

Photons to formate: Efficient electrochemical solar energy conversion via reduction of carbon dioxide



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ABSTRACT

The storage of solar energy as formic acid generated electrochemically from carbon dioxide has been identified as a viable solar fuel pathway. We report that this transformation can be accomplished by separating light absorption and CO₂ reduction through the use of a commercial solar panel illuminated with natural AM1.5 sunlight to power a custom closed-loop electrochemical flow cell stack. Faradaic yields for formate of up to 67% have been demonstrated in this system, yielding a solar energy to fuel thermionic conversion efficiency above 1.8%.

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1. Introduction

Artificial photosynthesis is often associated with schemes that utilize light to split water, generating hydrogen as a fuel. However, over the past decade, interest in the generation of liquid solar fuels has grown due to their enhanced energy density and improved storage properties, both of which are important attributes for dispatchable power [1]. In addition to liquid fuels, the generation of energy-dense carbon-based products provides a new source of chemical feedstocks derived from precursors other than fossil fuels [2]. However, a practical system must exceed the efficiency of natural photosynthesis, which converts up to 1% of incident sunlight to biomass [3]. Since CO₂ can be recovered in a relatively pure form from a variety of industrial processes [4], it is a prime candidate for a feedstock for solar fuel production. A second advantage to this approach is the mitigation of anthropogenically produced carbon dioxide, a greenhouse gas whose atmospheric concentrations have drastically increased in the past 200 years.

Several approaches have been employed in the light-assisted reduction of CO₂ using illuminated semiconductor electrodes, both with photoanodes to supply electrons to a dark cathode and with photocathodes to reduce the CO₂ directly [5–7]. Recently,

Panasonic claimed “a world’s top efficiency” of solar energy to formic acid conversion of 0.2% using an *n*-GaN photoanode to drive an indium cathode [8,9]. Although the long term stability of this system has not been reported, similar III–V *n*-type semiconductors tend to photodegrade in aqueous solution, limiting their usability [10].

An alternative to a photoelectrochemical system is to use an external photovoltaic (PV) array to power an electrolyzer utilizing metallic electrodes [11,12]. Only limited research has been reported using this approach [13–15]. A variety of metal electrodes have been previously examined for the generation of formate from CO₂ [16–20]. However, in general, these systems have required relatively large overpotentials, and have exhibited limited operational lifetime.

There are benefits and drawbacks to both photoelectrochemical (PEC) and coupled photovoltaic–electrochemical (PV–EC) systems, and the relative merits of both have been discussed for years, without resolution, since the cost–benefit analysis depends subtly on project specific details that may not directly be controlled by the chemistry and physics of the solar converting elements [21]. PEC cells are self-contained and do not require a separate set of electrodes to perform the electrochemical transformation. As a result, PEC systems have lower balance-of-plant costs and a higher theoretical system efficiency. However, PEC cells have severe materials constraints. High efficiency PEC cells are often achieved in the laboratory by employing single-crystal semiconductors as electrodes. Scale-up to a field-implementable system requires developing either polycrystalline, nanostructured or thin-film semiconductor electrodes. Such electrodes typically yield reduced

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activity compared to their monocrystalline counterparts. Further, it has been empirically and theoretically found [22,23] that photocorrosion is a major problem for semiconductor electrodes having band gaps providing an optical response well matched to the solar spectrum. Although a variety of chemistries have been developed to circumvent this problem, long-term cell stability can still be an issue.

PV-EC systems, such as the one described herein, do have the disadvantages of greater balance-of-plant costs and increased complexity due to the need to impedance match the various components between the photovoltaic and electrochemical cells. Proper mating of PV power output with the number and sizes of the EC cells is also difficult and may require an additional conversion step between the two. The coupling of the components, regardless of power-matching, leads to losses in the photogenerated electricity that do not occur with the simpler PEC cells [24]. However, the separation of light collection and carbon dioxide reduction into two distinct systems makes the coupling of the two into a single efficient system attractive since each subsystem can be independently optimized. The use of metal-based electrodes, in place of the semiconductor-based electrodes needed in a PEC cell allows for a high degree of control over the interfacial chemistry. This becomes especially important when one wishes to develop a system that carries out a complex chemical process such as the multielectron, multi-proton reduction of CO₂. Metal electrodes also enable a high degree of scalability with respect to both electrode area and multi-cell stack designs [25].

The present work investigates the chemical output and efficiency of an integrated system comprised of a silicon photovoltaic solar array coupled to an indium cathode-based electrochemical flow system [26] consisting of a stack of three 109 cm² electrochemical cells in series that sustainably converts carbon dioxide to formate. In this paper, we consider what should be a reasonable performance level for the integrated PV-electrolyzer system. However, the output parameters reported here provide a pragmatic base standard for all light-based CO₂ conversion systems. Only photoconversion systems, independent of design, either PV-EC or PEC, that outperform the system reported here represent a real world advancement in the production of carbon-based solar fuels.

2. Experimental

2.1. Electrochemical flow system

Three 109 cm² planar area two-electrode cells were assembled using PVC or polypropylene frames (Fig. 1), similar in design to those previously described [27]. In each cell a 0.254 cm thick expanded metal titanium folded screen with an iridium oxide electrocatalyst coating served as a spring compression anode (De Nora Tech). The back side of the anode was placed in contact with an iridium oxide-coated titanium current collector. The cathodes were each composed of an indium-based electrocatalyst coating deposited on a three-dimensional high surface area copper mesh in contact with a backplate composed of 0.0254 cm thick indium foil bonded to a 316 stainless steel current collector with silver epoxy. The total surface area of the high surface area cathode mesh is approximately 3.2×10^3 cm².

DuPont Nafion[®] 324 (Ion Power, Inc.) reinforced proton-exchange membrane was used as the cell separator. The cells were connected electrically in series and the anolyte and catholyte streams were connected in a flow system manifold that was plumbed in parallel, as depicted in Scheme 1. The flow system was constructed of ½ in. (1.27 cm) schedule 40 PVC pipe and was connected to the cells with ½ in. OD Tygon tubing. A Lightobject EWP-381312V inline pump powered by a Caswell SPC 9250

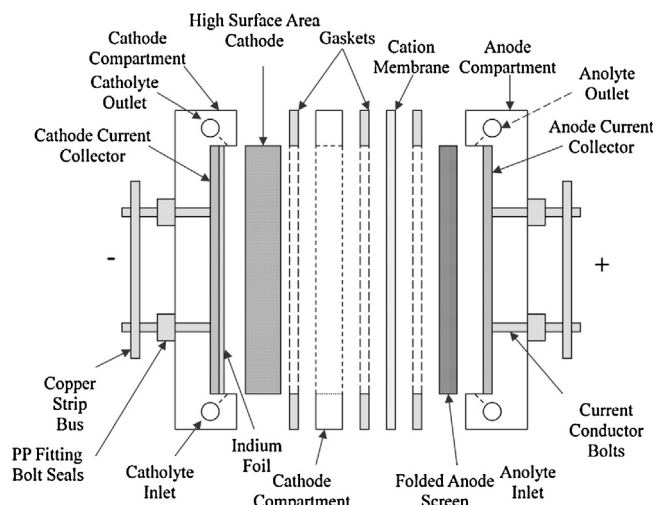
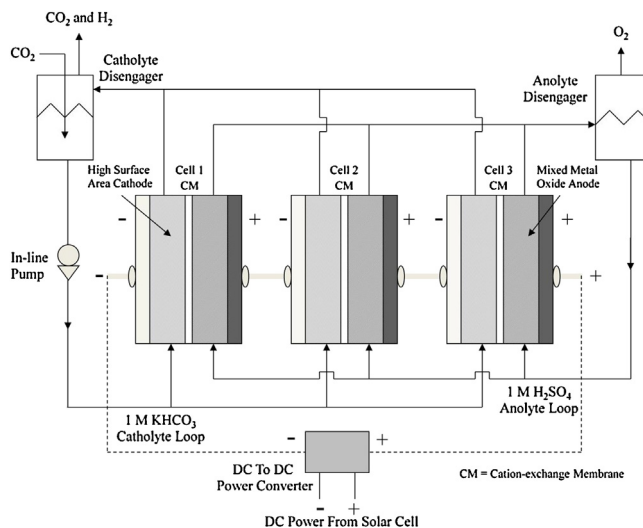


Fig. 1. Electrochemical cell configuration side view.



Scheme 1. Three cell stack wired in series with indium-based cathodes, iridium oxide-coated anodes, Nafion[®] 324 membranes, and associated anolyte and catholyte flow systems.

external power supply (12 V, 1.3 A) circulated the catholyte volume at a rate of 9 L/min, which was distributed at a rate of 3 L/min to each cell. The anolyte was not actively pumped; instead, it moved by convective gas lift circulation.

All electrolyte solutions were made using Millipore deionized water (>18 MΩ). 1 M potassium bicarbonate prepared from KHCO₃ (City Chemical, ACS reagent grade) and 1 M H₂SO₄ (95–98% sulfuric acid, Acros Organics) were used as the catholyte and anolyte, respectively. Approximately 1 L of each solution was used per run. Carbon dioxide (Atlantic States Specialty Gases, Bone Dry Grade) was bubbled into the flowing catholyte in the disengager (see Scheme 1) to maintain saturation. The anolyte was not degassed. Between runs, the cathode compartment was rinsed and kept full of deionized H₂O to prevent membrane drying and shrinking.

2.2. Power supply

The electrical system was connected as shown in Scheme 2. A 1.47 m² Suntech STP-200-18/UB-1 polycrystalline silicon solar panel (Petra Solar) was employed as the power source. Experiments were conducted under AM1.5 conditions in Monmouth Junction, New Jersey. A Mean Well SD-200B-12 DC–DC converter was connected to the solar panel through a RC Electronics R102v2

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