



ELSEVIER

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 29 (2012) 522 – 531

Energy

Procedia

World Hydrogen Energy Conference 2012

Development of a hydrogen evolving photocatalytic membrane

Stephen L. N. H. Rhoden*, Howard D. Mettee and Clovis A. Linkous

Youngstown State University, 1 University Plaza, Youngstown Ohio, 44515, U.S.A.

Abstract

Photoelectrochemical cells have a fundamental problem in that the thin, closely spaced laminar phases normally comprising an electrochemical cell do not readily lend themselves to penetration by external light as part of a solar energy conversion scheme. This has led to novel cell configurations that are more amenable to solar absorption. We are working on a “photocatalytic membrane,” where a single sheet comprised of two semiconductor layers combine their photopotentials to achieve a water-splitting voltage. A schematic depicting how the membrane might be configured is shown below. Light absorption in respective semiconductor layers drives oxidation on one side of the membrane and reduction on the other. Perforations filled with ion-exchange polymer allow the flow of ionic charge carriers (hydronium ion in acidic media) between anolyte and catholyte compartments. To fabricate such a photocatalytic membrane, a sequence of deposition steps must be developed where each subsequent step is compatible with the previous ones. Our strategy is to build n-type and p-type layers on opposite sides of a thin, perforated metallic sheet. A prototype device involving electrodeposition of n-WO₃ and p-CdTe on mechanically perforated stainless #304 has been fabricated. A net photovoltage of 0.8 V in aqueous acidic electrolyte was estimated.

© 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of Canadian Hydrogen and Fuel Cell Association Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: CdTe, photochemical, photochemistry, tungsten oxide, cadmium telluride, WO₃

1. Introduction

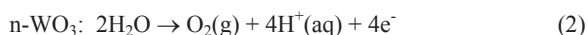
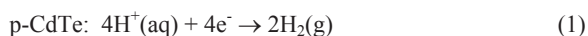
In recent years, research towards the sustainable production of hydrogen gas has increased significantly. It is widely thought that efficiently harnessing the earth’s primary source of energy (the

* Corresponding author Tel.: 1-330-941-2261; fax: 1-330-941-1579.

E-mail address: slrhoden@ysu.edu.

sun), would potentially produce enough H₂ to power the world's domestic, industrial and transport systems [1, 2, 3]. Photoelectrochemical (PEC) and photocatalytic semiconductor-based processes, optimized for performing water-splitting and CO₂ reduction, would work directly into the current photosynthetic cycle. Since the first reported photoelectrochemical solar cell [4], many reviews relating to the construction of liquid-junction semiconductor electrodes have been published [5, 6]. To this end, an ideal photochemical cell used for water-splitting will have to generate a minimum photovoltage of 1.23 V for water splitting, while demonstrating chemical stability in the PEC electrolyte and practical quantum yields. To date no single semiconductor material has proven to be robust while generating the water-splitting voltage.

A hetero-type photochemical diode should be able to overcome the water-splitting energy barrier by combining the voltage of a p-type and an n-type semiconductor connected through an ohmic contact. The critical dependence of the stability of such cells on these interfaces has also been previously discussed [7, 8]. Suitable tandem semiconductors must therefore harness the available photon energies, which are ideally equivalent to the sum of the band gaps of the n- and p-type semiconductors [9, 10, 11]. Tungsten trioxide (WO₃) and cadmium telluride (CdTe) are known stable photoelectrodes with band gaps of 2.2 eV and 1.4 eV respectively, both well suited to absorb most of the solar spectrum [12, 13]. With the photovoltages being additive, it is possible to build a semiconductor device which under illumination produces more than the 1.23 V necessary for splitting water, while remaining stable in the electrolyte of choice (shown in Equations 1 and 2).



Tungsten trioxide is one of the few semiconductors with a band gap smaller than that of titanium dioxide (TiO₂) that has successfully demonstrated the photooxidation of water [14].

Preparation of semiconductor electrodes has been accomplished by a wide variety of methods, including closed space sublimation, sol-gel films and chemical bath and vapor deposition techniques, with the semiconductor being deposited on a conducting glass substrate [15]. For the most part, these methods produce stable films, albeit at high materials and energy costs. Electrodeposition has been seen as a practical alternative, as it provides numerous advantages: film growth of any shape and size, ambient temperature deposition, and film properties can be easily altered based on bath composition, applied voltage and deposition period.

Nomenclature	
Normal hydrogen electrode	NHE
Photoelectrochemical	PEC
Saturated calomel electrode	SCE
Stainless steel	SS
Stainless steel etched with HCl	SS-HCl

2. Experimental Procedure

Stainless steel substrates were obtained from Cubbison LLC. Cadmium sulfate (CdSO_4), chloroplatinic acid hexahydrate (H_2PtCl_6) and sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) were obtained from Sigma Aldrich. Tellurium oxide (TeO_2) was obtained from Alfa Aesar. Hydrochloric acid, 30% hydrogen peroxide (H_2O_2), perchloric acid (HClO_4) and sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) were all obtained from Fisher Scientific Chemicals. Sodium hydroxide (NaOH) was purchased from VWR International LLC. Sulfuric acid (H_2SO_4) was acquired from Pharmco Aaper Co. De-ionized (DI) water was used for all rinsing, cleaning and solutions made.

Stainless steel squares (1" x 1") were first cleaned with detergent, acetone, ethanol, and were finally rinsed in DI water and then dried carefully. The stainless steel (SS) was submersed and etched in 10% v/v HCl solution (SS-HCl), followed by washing with DI water and consequent drying of surface water. The deposition of WO_3 has been adapted mainly from the work of Pauporté [16]. Enough 30% H_2O_2 was added to 25 mM Na_2WO_4 solution to achieve a concentration ratio of 0.8 of the latter to the former. This yielded a solution with a pH about 10.60. The solution was then allowed to stir vigorously while in contact with a platinum mesh for 15 minutes to allow for reduced oxygen gas evolution during electrodeposition. The solution was then acidified with perchloric acid to a pH of 1.20. Solutions were only kept for one day, and were generally made just prior to the time of the electrodeposition. Electrodeposition and photoelectrochemical experiments were done using a PAR 273A potentiostat from Ametek Inc., while stirring in a conventional 3-electrode system: SS-HCl, saturated calomel electrode (SCE) (0.2412 V vs. NHE) and a platinum gauze (110 cm^2 geometrical surface area) were the working electrode, reference electrode and counter electrode respectively. All solutions were purged with argon gas for at least 10 minutes before any experiments were done.

One side of the SS-HCl substrate was covered with Parafilm[®], and WO_3 was deposited on the other side at -0.46 V vs. SCE over a period of 1.5 hours (SS-HCl- WO_3) at 25 °C; upon completion the electrode surface was washed with ethanol, then DI water and allowed to air dry. The Parafilm was removed and the as-deposited SS-HCl- WO_3 samples were annealed at 450 °C for 1 hour. The WO_3 layer of the electrode was covered with an easily removable rubber cement, and was then allowed to air-dry overnight.

The covered SS-HCl- WO_3 was then placed in 10% v/v HCl for 10 minutes to remove the oxide layer formed on the SS-HCl face opposite WO_3 after annealing. A 1.0×10^{-4} M TeO_2 solution was made and acidified to pH 1.8 using H_2SO_4 . A water bath was used to equilibrate the temperature at 85 °C. Tellurium was cathodically deposited on the SS-HCl substrate at -0.5 V for 1 minute (Te-SS-HCl- WO_3). Immediately after Te deposition, the electrode was removed and placed into a solution of 0.5 M CdSO_4 and 1×10^{-4} M TeO_2 that had been acidified to a pH of 1.8 with sulfuric acid and heated to 85 °C. CdTe was electrodeposited from this solution onto the Te surface by holding the working Te-SS-HCl- WO_3 electrode at -0.52 V for 2 hours.

For some samples, the CdTe surface was functionalized with platinum. During the last three minutes of the CdTe electrodeposition, the solution was cooled to 25 °C and H_2PtCl_6 was added to make the solution 25 mM in the acid. The increase in current density was used to determine the amount of deposited Pt. Both Te and CdTe deposition was done with moderate stirring using a Teflon[®]-coated stir bar, while WO_3 was deposited without stirring. After the final deposition, CdTe-Te-SS-HCl- WO_3 electrode was rinsed with ethanol, then DI water and subsequently allowed to air dry. The rubber cement

layer placed on the WO_3 was removed before a final annealing of the dual sided electrode was performed at $350\text{ }^\circ\text{C}$ under an argon atmosphere. We may have included some air in our oven, as it was not air tight; this however, will be discussed later.

Photoelectrochemical hydrogen production was done in various electrolytes, using a two-sided Teflon[®] cell with Pyrex[®] windows, but once the electrode was placed inside, did not allow mixing of solutions in each half-cell. An inlet and an outlet were drilled into both sides of the half-cell. Hydrogen and oxygen gas evolution were measured using an Inficon Ecotec 3000 leak detection system with gas sniffer probe. X-ray diffraction patterns were taken using Bruker-Nonius D8 Advance Powder Diffractometer with Cu K- α radiation, with diffraction patterns obtained between a 2θ range from 20 to 80 degrees. Analytical electron microscopy images were taken using a JEOL JIB 4500 Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) with energy dispersive x-rays (EDX) detector for elemental analysis.

3. Results and discussion

3.1. Electrode schematics

The aim of this work was to produce a hetero-type PEC test electrode such as the schematic shown in Figure 1. Careful engineering of such an electrode would require sequential deposition of layers on the substrate, by masking the side opposite to which the deposition is to be effected. It was noted that CdTe directly electrodeposited onto SS (1a) did not make good ohmic contact. It was necessary to pre-deposit a layer of Te or another high work-function metal, as shown in Figure 1b. Similar findings have been made recently by others [17, 18, 19]. Initiating structural conversion of the as-deposited WO_3 and CdTe samples was frequently done, by annealing at $450\text{ }^\circ\text{C}$ and then $350\text{ }^\circ\text{C}$ respective to each semiconductor.



Figure 1. Cross-sectional schematic of hetero-type PEC electrodes with n-type tungsten oxide and p-type cadmium telluride on opposite sides of a stainless steel substrate.

3.2. Scanning electron microscopy and energy dispersive x-ray studies

Electrodeposition of amorphous WO_3 from Na_2WO_4 solutions followed by annealing has been demonstrated in previous work [16] as an efficient and controlled method of producing highly crystalline photoactive WO_3 films on indium-doped tin oxide (ITO). Similar results have been achieved by our research group, but on HCl-etched, stainless steel substrates. In the SEM micrographs of SS-HCl- WO_3 shown in Figure 2, it is demonstrated that the process developed for regular ITO previously used by Pauporté can be adapted to SS-HCl substrates. There is also the possibility that an ITO conducting layer may degrade the WO_3 layer by sodium ion migration from the soda lime glass to form Na_2WO_4 , which is highly soluble in aqueous media [20].

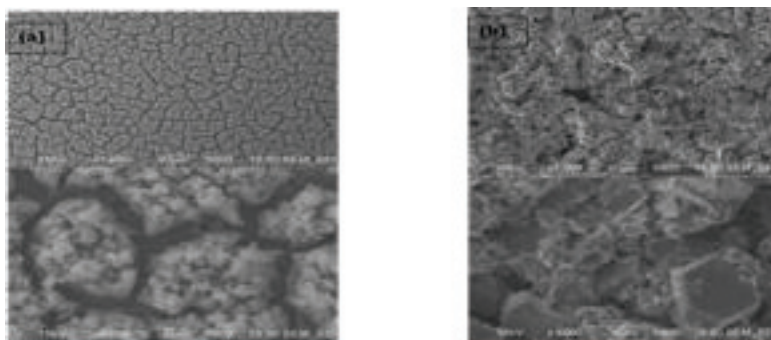


Figure 2. SEM pictures of SS-HCl- WO_3 as deposited from 25 mM Na_2WO_4 in 30% H_2O_2 , (concentration ratio of 0.8) acidified to a pH of 1.20 with H_2SO_4 . In a) before annealing, and b) after 450 °C annealing.

Electrodeposition of CdTe has been known for some time [21,22]. In our studies the deposition of Te from HTeO_2^+ -containing solutions occurred at less negative potentials in comparison to the deposition of Cd ions on the SS-HCl substrate. Good quality continuous films could be deposited by holding the potential at -0.46 V vs SCE for various times. The electrodeposition potential determines the relative amounts of Cd and Te, with potentials negative of -0.50 V giving films rich in Cd, and those more positive of -0.42 V giving films rich in Te. The films electrodeposited at -0.46 V were shown to have equal amounts of Cd and Te.

Representative EDX mapping data of CdTe photocathodes deposited on SS-HCl and on SS-HCl-Te-CdTe substrates are shown in Table 1. The Cd and Te were almost stoichiometric in content as measured by EDX in samples b and c. Sample c had a higher Te atomic percent, which is attributed to the deposition of the Te underlayer used to make an ohmic contact to the surface. All the other elements found are known to be characteristic of stainless steel 304. Carbon present in the spectrum was from using carbon tape for sample adhesion to the SEM sample platform. Oxygen present in the spectra may have been due to the negligible formation of some surface cadmium tellurates and possibly cadmium oxide [23]. This oxygen may have been from the atmosphere, as a non-airtight oven was used for annealing. Notwithstanding, electrodeposition does give excellent control for producing high purity CdTe thin films. The deposition of Cd metal is favored the further negative the voltage is held, while Te metal deposition is preferred at more positive potentials. Deposition potential, hydrodynamic conditions,

temperature and solution concentration all have a bearing on CdTe semiconductor thin film composition [24, 25]. One may target a specific composition of the p-type CdTe films to a very high degree. Our chosen conditions of 85 °C, 0.5 M CdSO₄, 1 x 10⁻⁴ M TeO₂, a slow stir rate, and a pH of 1.8 gave reproducible films which were robust enough for PEC testing after annealing.

Table 1. EDX mapping of CdTe photocathodes deposited on SS-HCl and on SS-HCl-Te-CdTe substrates.

a) SS-HCl			b) SS-HCl-CdTe			SS-HCl-Te-CdTe		
Element	Wt%	At%	Element	Wt%	At%	Element	Wt%	At%
C _K	3.47	12.53	C _K	10.97	35.41	C _K	10.97	34.43
O _K	6.10	16.54	O _K	4.18	10.13	O _K	6.32	14.89
Al _K	0.33	0.45	Al _K	0.32	0.46	Al _K	0.38	0.53
Si _K	0.40	0.48	Si _K	0.42	0.58	Si _K	0.81	1.09
Mo _K	0.32	0.13	Mo _L	0.74	0.30	Mo _L	0.44	0.17
Cr _K	16.00	13.42	Cd _L	7.33	2.53	Cd _L	7.52	2.52
Fe _K	65.04	51.01	Te _L	7.48	2.27	Te _L	10.44	3.08
Ni _K	8.34	5.44	Cr _K	14.61	10.89	Cr _K	13.89	10.06
			Fe _K	53.95	37.43	Fe _K	49.23	33.22

The SEM micrographs in Figure 3 show the effect of heat treatment on the SS-HCl-Te-CdTe electrodes deposited at 0.50 V relative to SCE. The images are very typical of electrodeposited CdTe thin films, almost identical to those taken by Rajeshwar [26]. A decrease in the cracks and/or grain boundaries in the annealed SS-HCl-Te-CdTe thin film (Figure 3b), as compared to the as-deposited sample (Figure 3a) was observed. Also, the micrographs show very small particle size, which may improve the number of catalytic sites for water-splitting.

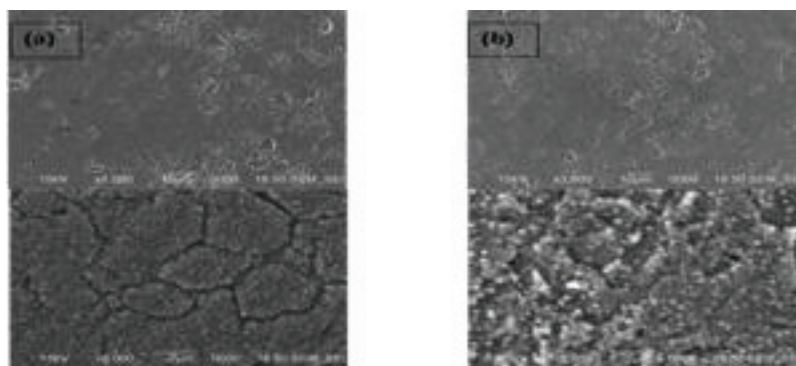


Figure 3. Scanning electron micrographs of a) as-deposited SS-HCl-Te-CdTe , and b) SS-HCl-Te-CdTe after annealing at 350 °C in argon.

3.3. X-ray diffraction analysis

XRD analysis, shown in Figure 4, has diffraction peaks characteristic of a hexagonal CdTe structure. Peaks for an Fe-Cr alloy are noted in all samples from the substrate SS-HCl ($2\theta = 43^\circ$, 52° and 75°). Tellurium deposition on the substrate gave a peak at about $2\theta = 27^\circ$, and was found in all SS-HCl-Te based photocathodes produced. Signature peaks for CdTe were found at $2\theta = 24^\circ$, 39° , 47° and 76° which are consistent with the structure assumed [26, 27]. A peak related to CdO was found at $2\theta = 44^\circ$.

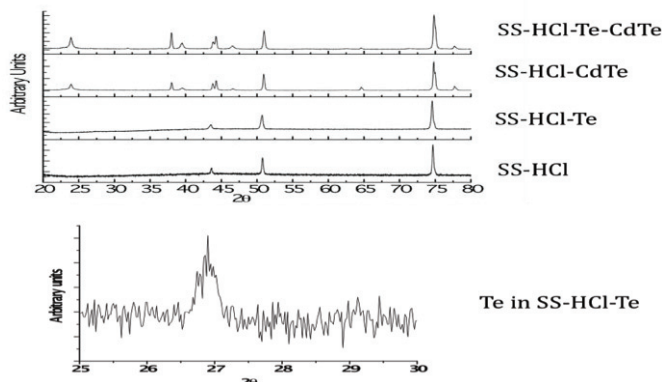


Figure 4. X-ray diffraction patterns of a) SS-HCl, b) SS-HCl-Te, c) SS-HCl-CdTe, and d) SS-HCl-Te-CdTe. The inset shows the presence of Te in the thin films.

3.4. Photoelectrochemistry

SS-HCl- WO_3 electrodes demonstrated high stability in 0.1 M H_2SO_4 within the cyclic voltammetric testing range (Figure 5). The stability of WO_3 in acidic media was demonstrated over 10 cycles sweeping from -0.3 V to +1.0 V (not shown here). Cyclic voltammetry experiments were done using a SS-based working electrode, SCE reference and platinum gauze as the counter electrode for all experiments. Under illumination, a -0.6 V photovoltage was measured for the onset of oxygen evolution

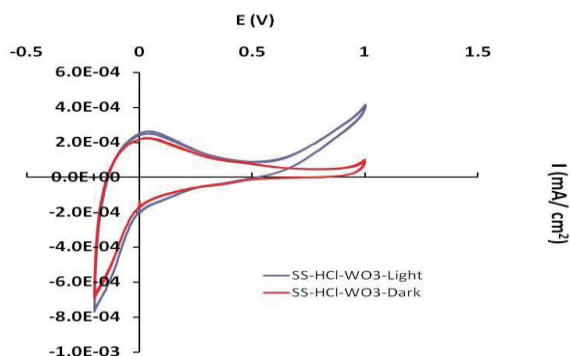


Figure 5. Photoelectrochemistry of SS-HCl- WO_3 . Conditions: 0.1 M H_2SO_4 sweep rate 10 mV/s from -0.3 to +1.3 V vs SCE, dark and under illumination.

under illumination from the light source. Optimization of this SS-HCl-WO₃ electrode could lead to a lower onset voltage of the oxygen evolution reaction, giving greater than half the potential necessary for splitting water.

Figure 6a shows the cyclic voltammetric I-V curve for SS-HCl-CdTe in 0.1 M H₂SO₄. Hydrogen evolution onset occurred at -0.2 V, and further sweeping negative gave a significant photoinduced current. Samples illuminated with the 1000 W continuous spectrum light source demonstrated a 3×10^{-3} mA/cm² amplitude increase at 1.0 V. In Figure 6b shows that when Te ohmic contacts were electrodeposited between the semiconductor and the SS-HCl substrates (SS-HCl-Te-CdTe), about a +0.2 V photovoltage was realized when its surface was illuminated. For samples functionalized with Pt electrocatalyst, there was an almost three-fold increase in the photocurrent realized for the SS-HCl-Te-CdTe electrodes. The platinization of the CdTe semiconductor increased kinetics of H₂ gas evolution significantly, although optimization of catalyst loading is important if low production costs are to be achieved.

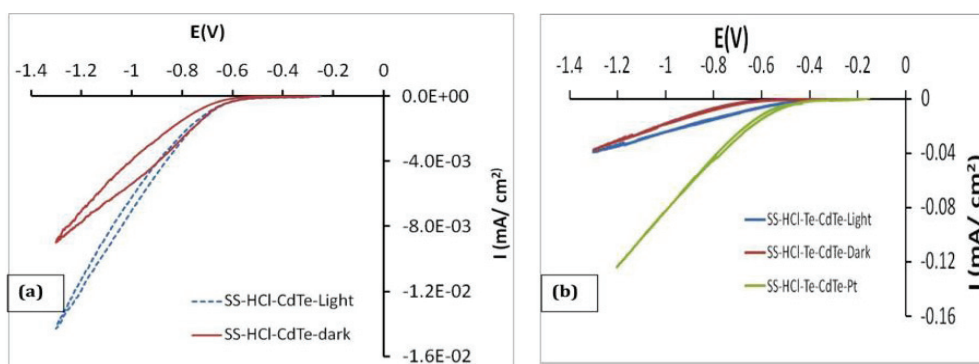


Figure 6. Photoelectrochemistry of a) SS-HCl-CdTe and b) SS-HCl-Te-CdTe with and without platinum. Conditions: 0.1 M H₂SO₄ sweep rate 10 mV/s from -0.3 to -1.3 V vs SCE, in the dark and under illumination.

Having tested both of the electrodeposited semiconductor electrodes separately, it was time to prepare and test the dual sided photocatalytic membrane, where p-type and n-type layers are placed on opposite sides of the stainless steel substrate. Accordingly, n-WO₃ and platinized p-CdTe with Te underlayer were deposited as described previously onto a 6.25 cm² square substrate and mounted in a Teflon cell with windows on both sides for dual face illumination. Gases detected by the gas leak mass spectrometer and the expected potential for performing redox chemistry on the specific electrolyte with the dual-sided electrode under 1000 W illumination are organized in Table 2.

Table 2. Gas evolution experiments based on gas leak detector from dual 1000W illumination WO₃-SS-HCl-Te-CdTe cell.

Electrolyte	Gas Detected/ Comments	Standard Reduction Potential (V vs NHE)
0.001 M benzhydroquinone	H ₂ /colorless to brown	0.599
1 M (HD ₂ O ⁺) ₂ (SO ₄ ²⁻)	H ₂ /HD/O ₂	1.230

The dual sided electrode evolved H₂ gas from the CdTe side of the cell while hydroquinone was oxidized to benzoquinone on the WO₃ side. For experiments done in acidified D₂O solution, the electrode evolved H₂, HD and O₂ from both its faces. The SS-HCl-Te-CdTe electrode showed some visible decay after testing in the acidified solution. The SS-HCl-WO₃ electrode did not however show any difference in its physical appearance. It should also be noted, that on electrolyzing hydroquinone, both faces of the electrode did not show any noticeable decomposition based on visual inspection. This system has shown utility and stability for performing redox chemistry on organic molecules, and should require further study to ascertain its sustainability if introduced to a prolonged testing environment.

Conclusion

Controlling microstructure and composition in an attempt to increase ohmic contact between semiconductor and substrate was demonstrated in the abovementioned research. A 200 mV photovoltage was seen on illumination of SS-HCl-Te-CdTe. This approach is similar to that studied by Mettee et al., who previously showed that n-type Fe₂O₃ and p-type GaP as paired electrodes could effectively evolve H₂ gas from Na₂SO₄ solutions upon illumination [28]. Achieving a steady-state photopotential that can split water into H₂ and O₂ gas is of much interest. Our work in the future would necessitate the separation of the electrodes into separate compartments using a novel membrane with perforations.

Acknowledgments

The authors would like to thank Paul Zandhuis, Charles Taylor and Christopher Matranga at the National Energy Technology Lab, Pittsburgh, PA, for their many helpful suggestions. Many thanks go to the YSU Structure & Chemical Instrumentation facility and its personnel for their effort and time. Funding from the U.S. Department of Energy under contract number DE-EE-0004094, "Advanced Automotive Fuels," and URS subcontract #RES1000286 in support of National Energy Technology Laboratory is gratefully acknowledged.

References

- [1] Licht S, Chitayat O, Bergmann H, Dick A, Ayub H, Ghosh S. Efficient STEP (solar thermal electrochemical photo) production of hydrogen – an economic assessment. *Int J Hydrogen Energy* 2010;35: 10867.
- [2] Nozik A, Miller J. Introduction to solar photon conversion. *Chem Rev* 2010;110:6443.
- [3] Bockris JO'M, Handley L. On photo fuel. *Energy Conv* 1978;18:1.
- [4] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972;238:37.
- [5] Chen X, Shen S, Guo L, Mao S. Semiconductor-based photocatalytic hydrogen generation. *Chem Rev* 2010;110:6570.
- [6] Nozik AJ, Memming R. Physical chemistry of semiconductor–liquid interfaces. *Phys Chem* 1996;100:13061.
- [7] Gerischer H. Electrochemical photo and solar cells principles and some experiments. *J Electroanal Chem* 1975;58:263.
- [8] Park S, Barber, Thermodynamic stabilities of semiconductor electrodes. *J. Electroanal Chem* 1979;99:67.
- [9] Nozik AJ. Photochemical diodes. *App Phys Lett* 1977;30:567.
- [10] Bard AJ. Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. *J Photochem* 1979;10:59.
- [11] Wrighton MS, Bocarsly AB, Bolts JM, Ellis AB, Legg KD. *Electrochem Soc Proc* 1977;77-3:138.
- [12] Alexander BD, Kuelsza PJ, Rutkowska I, Solarska R, Augustynski J. Metal oxide photoanodes for solar hydrogen production. *J Mater Chem* 2008;18:2298.

-
- [13] Santato C, Odziemkowski M, Ulmann M, Augustynski J. Crystallographically oriented mesoporous WO₃ films: synthesis, characterization, and applications. *J Am Chem Soc* 2001;123:10639.
- [14] Ostachaviciute S, Baltrusaitis J, Valatka E. Photoactive WO₃ and Se-WO₃ thin films for photoelectrochemical oxidation of organic compounds. *J Appl Electrochem* 2010;40:1337.
- [15] Granqvist C. Electrochromic tungsten oxide films: Review of progress 1993–1998. *Sol Energy Mater Sol Cells* 2000;60:201.
- [16] Pauporté T. A Simplified method for WO₃ electrodeposition. *J Electrochem Soc* 2002;149: C539-C545.
- [17] Rakshani AE, Makdisi Y, Mathew X, Mathews N.R. Charge transport mechanisms in Au–CdTe space-charge-limited schottky diodes. *Phy Stat Sol* 1998;168:177.
- [18] Gregory BW, Norton ML, Stickney JL. Thin-layer electrochemical studies of the underpotential deposition of cadmium and tellurium on polycrystalline Au, Pt and Cu electrodes. *J Electroanal Chem* 1990;293:85.
- [19] Chen JH, Wan CC. Dependence of the composition of CdTe semiconductor on conditions of electrodeposition. *J Electroanal Chem* 1994;365:87.
- [20] Yamanaka K. Degradation caused by substrate glass in WO₃ electrochromic devices. *J Appl Phys* 1983;54:1128.
- [21] Panicker MPR, Knaster M, Kroger F. Cathodic deposition of CdTe from aqueous electrolytes. *J Electrochem Soc* 1978;125:566.
- [22] Gregory BW, Stickney J L. Electrochemical atomic layer epitaxy (ECALE). *J Electroanal Chem* 1991;300:543.
- [23] Sharma RK, Singh G, Rastogi AC. Pulsed electrodeposition of CdTe thin films: effect of pulse parameters over structure, stoichiometry and optical absorption. *Sol Energy Mater & Sol Cells* 2004;82:201.
- [24] Lepellier C, Lincot D. New facets of CdTe electrodeposition in acidic solutions with higher tellurium concentrations. *J Electrochem Soc* 2004;151:C348.
- [25] Lepellier C, Cowache P, Guillemoles JF, Gibson N, Özsan E, Lincot D. Fast electrodeposition route for cadmium telluride solar cells . *Thin Solid Films* 2000;361-362:118.
- [26] Bhattacharya RN, Rajeshwar K. Electrodeposition of CdTe thin films. *J Electrochem Soc* 1984;131:2032.
- [27] Yang S, Chou J, Ueng H. Influence of electrodeposition potential and heat treatment on structural properties of CdTe films . *Thin Solid Films* 2010;518:4197.
- [28] Mettee HD, Otvos JW and Calvin M. Solar induced water splitting with p/n heterotype photochemical diodes: n-Fe₂O₃/p-GaP . *Sol Energy Mater* 1981;4:443.