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MINI REVIEW

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# Revisiting solar hydrogen production through photovoltaic-electrocatalytic and photoelectrochemical water splitting



**Abstract** Photoelectrochemical (PEC) water splitting is regarded as a promising way for solar hydrogen production, while the fast development of photovoltaic-electrolysis (PV-EC) has pushed PEC research into an embarrassed situation. In this paper, a comparison of PEC and PV-EC in terms of efficiency, cost, and stability is conducted and briefly discussed. It is suggested that the PEC should target on high solar-to-hydrogen efficiency based on cheap semiconductors in order to maintain its role in the technological race of sustainable hydrogen production.

**Keywords** hydrogen production, photovoltaic, electrocatalysis, photoelectrocatalysis, water splitting

The development of solar driven water splitting for hydrogen production has paved to be a clean and promising route toward sustainable energy supply. Among various candidate methods, the photoelectrocatalysis (PEC) and photovoltaic-electrocatalysis (PV-EC) have shown much higher efficiency. As shown in Fig. 1, the PEC process is based on the all-in-one photoelectrode where the light harvesting and water electrolysis occur in the same component. Meanwhile, the PV-EC process is based on separated modules of PV part and EC part for solar-to-electricity conversion and water splitting, respectively. These features distinguish PEC from PV-EC when taking efficiency, stability, and cost into consideration.

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The development of PEC can be dated back to 1950s. Ever since the emergence of semiconductor based electrodes, the unique response of electrodes to illumination has been noticed, which makes them apparently different from the traditional metal electrodes [1–4]. At the early stage of PEC, researches were targeted at the electrochemical response of redox couples (e.g., $Se/Se^{2-}$, $Fe(CN)_6^{3-/4-}$) [5,6]. For example, the Gartner Model were established to predict the theoretical PEC response. Memming [7], Nozik [8], Gerischer and Tobias [9], Bard [10] engaged in discovering fundamental frameworks of PEC research, such as investigating the carrier density, doping effect, and surface states influence etc. Based on these efforts, numerous concepts were developed as comprehensively summarized in the book of *Electrochemistry at Semiconductor and Oxidized Metal Electrodes* [11]. With these pioneers' work, Fujishima and Honda were able to achieve PEC water splitting for hydrogen production [12]. It brought more expectation to the public than to the scientific research community under the background of the First Petroleum Crisis (1973–1974). After that, PEC water splitting started to bloom and have lasted for decades.

Along with the PEC development, another solar conversion process, the solar to electricity conversion based on solar cell, has experienced a continuing and steady development. The power conversion efficiency (PCE) of the typical single crystal Si solar cell has continually grown from less than 15% to over 26% as summarized in the "*Best research cell efficiencies*" launched by NREL [13]. The fast development of solar cell naturally fertilizes the alternative solar hydrogen production method, which is PV driven electrolysis (PV-EC). The well-developed water electrolysis process makes the PV-EC process a very efficient route to produce solar hydrogen [14–16]. For example, Khaselev and Turner achieved a solar-to-hydrogen (STH) efficiency of 12.4% by combining the GaAs/GaInP based tandem solar cell with Pt as cocatalyst over 20 years ago [17]. In 2016, Jaramillo's group reported a STH efficiency over 30%

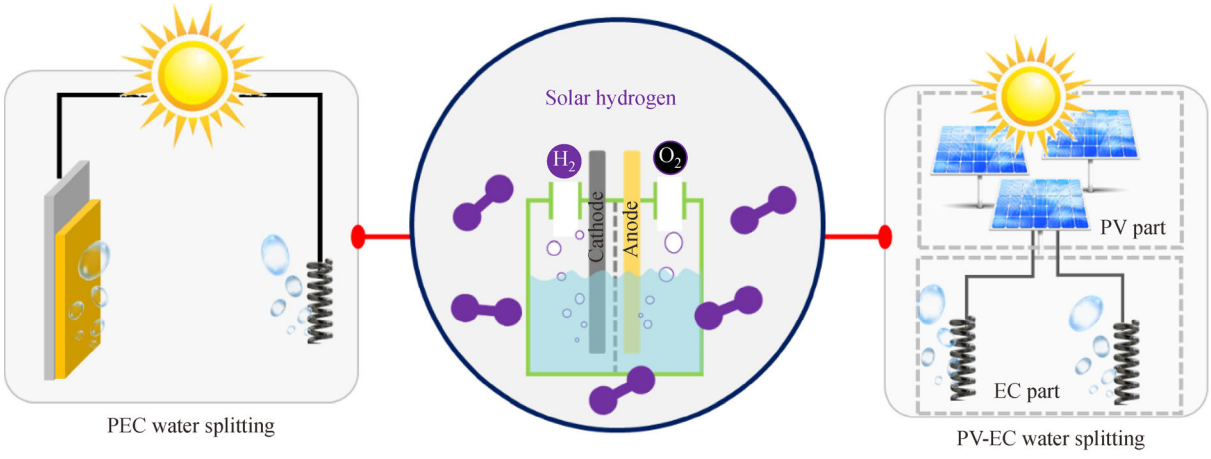


**Fig. 1** Two pathways for solar hydrogen production by PEC and PV-EC water splitting.

through the PV-EC route [18]. But the highest STH efficiency in traditional PEC water splitting is still within 3% [19], which is far behind the development of PV-EC in regard of the STH efficiency.

Considering the relatively mature development of water electrolysis, the PV-EC process faces limited technical difficulties for green hydrogen production. It has achieved a very high technology-readiness level (TRL) since both PV and EC are commercially available [20]. It can easily achieve an STH efficiency of over 10%, which is regarded as an important milestone for PEC yet to achieve. But the high price of solar cell has become the biggest barrier for the application of the PV-EC system for solar hydrogen production in the past decades. This leaves the room for the development of PEC research using more cost-effective materials, like $Fe_2O_3$, $WO_3$, etc. [21]. In this regard, applying relatively expensive PV based materials for PEC purpose has been biased from the initial motivation of PEC, which is to apply cheap materials for solar hydrogen production.

However, since the beginning of this century, the development of the PV market mainly driven by China has dramatically decreased the cost for solar cell fabrication [22]. Especially in the Si based solar cell modules, both the energy consumption and capital investment have been decreased significantly. The price of a single crystal module has been reduced to approximately US $ 0.3 per Watt (Year 2020) from approximately US $76 per Watt (Year 1977) [23,24]. In this scenario, the advantage of PEC over PV-EC in materials cost is diminished. The fast exploration in cheap and efficient electrocatalysts, and the continuing growth of PCE of solar cells have together made PV-EC a very promising method to realize sustainable solar hydrogen production. An economic-technology estimation of the solar hydrogen production by PV-EC approximates to US $6.22/kg $H_2$, which is lower than the PEC process (approximately US $8.43/kg $H_2$) with a similar STH of 10% on Si based PV or photoelectrodes [25,26]. Thus, a critical comparison of PEC and PV-EC have become important for the further development of solar hydrogen production.

Generally, the semiconductors of the PEC process have a higher tolerance of defects than the PV process. Therefore, many simple semiconductor metal oxides can be applied in PEC research. This feature has made PEC advantageous over PV-EC which closely relies on high quality semiconductors. However, low-quality semiconductors also seriously limit the efficiency of PEC. More efficient strategies in addressing the issues caused by low-quality semiconductors, like weak light absorption capability and serious charge recombination, should be developed in a timely manner [27,28].

Even though there are still many fundamental challenges, PEC water splitting should be an application-driven research. Therefore, it needs to consider the levelized cost of hydrogen production of PEC and PV-EC by taking the three criteria, i.e., land availability, sunlight intensity, and water supply, into consideration. One of the major capital investments is the land cost for the installation of solar capture modules. The land with a low price is normally far away from the populated residential regions. The integration of light absorbers and surface catalysts of PEC indicates that the produced solar $H_2$ will be far away from customers, which will require an additional transportation cost. Moreover, finding a site with a cheap land price and an abundant water and solar energy is not an easy task. In contrast, for the PV-EC process, the PV module can be connected to EC module with the existing electricity grid through a long distance.

In this way, the PV-EC is more flexible in realizing solar $H_2$ production in a more economical way. Besides the land cost and water availability, the space-time yield of hydrogen production (amount of hydrogen produced per hour per volume of reactor) is another significant factor. It

**Table 1** Comparison of PEC and PV-EC targeted on practical solar hydrogen production

| | PEC | PV-EC |
|---|---|---|
| Highest reported STH efficiency | 3% | 30% |
| Predicted $H_2$ price at 10% STH | > US \$8.43/kg $H_2$ | About US \$6.22/kg $H_2$ |
| Stability | About 1000 light hours[a] | > 10000 h (based on EC)[b] |
| Highest current density | About 25 mA/cm$^2$ | > 500 mA/cm$^2$ (based on EC) |
| EPT | > 5 a | About 1 a |
| TRL[c] | 3–4 | 8–9 |

**Notes:** a: This is timed under continually illumination; b: If based on Si based PV, it can last for over 10 a; c: The technology readiness level is based on the NASA TRL scale.

will determine the payback time of the invested capital and energy. Taking the commercialized water electrolysis as an example, the electrolyser is operated at a current density of over 1 A/cm$^2$ at a temperature over 70°C [15]. The huge current density is not achievable for any single semiconductor in PEC. To realize a comparable hydrogen rate, for the PEC process, the only available way is to increase the reaction area, which means more land cost. But for the PV-EC process, it is possible to achieve the required photocurrent density through the current transformer. In this case, the required area for PEC may be over tens of times that of PV-EC. In conclusion, the all-in-one PEC system may reduce the system complexity, but the critical requirement of land, sunlight, and water makes the PEC system have limited social benefit. For the PV-EC process, it takes advantage of different sites to produce a broad benefit for different fields, which can bring more profound influence on the society.

Another challenge for PEC water splitting is the stability issue at a high operating current density. A comparison of the lifetime of the PEC system and the energy payback time (EPT) will indicate whether the whole process is energy consuming or saving. A previous research has indicated that the EPT of the PEC system (STH about 10%) will be over 5 a [20], which is far more than any of the present reported PEC system (The maximum stability is about 1000 illuminated hours [29].). However, for the PV system, the EPT of the crystal Si PV panel is around one year due to its much higher PCE [30]. Even though the integration of EC system will extend the EPT of PV-EC system, the much higher STH efficiency will result in a much shorter EPT than the PEC system. Taking this into consideration, the PEC system may not achieve a net solar energy storage if all the energy budget of the PEC system is to be accounted. But the PV-EC can easily realize the net solar energy conversion due to the long lifetime of the commercial Si module and electrocatalysts.

The three critical criteria of performance gold triangle (the cost, efficiency, and stability) are equally important for solar hydrogen production research. PEC has the advantage in cost, but its poor efficiency and stability have been the bottlenecks for this field. Some key features of PEC and PV-EC for water splitting hydrogen production have been summarized in Table 1. With the further development of PV and EC to reduce the cost, the STH efficiency limitation of PEC is increasingly becoming an urgent task for the research community to battle. Besides the more efficient water splitting, the PEC research is also expected to target at the high-value compounds production, for example $CO_2$ reduction reaction, hydrogen peroxide production, organic synthesis and so on. Moreover, compared to the mature development of EC, deeper insights are still needed into the fundamentals of PEC research in terms of the occurrence of the charge transfer in the photoelectrodes, the role of surface states, the influence of external field (e.g., magnetron, electric field, sonic), etc. These findings will benefit not only PEC research, but also a broader field of materials, catalysis, and energy.

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