂R reaction and one for the OER, that typically operate at mutually different pH values and produced a lower total cell overvoltage than known single-electrolyte CO₂R systems while exhibiting ∼10% solar-to-fuels energy-conversion efficiency.

The sustainable electrochemical reduction of CO₂ requires utilization of CO₂ from the atmosphere as well as use of the electrons and protons produced by the oxidation of water to O₂(g). However, CO₂ reduction (CO₂R) involves very different optimal electrolyte conditions than oxidation of water. For the cathodic CO₂R reaction in alkaline conditions (e.g., pH > 10), the low concentration of dissolved CO₂ imposes severe mass-transport limitations on the electroactive reagent, whereas in acidic conditions (e.g., pH < 1), the high proton concentration favors the competing hydrogen-evolution reaction (HER). Hence, the development of catalysts for CO₂R has generally focused on electrolytes having near-neutral pH values. At present, in near-neutral pH electrolytes, only electrochemical processes that involve the two-electron/two-proton reduction of CO₂ to produce either CO or formate, can be performed efficiently and selectively at an operating current density of 10¹ mA cm⁻². In contrast, for the oxygen-evolution reaction (OER), mixed-metal oxides have been extensively studied in strongly alkaline conditions (1.0 M KOH(aq)), with state-of-the-art catalysts exhibiting ∼250–300 mV overpotentials at 10 mA cm⁻² of anodic current density. Electro catalysts for the OER in near-neutral electrolytes exhibit substantially larger overpotentials than OER electro catalysts in alkaline electrolytes because the negatively charged hydroxide ion is more readily oxidized than a neutral water molecule, and because hydroxide is present in high concentration in alkaline solutions.

Most laboratory demonstrations of solar-driven CO₂R devices have used a single electrolyte at near-neutral pH values but consequently suffer substantial overpotential losses for the OER. For example, a 6.5% solar-to-fuel conversion efficiency, ηSTF, was reported using an Au catalyst for CO
generation in 0.5 M NaHCO₃(aq) electrolyte. A value of η_STF = 4.6% was obtained using a polymeric Ru complex for formate generation in 0.1 M aqueous phosphate buffer. In addition to requiring effective ionic coupling between the catholyte and anolyte, a full solar-driven CO₂R system also requires a robust means to separate the products as well as facile collection of the reduced fuels. We demonstrate herein the performance of a photovoltaic-assisted electrosynthetic cell in which the photoanode is operated in 1.0 M KOH(aq) (pH = 13.7) to perform the OER while the cathode performs the CO₂R reaction in 2.8 M KHCO₃(aq) (pH = 8.0) under 1 atm of CO₂(g). The pH difference between the cathode chamber and the anode chamber was sustained at steady state with no accompanying chemical bias voltage by use of a bipolar membrane (fumasep FBM). Hence, two electrolytes having mutually different pH values, with each electrolyte individually optimized for the CO₂R reaction or the OER, were effectively coupled together to produce a modest combined cell overvoltage at the desired operational current density.

The photoanode (GaAs/InGaP/TiO₂/Ni) consisted of a tandem-junction III–V photoabsorber, an amorphous hole-conductive TiO₂ protection layer, and a thin catalyst layer to facilitate the OER. Details of the fabrication of the photoanode are described in the Supporting Information.
The water-oxidation behavior of the photoanode in 1.0 M KOH(aq) under simulated 1 sun illumination has been characterized previously, and the photoanode exhibited a light-limited photocurrent density of ∼8.5 mA cm⁻² and an equivalent open-circuit voltage of ∼2.4 V (Figure S1), in accord with prior results.

Figure 1A shows the cyclic voltammetry, at a scan rate of 10 mV s⁻¹ without correction for uncompensated resistance (see Figure S2A for an illustration of the three-electrode electrochemical measurement setup), of a Pd/C nanoparticle-coated Ti mesh cathode with a Pd mass loading of 250 μg cm⁻² (red) and a Pd/C-coated Ti foil with a Pd mass loading of 50 μg cm⁻² (black) in 2.8 M KHCO₃(aq) (pH = 8) that was saturated with a stream of 1 atm of CO₂(g). The Pd/C cathode was fabricated by drop-casting a solution containing 2 mg mL⁻¹ Pd/C nanoparticles and ∼0.15 wt % Nafion in isopropanol on a Ti mesh or a Ti foil. The Pd/C-coated Ti foil (black curve in Figure 1A) exhibited very similar electrocatalytic activity to that reported previously. The Pd/C-coated stacked Ti mesh electrode exhibited improved performance because of the increased mass loading and larger electrochemically accessible surface area for CO₂R reduction. The forward scan indicated that the onset potential of the cathodic current was close to the equilibrium potential for CO₂ reduction to formate (E°(CO₂/HCOO⁻) = −0.687 V versus the Ag/AgCl reference electrode). An overpotential of ∼57 ± 8 mV was required to drive CO₂R at a cathodic geometric current density of 10 mA cm⁻². Figure 1B shows the Faradaic efficiency for the production of formate using the Pd/C nanoparticle-coated Ti mesh cathode in CO₂-saturated 2.8 M KHCO₃(aq) as a function of time, at four different overpotentials. At all overpotentials, near-unity Faradaic efficiency was observed for the first 60 min of operation. The Faradaic efficiency then decreased slowly for overpotentials between −45 and −120 mV, but still exceeded ≥94% after 3 h of electrolysis (Figure 1B). In contrast, when the electrode was held at −170 mV vs E°(CO₂/HCOO⁻), the Faradaic efficiency decayed quickly after 90 min and decreased to ∼80% after 3 h of continuous operation (see the SI for discussion about the time dependence of the Faradaic efficiency). The decrease of the Faradaic efficiency for formate production is consistent with the accumulation of CO at the surface of the Pd nanoparticles.

To characterize in detail the performance of the protection layer and electrolytically active components of the anode, Figure 1C shows the current density vs potential (J–E) behavior of a p⁺-Si/TiO₂/Ni dark anode affecting the OER in 1.0 M KOH(aq) (black) and in 2.8 M KHCO₃(aq) (red) without any correction for uncompensated resistance. The J–E behavior of the p⁺-Si/TiO₂/Ni dark electrode was used to provide a measure of the overpotentials of the OER catalysts at 1.0 M KOH(aq) and in 2.8 M KHCO₃(aq) (see the SI for discussion of the nickel catalyst). As shown in Figure 1C, an overpotential of 330 ± 10 mV was required to produce a current density of 10 mA cm⁻² in 1.0 M KOH(aq), consistent with previous results. In contrast, an overpotential of 793 ± 26 mV was required in 2.8 M KHCO₃(aq) to produce 10 mA cm⁻² of current density.

With the anolyte at pH = 13.7 (1.0 M KOH(aq)) and the catholyte at pH = 8.0 (2.8 M KHCO₃(aq)), Figure 2A shows the membrane voltage loss (left axis), as well as the measured total membrane voltage (right axis) as a function of the current density normalized to the bipolar membrane (BPM) area (see Figure S2C for an illustration of the four-point measurement configuration). Two Luggin capillaries with Ag/AgCl reference electrodes were used to measure the electric potential drop across the BPM. The equilibrium potential, V_{membrane,eq} was calculated to be 0.336 V in the anolyte/catholyte system. At a current density of 10 mA cm⁻², the measured membrane total voltage was 0.843 ± 0.038 V. Hence, to drive the reduction of CO₂ to formate at steady state, the voltage loss in the BPM, V_{membrane,loss} = V_{membrane,eq} – V_{membrane,eq} = 0.843 V – [0.059 V × (13.7 − 8.0)], was 0.507 V. The voltage loss primarily resulted from the resistance loss of the BPM as well as from the overvoltage required for water dissociation at the transition region in the BPM. The observed membrane voltage losses in the 1.0 M KOH(aq) (pH = 13.7)/2.8 M KHCO₃(aq) (pH = 8.0) system were substantially smaller than those previously reported in 0.5 M KH₂BO₃(aq) (pH = 9.3)/1.0 M H₂SO₄(aq) (pH = 0) because the flexible Luggin capillaries used in the present study were placed very close to the membrane and minimized the resistive losses due to the solution. To evaluate the ion transport properties of the membrane, a cell with Pt mesh electrodes as the cathode and anode was operated continuously for 100 h at a current density of ∼8.5 mA cm⁻² normalized to the BPM area, with a resulting change by ∼0.01 unit in the pH of the anolyte. If 100% of the charge passed had been used for electrodialysis of the electrolytes, the pH of the anolyte would have changed by >1 unit. After continuous operation of this cell for 6 h at 8.5 mA cm⁻², the BPM voltage changed by <0.5% (Figure S3). Alternatively, for operation of CO₂R and OER in the same electrolyte, a cation-exchange membrane, for example, Nafion, could be used to separate the cathode chamber from the anode chamber. Figure 2B shows the measured total membrane voltage as a function of the current density normalized to the Nafion area, when both the anolyte and catholyte were 2.8 M KHCO₃(aq), but Nafion was used instead of a BPM. The total Nafion membrane voltage was equal to the Nafion membrane voltage loss, which largely arose due to the membrane resistance for transport of K⁺ ions. At a current density of 10 mA cm⁻², the voltage loss across the Nafion membrane was 214 ± 15 mV.

The ion-crossover fluxes in the BPM system were characterized using inductively coupled plasma mass spectrometry (ICPMS) in conjunction with a total inorganic carbon (TIC) analyzer to measure the ion concentrations in the catholyte and anolyte after charge was passed through the BPM at different current densities. Figure 2C–D shows the time dependence of the selectivity of the BPM for protons and hydroxide ions at two different operational current densities. Two major crossover pathways, cation crossover from the anolyte to the catholyte and anion crossover from the catholyte to the anolyte, were present under the electric field due to the imperfect permselectivity of the cation-exchange membrane and anion-exchange membrane portions of the BPM. To determine the cation crossover, the KHCO₃(aq) catholyte was replaced by CsHCO₃(aq), so that small increases in the K⁺ concentration could be detected. The measured K⁺ leak rate in the CsHCO₃(aq)/KOH(aq) configuration also presented an upper bound for the behavior of the KHCO₃(aq)/KOH(aq) configuration due to the absence of the diffusional driving force for K⁺ transport from the anolyte to the catholyte in the all-K⁺-containing system. The measured K⁺ selectivities, j_{K⁺}/j_{OH⁻}, were defined as the ratio of proton-carrying (hydroxide-carrying) charge passed relative to the total charge passed through the membrane. At an operational current density of 3 mA cm⁻², the potassium leak current and the bicarbonate leak current...
constituted 10–25% and 20–35%, respectively, of the total current passed through the BPM. When the membrane current density was increased to 8 mA cm\(^{-2}\), the membrane selectivity for protons increased to >90% and the membrane selectivity for hydroxide ions increased to >95%. The crossover of the formate product was low (Figure S4). In the three-electrode electrochemical measurement, the cathode compartment was separated from the Pt counter electrode by a BPM; therefore, the high Faradaic efficiency (>94%) measured in the cathode compartment at low overpotentials (from −45 to −120 mV; Figure 1B) also provides evidence for a low rate of formate crossover through the BPM. The product crossovers were minimal because the negatively charged formate ion was effectively blocked by the negatively charged cation-exchange membrane in the BPM system.

Figure 3A shows a schematic illustration of the two-electrode electrochemical setup. CO\(_2\) at 1 atm (ALPHAGAZ 1) was bubbled continuously into the 2.8 M KHCO\(_3\) (aq) catholyte. The blue tubes shown in the figure were connected to a peristaltic pumping system that facilitated removal of CO\(_2\) bubbles and thus minimized associated fluctuations in the cell voltage and current. The geometric areas of the GaAs/InGaP/TiO\(_2\)/Ni photoanode, BPM, Nafion membrane, and Pd/C/Ti cathode were mutually similar, at 0.030, 0.030, 0.030, and 0.040 cm\(^2\), respectively. The relatively small active device area was due to the behavior of the photoanode in 1.0 M KOH (aq). The electrocatalytic performance, stability, and Faradaic efficiency for product formation at the cathode, the \(J−E\) properties of the photoanode, and the current–voltage characteristics of the BPM were independent of the geometric areas of these cell components (Figure S5), but the stability of the photoanode was dependent on the electrode area due to pinholes and other defects at large electrode areas, providing a source for active dissolution and thus instability of the III–V semiconductors in 1.0 M KOH (aq) (see the SI). Small-area photoanodes have exhibited stable operation for >100 h with near-unity Faradaic efficiency for the OER,\(^{24,28}\) Figure 3B shows the current density vs voltage behavior of the GaAs/InGaP/TiO\(_2\)/Ni photoanode wired to a Pd/C-coated Ti mesh cathode was measured under 100 mW cm\(^{-2}\) of simulated AM1.5 illumination. The calculated current density–voltage characteristic of the solid-state tandem cell (orange).\(^{24,25}\)
mesh cathode under 100 mW cm$^{-2}$ of simulated Air Mass (AM) 1.5 illumination. The calculated two-electrode current density vs voltage behavior (dotted black) was obtained by using the current–voltage behavior of the tandem solid-state photoabsorber (dotted orange) in conjunction with the overall polarization characteristic of a p–Si/TiO$_2$/Ni anode and a Pd/C-coated Ti mesh cathode in the two-electrode BMP configuration (KHCO$_3$/BPM/KOH) (black). The calculated two-electrode current density vs voltage behavior was in good agreement with the experimental measurements. The electro-synthetic cell component required 2.04 V to operate at a current density of 8.5 mA cm$^{-2}$ and was thus well matched to the maximum power point of the photovoltaic tandem junction component of the photoanode. The electro-synthetic cell thus operated with an electrical-to-fuel conversion efficiency, $\eta_{\text{electrolyzer}}$ of 1.21 V/2.04 V = 59.3% at 8.5 mA cm$^{-2}$ current density. Figure 3C also shows the overall polarization characteristics of the two-electrode Nafion membrane configuration (KHCO$_3$/Nafion/KHCO$_3$) (blue) using the same electrode materials. Due to the large overpotential for the Ni catalyst to affect the OER at the near-neutral pH (Figure 1C), obtaining an operational current density of $\sim$8.5 mA cm$^{-2}$ to drive the overall CO$_2$R reaction in conjunction with the OER required an additional $\sim$180 mV of voltage in the Nafion-containing cell relative to the voltage required to operate the BPM-containing cell (Tables S1 and S2). For comparison, a Nafion-containing cell for the electrochemical reduction of 1 atm of CO$_2$ to CO while performing the OER at the anode in 0.4 M buffered KH$_2$PO$_4$)(aq) (pH = 7.3)/Nafion/0.5 M KHCO$_3$)(aq) (pH = 7.3) required 2.5 V to produce a current density of 1 mA cm$^{-2}$. Transport of K$^+$ between the anolyte and catholyte during steady-state operation would also electrodialyze the electrolytes in the Nafion-containing cell. Circulation or recirculation might potentially minimize the steady-state K$^+$ ion concentration polarization of the system, but would entail significant challenges in separation of the low concentration of the liquid product, formate, in the catholyte. In contrast, the robust product separation afforded by the BPM would allow for production of a high concentration of formate, which would be advantageous in a downstream separation process. Additionally, the Ni catalyst is not stable for OER at near-neutral pH. Use of the BPM thus relaxed the electrolyte constraints and allowed the incorporation of this active OER catalyst$^{33}$ in the device.

TiO$_2$-protected tandem III–V photoanodes have been used in a variety of cell configurations to construct high (>10%) efficiency solar-driven water-splitting cells$^{24,25}$. The $J$–$E$ performance of the cathodes in such systems$^{32,34}$ are comparable to the $J$–$E$ performance of the Pd/C nanoparticle-coated CO$_2$R cathodes used herein, providing a basis for comparison of the efficiency losses in each of the cell types in the limit of having a low overpotential, selective cathode in each system. Although the 10% efficiency for CO$_2$R reported herein is comparable in magnitude to the 10% efficiency reported for photoelectrosynthetic solar-driven water-splitting cells that use either anion exchange or BPMs$^{24,25,35}$, the efficiencies of these different electrolysers cannot be directly compared at the system level. Solar-driven water-splitting cells in alkaline electrolytes produce physically separate streams of H$_2$(g) and O$_2$(g) (either at 1 atm or under higher pressures due to electrochemical compression) from an abundant reagent (including liquid or vapor H$_2$O from humidified ambient air)$^{36,37}$ have minimal (<100 mV) voltage losses associated with the anion-exchange membrane and electrolyte, utilize relatively low (<300 mV) overpotential electrocatalysts for the OER, and thus will provide the highest $\eta_{\text{STP}}$.$^{24,38}$ Use of a BPM allows for operation of the photoanode in electrolytes at near-neutral pH values, which are less corrosive to photoelectrodes, especially for III–V compound semiconductors, relative to the alkaline electrolyte (e.g., 1.0 M KOH), and facilitates the use of relatively large area (~1 cm$^2$) photoelectrodes due to stabilization by TiO$_2$ protective coatings.$^{35}$ However, BPMs introduce additional membrane-derived voltage losses.$^{20}$ The near-neutral pH operation also entails increased overpotential losses due to the reduced activity of available OER catalysts operating under such conditions.$^{15,32,35,40}$ The available OER catalysts also obscure light and are semisoluble and unstable on the electrode surface during operation at near-neutral pH.$^{32}$ In addition, the finite ion crossovers in such cells would eventually lead to electrodialysis of the electrolyte during passive, long-term cell operation. The CO$_2$R cells evaluated herein share the same $\eta_{\text{STP}}$ limitations as solar-driven water-splitting systems that utilize a BPM having one electrolyte at near-neutral pH and the other electrolyte under either strongly alkaline or acidic conditions (Tables S1 and S2). The CO$_2$R cells moreover require that concentrated, purified (to eliminate highly electroactive, ambient O$_2$) CO$_2$ feeds are distributed over large electrode areas due to mass-transport limitations on the atmospheric CO$_2$ flux into aqueous electrolytes, and they also entail a loss of selectivity in reduction of CO$_2$ relative to H$_2$ production at atmospheric (400 ppmv) concentrations of CO$_2$ in the cathode feed. The formate would also have to be separated from the aqueous solution, as would any other water-soluble CO$_2$R product such as methanol, ethanol, or isopropanol, requiring an energy-intensive separation step. Use of flue gas as the (unsustainable) CO$_2$ source would require removal of the electroactive O$_2$ (g) as well as the flue-gas stream to remove NO$_x$, SO$_x$, Hg, and other trace flue-gas components that are either electroactive or that can poison the cathode. The gas stream would then need to be humidified and cooled to near-ambient temperatures, and the resulting gas feedstock distributed over the $\sim$10$^7$ m$^2$ area would be required to collect the incident solar photon flux necessary to reduce the CO$_2$ that is emitted from a 100 MW (electric) coal-fired power plant (see the SI for calculation details). Large storage reservoirs for the CO$_2$ would also be required to compensate for the 20% capacity factor of the solar-driven photoelectrosynthetic cell relative to the nearly continuous CO$_2$ emissions stream emanating from the power plant.

In summary, a solar-driven CO$_2$ reduction photovoltaic-assisted electrolysytic cell was demonstrated at a solar-to-fuel energy-conversion efficiency of 10% using a tandem GaAs/InGaP/TiO$_2$/NiO$_x$ photoanode in 1.0 M KOH(aq), a Pd/C nanoparticle-coated Ti mesh cathode in 2.8 M KHCO$_3$)(aq), and a BPM reducing a purified feed stream of 1 atm of CO$_2$(g). At the operational current density of 8.5 mA cm$^{-2}$, the cathode exhibited $<100$ mV overpotential and >94% Faradaic efficiency for CO$_2$ reduction to formate in 2.8 M KHCO$_3$)(aq) (pH = 8.0), the anode exhibited a $\sim$320 ± 7 mV overpotential for OER in 1.0 M KOH (aq) (pH = $\sim$13.7), and the BPM exhibited a $\sim$480 mV voltage loss with minimal product crossovers and $>$90 and $>$95% selectivity for proton and hydroxide ions, respectively. The BPM effectively coupled together two electrolysers that were separately effective for the CO$_2$R reaction and for the OER and produced lower total overpotentials and
higher efficiency than could at present be obtained in a single-electrolyte CO₂ reduction cell. The photoelectrosynthetic cells also allowed a comparative evaluation of the operational constraints associated with sustainable solar-driven CO₂ reduction systems relative to sustainable solar-driven water-splitting systems.

**ASSOCIATED CONTENT**

5 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00317.

Experimental details; calculation details; bipolar membrane and two-electrode configuration (Pd/C-coated Ti mesh/BPM/GaAs/InGaP/TiO₂/Ni) stability data; voltage loss comparison for three cell configurations; low formate crossover data; Faradaic efficiency data for large-area Pd/C-coated Ti mesh cathode and large-area bipolar membrane voltage loss data (PDF).

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The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This material is based on work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. S.A.F. acknowledges the Resnick Sustainability Institute at Caltech for a Postdoctoral Fellowship. The authors also thank N. Dalleska (Caltech) for his assistance with measurements and analysis of the ICPMS and TIC data.

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