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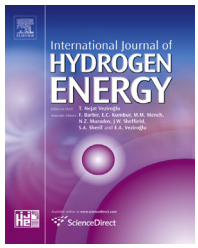

# Solar water splitting: Efficiency discussion

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ABSTRACT

The current state of the art in direct water splitting in photo-electrochemical cells (PECs) is presented together with: *(i)* a case study of water splitting using a simple solar cell with the most efficient water splitting electrodes and *(ii)* a detailed mechanism analysis. Detailed analysis of energy balance and efficiency of solar hydrogen production are presented. The role of hydrogen peroxide formation as an intermediate in oxygen evolution reaction is newly revealed and explains why an oxygen evolution is not taking place at the thermodynamically expected 1.23 V potential. Mechanism of cascading oxidation of water molecules via the peroxide stage is proposed and conforms with experimental observation.

Solar hydrogen production with electrical-to-hydrogen conversion efficiency of 52% is demonstrated using a simple ~0.7%-efficient n-Si/Ni Schottky solar cell connected to a water electrolysis cell. This case study shows that separation of the processes of solar harvesting and electrolysis avoids photo-electrode corrosion and utilizes optimal electrodes for hydrogen and oxygen evolution reactions and achieves ~10% efficiency in light-to-hydrogen conversion with a standard 18% efficient household roof Si-solar cells. Strategy to increase efficiency above 15% for a single junction cell is outlined.



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## Review: materials and cell configurations

A solar water splitting is decomposition of $H_2O$ molecules into molecular hydrogen and oxygen using solar energy. This process is expected to become foundation of a sustainable hydrogen-based energy economy, as it represents carbon-neutral way to produce hydrogen gas using the most abundant renewable resources, i.e., water and sunlight [1–3].

### *Early days of solar water splitting*

From the technical point of view, there are many ways to realize water splitting, however, the technology must be

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efficient and economically viable. Comprehensive review [1], dedicated to the problems of electrolysis of water on light-sensitive semiconductor surfaces covers the period between 1972, when the photoelectrochemical (PEC) water splitting was first discovered [4] and 2010. The authors survey the data related to thermodynamics of hydrogen and oxygen evolution reactions (HER and OER), performance of various semiconductors, configurations of photoelectrochemical cells, properties of catalyst materials, influence of various structural effects on the efficiency of the process. Values of the energy conversion efficiency or the so-called solar-to-hydrogen efficiency, $\eta_{STH}$, obtained for water splitting cells of different configurations are summarized [1]. The values vary between 0.01% and 18%, i.e., by a factor of about 2000, for PEC cells without surface catalysts and those with catalysts and buried photovoltaic (PV) junctions.

In terms of a technical realisation, direct solar-to-chemical energy conversion in PEC cell is considered to be more practical, efficient and less expensive method of $H_2$ production compared to electrolysis of water using PV-generated electricity, because the former integrates light energy collection and water splitting into one device [5–7,1]. This goal, however, poses serious material-related challenges: semiconductor photoelectrodes should efficiently harvest solar irradiation and drive water oxidation or reduction reactions in aqueous solutions at a sufficient rate at current densities of (10–15) mA $cm^{-2}$ under 1 Sun illumination without degrading for a sufficiently long period of time, i.e., more than 2000 h according to benchmarks of US Department of Energy [8]. Such a set of requirements simply cannot be met by a single material, therefore formation of various heterostructures [7,9–15], tandem devices [16–18], as well as methods for photocorrosion protection of semiconductors [19–23] have been very intensively explored over the period of recent years in 2010–2016, as can be seen from the list of the referenced literature.

### *Recent state-of-the-art in solar water splitting*

The highest solar-to-hydrogen efficiencies (STH), exceeding 10%, so far have been achieved using very expensive and unstable III–V group semiconductors [24,25]. Therefore the focus of undergoing research is to find economically viable, efficient and stable material compositions for PEC water splitting based on earth-abundant elements. A great deal of attention is being devoted to employment of Si photovoltaics in solar hydrogen production, as this technology is well-developed already and, more importantly, the price of crystalline silicon solar cells has decreased more than 7 times in the past several years [26]. Reece et al. [12] has reported fabrication of solar water-splitting cells, which consist of triple junction amorphous Si photovoltaic cell interfaced to cobalt borate and NiMoZn as oxygen and hydrogen evolution catalysts, respectively. The highest STH efficiency obtained was 4.7% under 1 Sun illumination, however, a stable operation of the device lasted only for 10 h. Another group [21] has successfully stabilized silicon photoanode by atomic layer deposition (ALD) of 2 nm thick layer of $TiO_2$ covered with 3 nm thick iridium film for the OER catalysis. Stable operation of the anode was observed for at least 24 h. Similarly, ALD-grown Al-doped ZnO (20 nm) and $TiO_2$ (20 nm) protective layers modified with Pt nanoparticles have been shown to effectively stabilize $Cu_2O$ photocathode [27,28] for $H_2$ production, which retained 62% of the initial photocurrent value after 10 h stability test. Recently, a 40-h-long stable operation of tandem-junction GaAs/InGaP photoanode, protected with ALD-formed $TiO_2$ layer, in conjunction with Ni-based HER and OER catalysts, was reported [29]. Kenney et al. [13] demonstrated a record 80-h-long direct water oxidation, using n-type Si photoanodes passivated with a 2 nm thick nickel film, which acts also as oxygen evolution catalyst.

Thus, one has to admit that significant progress has been made in recent years in the area of engineering the semiconductor electrodes for efficient solar water splitting, however, the fabrication of complex heterostructures usually involves such sophisticated techniques as ALD [22,21,29,27,28], which are totally incompatible with the larger area and mass production of the photoelectrodes, if solar energy is going to be collected on the terawatt scale. Moreover, the longevity of these state-of-the-art photoelectrodes is still far beyond the targeted 2000 h and the energy conversion efficiency achieves the pursued 10% [8] only when the most expensive III–V semiconductors are used [29].

In view of the above, the so-called "brute-force" or photovoltaic (PV) plus the electrolysis approach is lately being reconsidered [30,26,31]. The main advantage of this approach is that both processes, i.e., the photovoltaic and electrochemical energy conversion can be optimized independently. Moreover, the problems related with photo-corrosion of semiconductors and blocking of the light-sensitive surface with HER or OER catalyst particles are automatically avoided. In Ref. [32] $\eta_{STH} = 18\%$ was obtained using system integrating highly efficient, yet very expensive, group III–V semiconductor solar cells, optical concentrator and polymer electrolyte membrane electrolyzer. Quite recently [26] STH efficiency exceeding 10% has been achieved with a crystalline silicon PV module and noble metal-free, low cost HER and OER catalysts. The operation of the coupled system was stable for over a week at current density of ~8 mA $cm^{-2}$. Grätzel with co-workers [31] have demonstrated a 12.3% solar-to-hydrogen efficiency using low-cost perovskite photovoltaics and earth abundant catalysts. Though the results are promising, the instability of perovskite solar cell limits the lifetime of water splitting device. For practical applications an expectation of a lifetime for a solar energy converter is dictated by solar cells and has to be 25 years. Thus, it is evident, that in construction of efficient solar water splitting system, a trade-off between efficiency, cost and longevity must be achieved. The highest efficiency of solar-to-hydrogen conversion to date 24.4% was achieved using concentrator optics and triple junction solar cell [33].

Here, we explicitly demonstrate that by separating steps of: *(1)* solar-to-electrical and *(2)* electrical-to-hydrogen conversion the highest overall solar-to-hydrogen efficiency $\eta_{STH}$ can be achieved. As tutorial case study, we choose a simple Si/Ni Schottky solar cell *(1)* and the most efficient Pt and Ti/Ir–Ta oxide electrodes as HER and OER catalysts for the process *(2)*. The mechanism of water splitting reactions based on the principles of thermodynamics is revealed and the reason of absence of water oxidation at the thermodynamically

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