

Waste-to-Energy Conversion for Sustainability: Production of Hydrogen and Elimination of Chemical Wastes in Water with Solar Light

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ABSTRACT: *A Bi-doped TiO₂ anode, which is prepared from a mixed metal oxide coating deposited on Ti metal, is shown to be efficient for conventional water splitting. In this hybrid photovoltaic – electrochemical system, a photovoltaic (PV) cell is used to convert solar light to electricity which is then used to oxidize a series of phenolic compounds at the semiconductor anode to carbon dioxide with the simultaneous production of molecular hydrogen from water/proton reduction at the stainless steel cathode. Degradation of phenol in the presence of a background NaCl electrolyte produces chlorinated phenols as reaction intermediates which are subsequently oxidized completely to carbon dioxide and low-molecular weight carboxylic acids. The anodic current efficiency for the complete oxidation of phenolic compounds ranges from 3 to 17%, while the cathodic current efficiency and the energy efficiency for hydrogen gas generation range from 68 to 95% and from 30 to 70%, respectively.*

Keywords: Hydrogen, Production, Sunlight, Water Purification, Treatment, Electrochemical Water Splitting

1. INTRODUCTION

Sustainability, in general, is a very broad and loosely defined concept about ecological and environmental conservation such that vital resources that are needed for sustaining life are recycled in a nominal closed-loop cycle. The earth's hydrological cycle provides a simple roadmap. In the case of "sustainable energy" the goal is to find a renewable and sustainable source of energy that is able to be recycled in an efficient way. The generation of energy

from water, which is recycled naturally and artificially, should lead to long-term "energy sustainability."

Electrochemical water splitting powered by conventional electricity or photovoltaic arrays produces molecular hydrogen at the cathode, while water oxidation under mild conditions to oxygen, takes place at the anode in competition with the production of oxygen. An electrolytic cell, which is based on the coupling of bismuth-doped titanium dioxide anodes (BiO_x-TiO₂) with stainless

steel cathodes (SS), is characterized in terms of hydrogen and oxygen production efficiency [1-8]. In a solar-powered PV-electrochemical system, the production of molecular oxygen at the anode can be suppressed by the simultaneous oxidation and mineralization of organic compounds dissolved in water. In addition, the anodic oxidation of organic substrates will have a synergistic effect on hydrogen production at the cathode that can result in increases in the energy efficiency for H_2 generation at circum-neutral pH in the presence of dilute electrolyte solutions.

2. EXPERIMENTAL APPROACH

2.1 General Approach

The BiO_x - TiO_2 anode and SS cathode couple was immersed in the electrolyte of 50 mM NaCl (200 mL or 20 L) and the electrolyte was stirred under the continuous purging with air or nitrogen as a background carrier gas. The target substrates (e.g., phenol) were mixed in with a background electrolyte or added during the course of electrolysis. A constant cell voltage or current was applied to the electrodes with a DC power supply (HP 6263B and 6260B). For the PV-powered electrolyses, a commercial thin film, amorphous silicon PV (Silicon Solar Inc.) with a peak power output of 6.4 W_{peak} ($PV_{peak} = E_{peak} \times I_{peak}$; $E_{peak} = 8 - 10$ V; $I_{peak} = 0.95$ A) and with active surface area of 1280 cm² was used (Figure 1). A real-time solar radiation was monitored and recorded with a pyranometer (Apogee) connected to a datalogger (Campbell Scientific). Cell voltage (E_{cell}) and cell current (I_{cell}) were measured by multimeters (Fluke).

2.2 Electrode Details

The anode was prepared as follows: 1) A Ti metal sheet (Ti-Gr.2 sheet, 0.50 mm thick) was cleaned using SiC paper (120 to 240 grit) before coating with a sequence of substrates (Scheme 2a). 2) An initial surface

coating containing Ir and Ta at an Ir:Ta = mole ratio of 0.67:0.33 is deposited and annealed to the Ti base. 3) The initial metal oxide coating is sealed with SnO_2 doped with Bi at a Sn:Bi mole ratio of 0.9:0.1. 4) A tertiary surface coating of TiO_2 that is doped with Bi at a Ti:Bi mole ratio of 0.96:0.04 is layered down next with high temperature annealing. 5) The final step involves the deposition of an overcoat that contains a mixture of oxides of Ti and Bi at a Ti:Bi mole ratio of 0.9:0.1. Each successive step of coating requires a specific heat treatment regime at different temperatures and durations. Details are provided elsewhere. Two types of anode-cathode couples were used for the experiments reported herein. The first couple is composed of a single anode with an active area of contact with the electrolyte solution of 10.0×2.0 cm² and two pieces stainless steel (SS) cathodes (Hastelloy C-22) of the same size facing the both sides (i.e., a sandwich configuration) of the doubly coated anode plate with a distance of separation of 2 mm. The second configuration involves a small pilot scale reactor consisting of 5 anode plates (5 pieces $\times$ 800 cm²/piece) and 6 stainless steel cathode plates that face each other with a distance of separation of 2 mm (Scheme 2b).

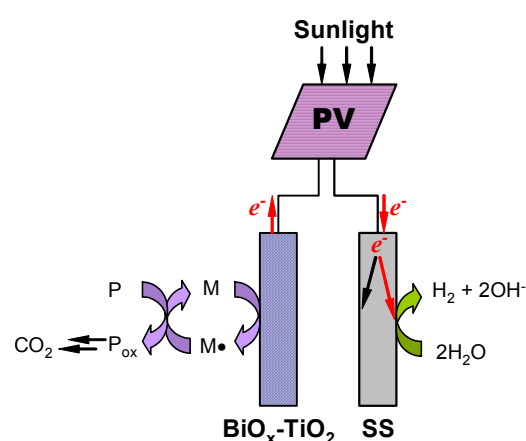


Figure 1: Schematic diagram of the hybrid PV-electrochemical system. P: pollutants, n-TiO₂: BiO_x - TiO_2 /Ti anode, SS: stainless steel cathode.

2.3 Analytical Details

The core electrochemical reactor was sealed from the ambient atmosphere. At a given rate, the headspace gas of the reactor was extracted with a peristaltic pump and pushed through a membrane inlet into a quadrupole mass spectrometry (Balzers) via a turbo pump (Pfeiffer; 5.0×10^{-6} torr). The volume percent of the headspace was calculated assuming that it was directly proportional to the ion current measured by the mass spectrometer and that the transfer of all gases through the membrane and their 70 eV electron ionization cross-sections were approximately equivalent. This assumption was validated in part since ambient air was measured to be 77% nitrogen, 17% oxygen, 5% water vapor, and 1% argon.

Aqueous organic compounds including intermediates were analyzed by a high performance liquid chromatography (HPLC, Agilent 1100 series) with a C18 column. The eluent was composed of 55% Milli-Q water (0.1 wt% acetic acid) and 45% acetonitrile at flow rate of 0.7 mL/min. Total organic carbon was determined (TOC, OI Analytical Aurora Model 1030) with an autosampler (OI Analytical Model 1096).

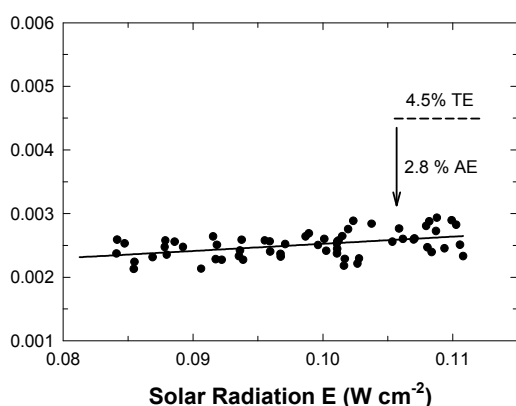


Figure 2. PV performance as a function of solar radiation. Theoretical energy conversion efficiency (TE) of the employed PV is around 4.5% and actual efficiency (AE) is about 3%.

2.4 20 L Pilot-Scale Reactor

For application to pilot or sub-pilot scale, a batch reactor of 20 L-size was prepared

where 5 anodes (each, 800 cm²) and 6 cathodes of the same size are arranged to alternatively face each other. At 60W (3V×20A) of power supply, carbon dioxide starts being released after 20 min and the rate of hydrogen production reaches ca. 3.5×10^{-3} mol/min along with hydrogen energy efficiency of 30%. The half life time of 1 mM phenol in a total volume of 20 L is < 2 min. Based on this operation condition, we can estimate the required PV areas with different efficiencies ($PV\% = P_{PV,max}/(I_{S,0} \times PV \text{ area}) \times 100$) for treating variable capacity of water/wastewater contaminated with 1 mM phenol. It is clear water treatment capacity is strongly related to the PV area and efficiency. For example, treatment of 16 metric tons of water (i.e., 1.6 kg phenol) daily (i.e., operation for 9 h/day) needs a 62 m² PV panel operating at 10% efficiency. Currently, the PV efficiencies are being improved and the 10% efficiency is most readily available. In addition, hydrogen is obtained as a potentially useful byproduct. Hydrogen production rates are affected both by the water treatment capacity and H₂ energy efficiency. Small-scale reactors are usually better than large reactors for the energy efficiency. At a H₂ energy efficiency of 60%, the treatment of 16 tons of water with a PV of 10% efficiency will yield around 1 kg of H₂ daily.

3. EXPERIMENTAL RESULTS

3.1 Overview

This hybrid photovoltaic electrochemical system is used to oxidize a series of phenolic compounds at the semiconductor anode to carbon dioxide with the simultaneous production of molecular hydrogen from water/proton reduction at the stainless steel cathode. Degradation of phenol in the presence of a background NaCl electrolyte produces chlorinated phenols as reaction intermediates which are subsequently oxidized completely to carbon

dioxide and low-molecular weight carboxylic acids.

The electrochemical degradation kinetics of a variety of organic substrates was investigated as a function of a background electrolyte NaCl vs. Na₂SO₄. The substrate degradation kinetics is found to correlate well with cell current (I_{cell}) and H₂ production energy efficiency (EE) in the presence of NaCl as the background electrolyte. In the case of Na₂SO₄, no correlation is observed and the degradation rates are substantially lower. This suggests the primary chemical oxidant is electrolyte-dependent. For example, the observed rate constants are found to be proportional to bimolecular rate constants of the chlorine radical anion and substrate-induced ΔEEs (EE with substrate – EE without substrate) in the presence of NaCl. The ΔEE arises from the active chlorine species acting as an electron shuttle with competing with the H₂ production for electrons. In the presence of the organic substrates, the active chlorine species are quenched increasing the fraction of electrons utilized for the H₂ production. be justified.

3.2 Phenolic Compound Oxidation

The degradation of the phenolic substrates follows pseudo first-order kinetics (reaction 3). The observed reaction rates ($-k_{\text{obs}}^{\text{S}}$) are structural-dependent under similar electrolysis conditions ($I_{\text{cell}} = 14 \text{ mA/cm}^2$; 50 mM NaCl).

$$\frac{d[\text{S}]}{dt} = -k_{\text{obs}}^{\text{S}}[\text{S}]$$

For example, the degradation rates of hydroquinone and 2,4,6-trichlorophenol are 4.6 and 3.7 times faster than that of phenol, respectively. On the other hand, the degradation rates of salicylic acid and benzoic acid are 2 and 250 times slower than phenol, respectively. It appears that the presence of substitution groups such as chloride and hydroxyl enhances the

degradation rate but the presence of carboxyl group decreases the rate with respect to phenol itself. Carboxylated benzene (i.e., benzoic acid) has much lower reactivity than the hydroxylated analogue (i.e., phenol), indicating the oxidative species generated at the anode have substitution group-dependent reactivity.

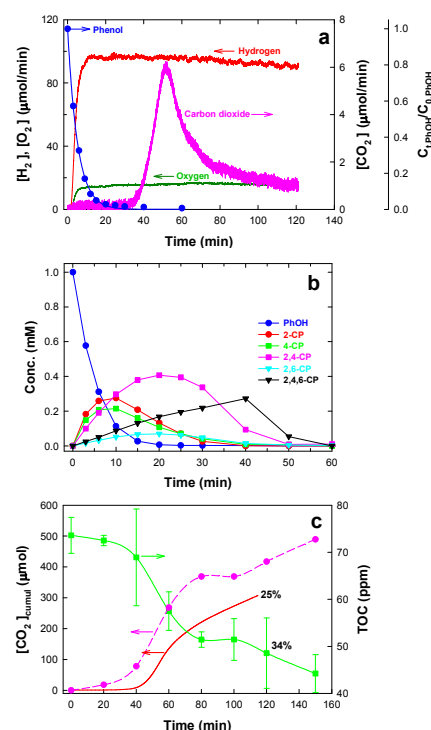


Figure 3. (a) Electrochemical oxidation of phenol to carbon dioxide and simultaneous generation of hydrogen and oxygen at $I_{\text{cell}} = 14 \text{ mA/cm}^2$. (b) Time profiles of intermediates generated during the oxidation of phenol. (c) Time profiles of accumulation of carbon dioxide and TOC decrease. $[\text{phenol}]_0 = 1 \text{ mM}$ (0.2 L); $[\text{NaCl}] = 50 \text{ mM}$; nitrogen purged continuously.

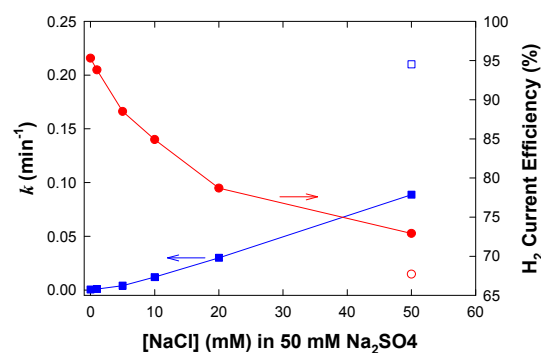


Figure 4. Effect of sodium chloride concentrations on the degradation rate (k) of phenol (■) and the current efficiency for hydrogen production (●) in 50 mM Na₂SO₄. For comparison, effect of 50 mM NaCl without Na₂SO₄ was also shown for k (□) and hydrogen production (○).

3.3 Role of Organic Compounds on H₂ Production

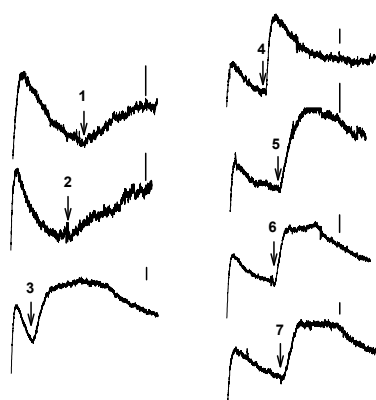


Figure 4. The relative effects of organic reductants on H₂ production rates are shown above. 1: maleic acid, 2: oxalic acid, 3: phenol, 4: catechol, 5: salicylic acid, 6: 2-chlorophenol, 7: 4-chlorophenol. The sidebars refer to hydrogen production rates of 5×10^{-6} mol/min.

In sodium sulfate medium, one-electron oxidized sulfate radical ($\text{SO}_4^{\bullet-}$) is expected to be the primary reactive species. In spite of the high redox potentials of the radical, the oxidation rates of the substrates are two orders of magnitude lower than those in the sodium chloride. There are two possibilities to explain this result. Firstly, sulfate radical is not produced at the anode surface. $\text{SO}_4^{\bullet-}$ is known to be one or two orders of magnitude faster than $\text{Cl}_2^{\bullet-}$ for the reaction with aromatic compounds.³⁴ Thus if the radical is produced, phenol degradation should have occurred. Secondly, as soon as

produced, the sulfate radical is transformed into persulfate (i.e., $\text{S}_2\text{O}_8^{2-}$). Persulfate can be homolytically split into two sulfate radicals either by photolysis or at high temperature,^{43,44} but is stable under ambient conditions. Otherwise it is readily transformed into two sulfate anions and oxygen (12) or hydrogen peroxide (13 & 14).

3.4 Demonstration & Pilot-Scale Systems

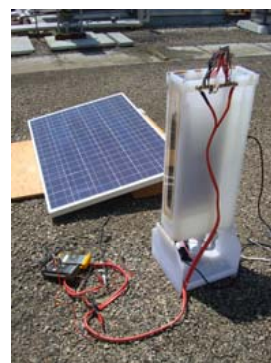


Figure 5. Photograph of a 20 L hybrid electrochemical reactor system exposed to June 2008 light in Pasadena, California.



Figure 6. Photograph of PV-driven gas bubble evolution off of an electrode array consisting of four double-sided anodes with matching stainless steel cathodes.

The sodium chloride concentration is observed to play a negative role in the cathodic hydrogen production when mixed with Na₂SO₄. At 0 mM NaCl (i.e., 50 mM Na₂SO₄ only), the current efficiency for the hydrogen production is around 96%,

whereas at 50 mM NaCl, the efficiency is lowered to be around 73%. When 50 mM NaCl and 50 mM NaCl + 50 mM Na₂O₄ are compared, the former has lower efficiency by 6 ~ 7%. This strongly confirms that the active chlorine species act as an electron-shuttle between the anode and the cathode whereas the active SO₄^{•-} radical does not act as the shuttle. When more Cl₂^{•-} radicals are generated, lower hydrogen production rates are obtained. A decrease of 23% of the hydrogen production efficiency in NaCl as compared in Na₂SO₄ might be due to the electron-shuttle effect by Cl₂^{•-} molecules. Therefore, electrolytic production of the long-lived active chlorine species has a negative effect on the cathodic process and a positive effect on the anodic oxidation process.

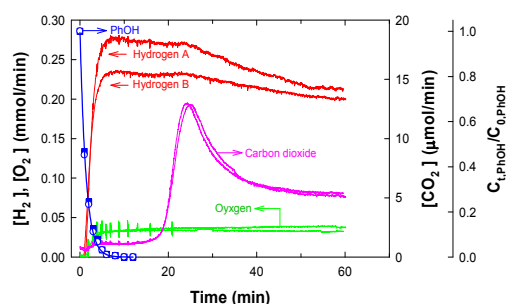


Figure 7. Solar powered oxidation of phenol to carbon dioxide and simultaneous non-stoichiometric water splitting. A 6.4W-rated photovoltaic cell with area of 1280 cm² is directly connected to the anode-cathode couple. Hydrogen A and B indicates the hydrogen production at solar energy of 1.00 ± 0.01 and 1.07 ± 0.01 W/cm², respectively.

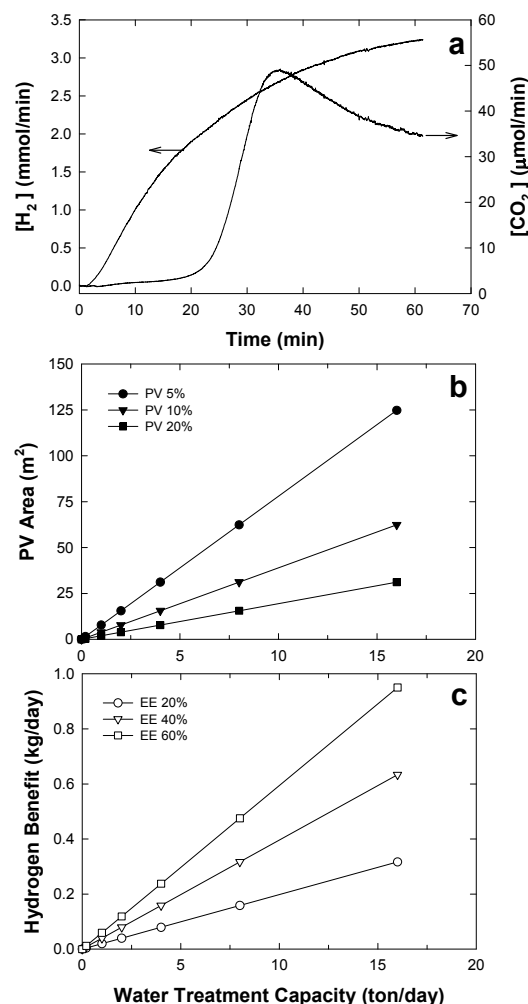


Figure 8 (a) A DC-powered electrochemical oxidation of phenol to carbon dioxide and generation of hydrogen in a sub-pilot scaled reactor (20L) at $E_{\text{cell}} = 3\text{V}$ and $I_{\text{cell}} = 20\text{A}$. $[\text{phenol}]_0 = 1\text{ mM}$. (b) Correlation between water treatment capacity and required PV area with different efficiencies. (c) Effects of water treatment capacity on the amount of hydrogen obtainable with different energy efficiencies at a PV of 10%. (b) and (c) were estimated based on the operation of the sub-pilot scaled reactor. Capacity of water treatment = 20L/h (1mM phenol) at 60W (3V×20A); daily solar utilization time (working hours) = 9 h (9 am to 6 pm, California); average solar energy input = 1100 W m^{-2} ; PV-driven energy output = $1100\text{ W/m}^2 \times \text{PV max efficiency (PV\%)} \times \text{application factor (0.7)}$.

4. DISCUSSION

It is quite feasible that the hybrid PV-electrochemical system described above could be employed for small-scale conventional water or wastewater treatment. A minimal background electrolyte (i.e., NaCl) concentration is intrinsically necessary for the electrolysis. However, sodium chloride is present in water and wastewater influents over the range of 1 to 9300 kg/day. Furthermore, wastewater inflows normally have a high conductivities in the range of 620 to 3550 $\mu\text{S}/\text{cm}$. The Caltech PV hybrid is found to work efficiently 20 mM NaCl ($\sim 1.2 \text{ g/L}$) and less. In addition, we have found detected any chlorinated gases such as methyl chloride, dichloromethane, chloroform, tetrachloride, phosgene, vinyl chloride, chlorine during the electrolysis in the presence of phenol. The chlorinated phenols, which are produced, are very rapidly converted to carbon dioxide (e.g., $k_{2,4,6\text{-ClPhOH}} / k_{\text{PhOH}} > 3.7$), water, and chloride.

Separation and purification of the evolved gas stream is the next major challenge. However, this should not prove to be difficult. Proton-exchange membranes or porous ceramic separators (e.g., Nafion or fine glass frits) can be used between the anode and cathode. Since oxygen and carbon dioxide are produced at the anode, both gases are effectively separated from hydrogen produced at the cathode provided that there is an appropriate membrane separating the two compartments. In addition, even if hydrogen is mixed with carbon dioxide, the CO_2 can be readily removed by chemical absorption process (e.g., flowing carbon dioxide gas through amine solution). This approach typically used as a CO_2 separation process in gas turbine power plants.

Current water and wastewater treatment processes include a series of pre-treatment steps to screen out solid debris and large particle suspended solids, physical

separation such as small particle coagulation, flocculation and sedimentation, floatation and clarification, biological treatment for removal of biological oxygen demand, and advanced oxidation treatment such as UV/ozone process for disinfection and reduction of chemical oxygen demand. Therefore no unit process itself could replace the overall wastewater treatment processes. The Caltech PV-electrolytic system could be used to replace conventional UV/ozone steps used for advanced oxidation and disinfection.

5. CONCLUSIONS

We have developed hybrid photovoltaic electrochemical device for the simultaneous treatment of aqueous chemical pollutants at metal-doped TiO_2 anodes coupled with the production of molecular hydrogen via water splitting at stainless steel cathodes. The anodic oxidation of aqueous chemical contaminants in water has a synergistic effect on hydrogen production that results in a 30 to 60 % increase in H_2 production efficiency. Overall energy efficiencies are comparable to those of conventional electrolysis. Similar systems could be applied directly for water and wastewater treatment where hydrogen fuel is produced as a useful, energy-rich by-product.

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