Importance of Oxygen Measurements during Photoelectrochemical Water-Splitting Reactions

In pursuit of clean and renewable energy sources, harvesting solar energy has been recognized as the most sustainable route. However, the diffuse and intermittent nature of solar energy reduces the overall dependency and utilization. A potential solution for maximum utilization of solar energy is to directly convert it into storable fuels in terms of chemical bonds (such as hydrogen from water). In this context, solar-driven photoelectrochemical (PEC) water splitting is a promising approach that can potentially commercialize hydrogen production from renewables. Since the demonstration of PEC water oxidation on an n-type rutile TiO$_2$ semiconductor electrode by Honda--Fujishima in the early 1970s, PEC water splitting on various semiconducting materials has been widely studied. A large fraction of technologically important semiconductors such as Si and other III--V semiconductors are not capable of driving unassisted (without bias) PEC water splitting due to their limited photocurrent produced by light illumination. Hence, it is important to utilize series-connected or tandem light-absorbing devices to achieve the photocurrent of ∼1.7−1.8 V that is required to perform unassisted PEC water-splitting reaction. Therefore, PEC devices based on tandem amorphous silicon (a-Si) and III–V-based semiconductors have been used for water splitting, and overall solar to hydrogen (SHT) efficiencies of above 10% have been reported.

However, the instability of these PEC devices prohibits their practical use for solar-driven water splitting. Almost all nonoxide semiconductors such as Si, Ge, GaAs, InGaN, GaP, etc. continue to suffer from photocorrosion under harsh reaction conditions (highly acidic/basic electrolytes at a potential > 1.8 V). In order to improve the stability of photoelectrodes, various protection layers including metals, metal oxides, and carbon materials have been widely implemented that enhanced the stability of photoelectrodes to a few hours. Yet, most of the PEC stability testing has been performed primarily by monitoring the photocurrent density or the amount of H$_2$ produced, and not much importance has been given to O$_2$ produced. Complications in measuring the O$_2$ during the reaction is understandable, but relying only on current density and H$_2$ production rate may be erroneous especially due to the probable oxidation of the semiconductor rather than water.

In this work, we provide evidence on the importance of O$_2$ measurements during PEC water-splitting experiments and demonstrate how the current density and H$_2$ measurements may distort and lead to erroneous stability data over time. To prove the concept, we performed a series of PEC water-splitting experiments by employing a triple-junction (3J) thin film as a surface-protection layer for the 3J photoanode. The PEC experiments with and without the surface-protection layer demonstrate that the 3J photoanode corrodes over time, indicating that the 3J photoanode does not oxidize the water, but as a sacrificial inorganic compound, the photoanode is corroded through self-oxidation. This can be evident only through O$_2$ measurements as we discovered how photocurrent or H$_2$ measurements could be misleading. Finally, we also employed a thick Ti foil (0.25 mm thickness) as a surface-protection layer for the 3J photoanode that showed true water-splitting activity, as evidenced by the stoichiometric ratio (2:1) of H$_2$ and O$_2$ gases. Overall, we believe that our finding will encourage researchers working in the field of water splitting to conduct the additionally desired step of measuring both the H$_2$ and O$_2$ gases and quantify them with the stoichiometric ratio of 2:1 to demonstrate the stability and set a standard method for evaluating the true water splitting.

Figure 1a presents the schematic structure of the 3J photoanode in which the light absorption takes place on the front side whereas water oxidation reaction takes place on the surface of the OER catalyst deposited on the back side of the cell. Before measuring the PEC performance, photovoltatic (PV) characteristics of the InGaP/InGaAs/Ge solar cell were measured in air under AM 1.5G illumination (Figure 1b).

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3J photoanode with and without a protection layer as follows: (a) a 3J photoanode without a surface-protection layer; (b) a 3J photoanode with an ALD ∼40 nm thick TiO2 protection layer; (c) a 3J photoanode with a thick Ti foil (0.25 mm) protection layer. All of the samples were coated with 5 nm thick sputtered Pt as an oxygen evolution reaction (OER) catalyst.

(A) PEC Water Splitting without a Surface-Protection Layer.

The PEC water-splitting performance of the 3J photoanode was tested using cyclic voltammetry (CV) in a gas-tight quartz cell without any uncompensated resistance (iR) correction. The three-electrode measurement setup consists of a Pt counter electrode, a Ag/AgCl reference electrode, and the 3J photoanode as a working electrode in 1.0 M Na2SO4 (pH ≈ 7) aqueous electrolyte under 1 sun AM 1.5G illumination. During PEC measurements, the light-harvesting side is illuminated through a thin quartz substrate (0.5 mm thick), while the Pt catalyst on the back side of the photoanode is in contact with the electrolyte to drive the OER. As shown in Figure 2a, the 3J photoanode exhibits a Jsc and Voc of 9.5 mA/cm2 and 2.2 V, respectively, and shows a maximum power conversion efficiency (PCE) of 12.4%. The Voc of 2.2 V for the PEC cell is ∼0.2 V less than the Voc measured for PV cell in air, which is mainly attributed to kinetic overpotential losses.33 The PEC stability is evaluated using a chronoamperometry (CA) test at a potential of 0.61 V vs RHE under 1 sun illumination (Figure 2b). As displayed in Figure 2b, the 3J photoanode without a protection layer exhibits stable photocurrent density for over 10 h of continuous reaction. Besides, H2 gas produced during the reaction was measured using an online GC. The H2 production rate is consistent with the photocurrent trend and also found to be stable as a function of reaction time (Figure 1b). Most of the articles published on PEC water splitting consistently report the photocurrent or H2 production-based results without accounting for the O2 production. We further measured the O2 production during the PEC water-splitting reaction to confirm whether the reaction occurred through a true water-splitting mechanism with a proper H2/O2 ratio of 2:1. Figure 2c shows the O2 production and H2/O2 ratio obtained during the PEC reaction using a Pt-coated 3J photoanode without a protection layer. Unexpectedly, O2 production significantly drops within 30 min of reaction time and no further O2 is detected. Thus, the H2/O2 ratio is quite deviated from the expected 2:1 ratio for water splitting. Therefore, only relying on photocurrent and H2 production measurements without considering O2 production can be misleading. Furthermore, this problem is accentuated when the experiment is conducted in a two-electrode setup without any applied bias (Supporting Information: Figure S1). As shown in Figure S1, the STH efficiency based on the photocurrent and H2 production rate was calculated to be ∼9.84 and 9.24%, respectively. Overall, the device is stable for more than 6 h without any obvious degradation in photocurrent density or H2 production rate. However, because no O2 was produced during the reaction, the STH efficiency numbers do not have any meaning. Here it also important to point out that accurate efficiency determination for water splitting becomes difficult when operated with a bias (in a three-electrode setup) and under half-cell conditions because the counter electrode is not maintained at a constant bias.

(B) PEC Water Splitting with ALD-TiO2 Protection.

ALD amorphous TiO2 thin films have been widely used to protect III–V-based PEC cells with reported stability up to 100 h.19,20 These thin TiO2 films are termed “leaky oxides”, referring to the increase in conductivity due to the amorphous nature.34–36 Therefore, we carried out PEC stability tests on an ALD-TiO2-protected 3J photoanode. The ALD-TiO2 films were deposited at 150 °C for 1000 cycles using titanium tetraisopropyl oxide.
(TIIP) as a precursor and H₂O as the reactant. The dosing time was kept at 1 s for TIIP and 0.1 s for H₂O. The thickness of the TiO₂ layer was ∼40 nm as determined by electron microscopy (Supporting Information: Figures S2 and S3). A 5 nm thick Pt catalyst was deposited (by sputtering) on top of TiO₂ as an OER catalyst. Figure 3a shows the CV curve of the ALD-TiO₂-protected 3J photoanode in 1.0 M Na₂SO₄ (pH ≈ 7) under AM 1.5G illumination. At 0 V vs RHE, we observed a photocurrent density of ∼7.7 mA/cm², and the light-limiting photocurrent saturated to ∼9.4 mA/cm² at 0.2 V vs RHE. The PEC stability measurement was carried out using a CA test under identical conditions as the previous test. The photocurrent density and H₂ production rate were found to be stable for up to 8 h (Figure 3b). However, as shown in Figure 3c, the stable O₂ production rate was observed during the initial ∼1.5 h with a H₂/O₂ ratio of 2:1, and afterward, the O₂ production rate abruptly dropped to zero. Yet, as noticed above, the photocurrent density and the H₂ production rate did not show evidence of instability. Hence, O₂ gas should be measured throughout the total duration of the experiment and not at a selected time frame.

The results of experiments (A) and (B) indicate that upon contact with the electrolyte the 3J photoanode does not oxidize water but acts as a sacrificial compound. Instead of water photo-oxidation, the preferred reaction could be the Ge photo-oxidation, which is similar to that of sacrificial agents in powder-based photocatalysts. To date, powder photocatalysts demonstrate very low solar energy conversion, which leads to the use of sacrificial agents as electron donors (hole traps) for H₂ production. The presence of sacrificial donors drove researchers to probe the reductive/oxidative cycles selectively and understand the electron-transfer mechanism. However, the use of sacrificial agents does not represent true water-splitting as the oxidative process involves oxidation of the sacrificial agent (forming CO₂) rather than oxidizing the water to form O₂. In principle, a water-splitting reaction should yield H₂ and O₂ in a stoichiometric ratio of 2:1, which is simply not in the case when employing any form of sacrificial agent. Such discrepancies have been recently highlighted, where the authors observed that the performance of the photocatalysts in the presence of electron donors is not comparable, and hence, the knowledge acquired by employing such electron donors may not be transferrable.

In this particular case, Ge was used as a sacrificial compound that eventually destroyed the photoelectrode. The photo-oxidation of the Ge layer during PEC reaction is illustrated in Scheme 1. Photogenerated holes (h⁺) oxidize the semiconductor first, rather than water molecules. This is dependent on the position of ϕ₉₉₉₉ (oxidation potential) relative to ϕ₉₉₉₉(O₂/H₂O) and ϕ₉₉₉₉(reduction) relative to ϕ₉₉₉₉(H⁺/H₂). For Ge, the oxidation potential is ∼−0.1 V vs NHE. Thus, photogenerated holes would rather oxidize Ge than water. In this case, the reaction may proceed as given in eqs 1–3

\[
\text{Ge} + 2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{GeO}_2 + 4\text{H}^+ \\
(E^\circ = -0.01; \Delta G^\circ = -nF \Delta E^\circ = 3.86 \text{ kJ/mol})
\]

\[
\text{Ge} + 3\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{H}_2\text{GeO}_3 + 4\text{H}^+ \\
(E^\circ = -0.13; \Delta G^\circ = -nF \Delta E^\circ = 50.18 \text{ kJ/mol})
\]

\[
\text{Ge} + \text{H}_2\text{O} + 2\text{h}^+ \rightarrow \text{GeO} + 2\text{H}^+ \\
(E^\circ = -0.29; \Delta G^\circ = -nF \Delta E^\circ = 55.97 \text{ kJ/mol})
\]

In the case of semiconductors like Si, the oxidation leads to the formation of metal oxide (SiO₂) on the surface, which acts...
as a passivation layer. However, in the case of Ge, the amorphous GeOx formed on the surface is known to be water-soluble, thus causing the entire layer to slowly disintegrate/etch away during reaction. We have observed that these unprotected 3J photoanode cells disintegrate during the PEC reaction and start breaking into small pieces.

To further analyze the corrosion process, the 3J photoanode was studied by scanning transmission electron microscopy (STEM). Figure 4a,b shows cross-sectional STEM high-angle annular dark-field imaging (HAADF) images of the 3J (InGaP/InGaAs/Ge/Au) cell after ~10 h of PEC reaction of Figure 2b. We observe that a thick irregular amorphous layer forms on the bottom surface of the 3J cell. Elemental mapping using energy filtering in Figure 4c gives a clear picture of the extent of corrosion. The elemental mapping indicates that the thick amorphous structure (marked as #1) is a mixture of GeOx/GaOx, as indicated by the presence of oxygen, gallium, and a small concentration of germanium and arsenic. Thus, the photocorrosion and mechanical disintegration of the 3J cell leads to loss of bottom subcells InGaAs and Ge, respectively. The second layer is observed to be the top subcell of InGaP, as indicated by the strong concentration of indium and phosphorus. Finally, the third layer (layer #3) looks like the capping layer, which is GaAs, as indicated by the presence of gallium and arsenic.

Scheme 1. Energy Diagram of the Oxidation (ϕox) and Reduction Potentials (ϕred) of Ge versus the Oxidation (O2/H2O) and Reduction (H+/H2) Potentials of Water

“Photogenerated holes (h+) from the 3J cell oxidize the semiconductor rather than water.

(C) PEC Water Splitting with Ti Foil Protection. Finally, we protected the 3J photoanode using a thin Ti foil (0.25 mm thick, 99% purity, ALFA AESAR) on which Pt was deposited in a similar manner. Ti is a widely studied protection layer for various photoelectrodes in different pH conditions. It forms a native oxide passivation layer ~2–4 nm thick, which further protects the PEC cell from corrosion. Figure 5a shows the CV curve of a Ti foil-protected 3J photoanode in 1.0 M...
**Figure 5.** (a) CV curve of a Pt catalyst-coated Ti foil-protected 3J photoanode measured under a three-electrode system in 1.0 M Na₂SO₄ (pH ≈ 7) under AM 1.5G illumination. (b) CA test of the system in (a) under AM 1.5G illumination in 1.0 M Na₂SO₄ (pH ≈ 7) at 0.61 V vs RHE in a three-electrode setup. The left axis shows the photocurrent density, while the right axis shows volumetric H₂ production rates during the reaction. (c) The left axis shows volumetric O₂ production rates during the CA experiment of (b). The right axis presents the calculated H₂/O₂ ratios.

Na₂SO₄ (pH ≈ 7) under similar experimental conditions as the previous experiments. The Pt/Ti/3J photoanode exhibits a maximum current density of ~4.6 mA/cm² at 0 V vs RHE, and the light-limiting photocurrent saturates to ~8.5 mA/cm² at 0.35 V vs RHE. As shown in Figure 5b, the Pt/Ti/3J photoanode displays a stable photocurrent density and H₂ production rate up to 24 h of continuous reaction time. More importantly, the O₂ production is stable during the entire reaction, as shown in Figure 5c. The H₂/O₂ ratio was 2:1, indicating the “true” water-splitting reaction on a Ti foil-protected 3J photoanode. From these results, it is clear that measurement of O₂ is vital to evaluate the stability of PEC photoelectrodes/devices.

Most PEC water-splitting studies report the photocurrent or H₂ gas measurements. These can be largely misleading because the complete catalytic cycle is not monitored nor given. It is important to measure molecular oxygen when working with unstable semiconductors such as Si, Ge, GaAs, and nitride or sulﬁde semiconductors for light-driven water-splitting applications. A catalytic reaction by deﬁnition means that a reactive site has contributed to the reaction without itself being destroyed. In that regard, a turnover number (which is the integration of the total amount of molecular hydrogen divided by the total number of atoms (not only on the surface) of the catalytic material used) needs to be given if measurements of molecular oxygen were found to be difﬁcult. Researchers, referees, and editors working and evaluating water-splitting performance would beneﬁt from a standard methodology for activity measurements. It is clear based on the above experiments that while photocurrent or H₂ measurements can be used for initial screening they cannot be relied on to evaluate stability, calculate reaction rates, or provide a STH efficiency number.

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**ASSOCIATED CONTENT**

**Supporting Information**
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Data for PEC stability testing of the 3J photoanode in a two-electrode setup and TEM images of a TiO₂-protected photoanode before and after PEC stability testing (PDF)

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