Comparative analysis of photoelectrocatalysis and photovoltaic-electrocatalysis and their applications

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Abstract. With the industrial development of mankind, large amounts of greenhouse gases are being released into the atmosphere, far beyond the limits of what the earth's ecological cycle can handle. In order to reduce carbon emissions, it needs to find zero-carbon energy technologies to replace existing fossil fuel technologies, in which photoelectrocatalysis (PEC) systems and photovoltaic-electrocatalysis (PV-EC) systems are the backbone of zero-carbon photovoltaic technologies. PV-EC systems and PV-EC systems share the common essence of converting solar energy into hydrogen, but the difference between PV-EC and PEC is that PV-EC can also provide electricity while producing hydrogen, which is an additional energy output option. However, the difference between PV-EC and PEC is that PV-EC can produce hydrogen and provide electricity at the same time, providing an additional energy output option than PEC systems. This research briefly discusses the mechanics and economics of the two systems and analyses the development trends of PV-EC systems in recent years. The author suggests that PV-EC systems take advantage of the diversity and modularity of energy output, break the limits of the earth's high-quality light source areas through energy conversion, and deploy PV-EC systems in a distributed manner to increase the efficiency of power generation and hydrogen production.

Keywords: photoelectrocatalysis, photovoltaic-electrocatalysis, Hydrogen produce, water electrolysis

1. Introduction

Zero-carbon energy sources are one of the avenues to solve the environmental issue. With the industrialization developing, the large amount of greenhouse gases is being emission. It causes the environmental problems becoming increasingly grim [1]. Various countries have taken the zero-carbon energy sources as the emphasis in the plan for optimizing the future energy structure [2]. Zero-carbon technology is an important part to human achieve the development of energy supply structure, which including both zero-carbon power generation technology and zero-carbon non-generating technology. The above two measures are inefficient when using independently. Therefore, it's important to develop the combined power generation technology. As a new measure to generate electricity, photovoltaic-electrocatalysis (PV-EC)-H_2 generation technology is gradually replacing the old way of combined power generation technology.

Sunlight is one of the most important part of zero-carbon energy source, which is expected to solve the energy and environmental problems faced by human society. According to the forecast from IEA, the total installed capacity of photovoltaic power generation will reach about 894.3 GW in 2021 [3]. Because of the wildly use of photovoltaic power generation, how to solve the power store problem is becoming more and more urgent. Hydrogen is chosen because of the adventure, such as environmentally friendly, high calorific value, non-toxic and cleaning reaction product.

In the past decade, hydrogen is produced in two main ways. One is to use the electric energy generated by thermal power generation to produce hydrogen by brine electrolysis of water, and the other is to use fossil fuels which originally containing hydrogen, such as steam-methane-reforming (SMR) to produce hydrogen [4]. Both of the above technologies consume the limited fossil fuels on earth and emit a large amount of carbon dioxide as the price of producing hydrogen, which would not be in accord with the definition of zero-carbon energy urgently needed today. At this moment, photoelectrocatalysis (PEC) hydrogen production came into people's sight. It is a hydrogen

production technology which combines light-collection and brine electrolysis water with photovoltaic electrode as the carrier. But the solar-to-hydrogen (STH) efficiency of this technology can only achieve to about 12.4%, which is not satisfactory. Nevertheless, the solar-to-hydrogen (STH) efficiency of PV-EC is up to 30% and still improving. At the beginning of this century, PEC was more competitive than PV-EC due to material cost. But in the nearly years, with China which is a huge player in the photovoltaic industry who enters the market, the price of a single crystal module materials was reduced from about 76 to 0.3 U.S. dollar/Watt by China [5]. In such a market environment, PV-EC has more price adventure than PEC. Therefore, PV-EC technology was coming back on the agenda [5].

Using PV-EC to brine electrolysis water and producing hydrogen is the most ideal way to achieve the "liquid sunlight" energy and storage program. As a third-generation solar energy technology, PEC brine electrolysis has the advantages of high economic benefit, environmental friendliness, high activity and high stability.

This research will analyze and compare the economics of PEC and PV-EC brine electrolysis for hydrogen production and present the material development of PV-EC photochemical hydrogen production to demonstrate PV-EC as a zero-carbon energy technology.

2. The mechanism and advantages of PEC and PV-EC

2.1. Mechanism

Before the introduction of PV-EC mechanism, the author must learn about the PEC which was previous generation technology. Figure 1 shows the mechanism membrane electrode assembly of a PEC reactor. The PEC process is based on an integrative photoelectrode system, which integrating both lights generating part and water electrolysis part into one reaction container [6]. When semiconductor-based electrodes come into people's sight, its specific response of illumination intensity was noticed by people who study photovoltaics [5].

In the typical PEC cell for water electrolysis, the electrons which lay on the photo-anode are being excited by photons. Electrons will escape from photo-anode when gathering enough power and transferred to the photo-cathode. The electrons move to the photocathode, bond with positively charged hydrogen in the H_2O molecule and drive H_2O reduction to produce H_2 [7]. At the same time, a photogenerated holes will be created on the photoanode. These photogeneration holes are employed for competing electrons from oxygen which inside the H_2O and oxidation them become O_2 [8]. However, this technique can only achieve a maximum of 3% of STH, which is limited by O_2 evolution reaction.

As a new photovoltaic hydrogen generation technology, PV-EC is different from PEC in principle. It is a solar energy conversion technology which based on photovoltaic cells and electrolysis. There are two parts of PV-EC, the first part is employed for generating photons and turning them into electric energy, part of electric energy will output to the user and rest of them will put into electrolysis system to produce hydrogen for storage. These two parts are mutually independent which can be built separately, to reduce the special requirement of construction area. The maximum STH of this technique is up to 30%, which limited by PV generation efficiency and the variety of electrolyte inside the electrolysis system. In closely decade, due to PV related material technology development and improvement in PV producing technology, the efficiency and cost of PV power generation technology has been drastically reduced. The solution of this difficulty breaks the maximum limit of PV-EC hydrogen production technology. The STH of PV-EC can easily breakthrough over 10% [5].

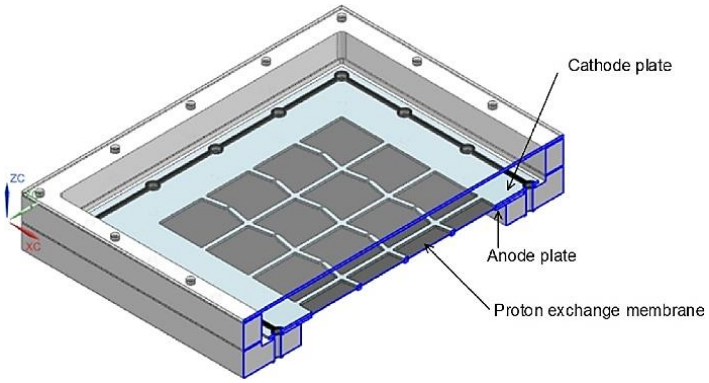


Figure 1 The principle of the PEC reactor [6].

2.2. Advantages

At the beginning of photovoltaic development course, PEC had more advantage than PV-EC whatever considered from the cost of construction or technology level of related materials. Compared with PV-EC process, the semiconductors of PEC process have a greater fault tolerance which means many semiconductors metal oxides could be approached when using PEC to produce hydrogen. However, the PV-EC is very sensitive to light absorption capability [5]. Therefore, PV-EC have to using high quality materials photovoltaic panel. But the photovoltaic panel which produced by low quality materials is also limit the upper limit of light absorption efficiency and cause a serious charge recombination which means that the system cannot sustaining large current densities. Because these two key defects, if people want to increase the STH of the PEC without greatly increasing the cost, people must increase a large area for the PEC to construction of photovoltaic panels.

However, when people built up the system which turns sunlight to hydrogen (Figure 2), the land cost, land suitability, water supply and sunlight intensity should be considered. Because PEC is an integrated system, it cannot be split. In order to ensure the performance of PEC, this system must be built in the area which satisfied following conditions: high light intensity, enough water supply and low land cost. However, the area which satisfying above conditions are less and also located on desolate and uninhabited places. If you want to translate the hydrogen to the densely populated residential area or the center of city, there are high additional hydrogen transport costs should be afforded.

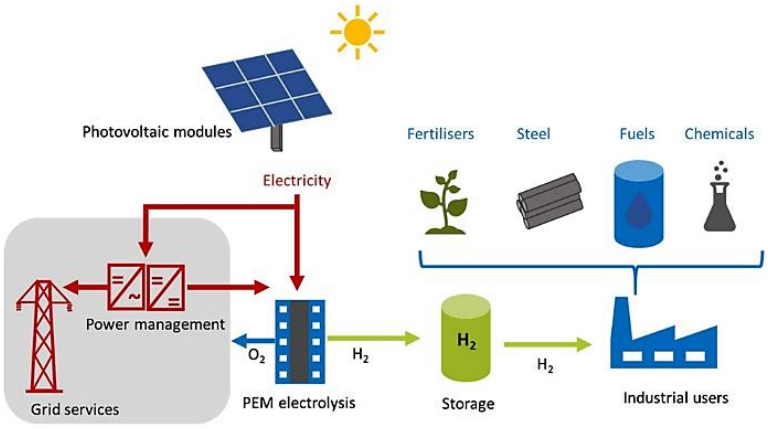


Figure 2 The designed system for H_2 production for industrial stakeholders [7].

The PV-EC system can be divided into two parts that can be independently constructed. People can build the PV system in the area with low land cost and abundant sunshine, and build the EC hydrogen production system in the place with sufficient water supply and close to the population concentration area. The two systems are connected by the power grid, which not only solves the problem of low flexibility in the construction of PEC. Replacing the high cost of transporting hydrogen with cheap electricity. At the same time, due to the development of PV material, the light

absorption efficiency of PV-EC system has significantly increasing. The other advance of PV-EC is the system can easily sustain large current densities. This further reduces the land cost of PV-EC when STH as same as PEC.

3. Application and DEVELOPMENT CURRENT SITUATION of PV-EC

In recent years, PV-EC has matured and a variety of materials have been used in the two main parts of the PV-EC system. One of these is the integration of molecular materials into the PV-EC's hydrolysis system, which can significantly improve the STH efficiency of the PV-EC. Using water oxidation catalysts (WOCs) made from molecular ruthenium, the researchers aim to solve the problem of the PV-EC maintaining a high hydrogen production efficiency even at low potentials in the PV section (i.e. in a low-light state), thus increasing the ability of the PV-EC to operate 24/7. Ideally, the pH of the electrolytic cell (EC) section should be close to 7, as this minimises the corrosion and dissolution effects of the electrodes at extreme pH conditions [9], as shown in Figure 3. If conventional metal catalysts such as iron, nickel or cobalt oxides are used, the electrodes will inevitably be exposed to extreme pH solutions such as $HCLO_4$ or KOH, which will accelerate the rate of catalyst damage or passivation. This can be avoided when using WOCs, where the STH efficiency can still exceed 20% even with small pH fluctuations. Properly functionalised and immobilised on the surface of a conductive graphite catalyst carrier as the anode of the electrolyzer, the WOCs show no signs of deactivation after more than one million cycles, a performance that exceeds the cycle life of existing solar cells such as Calcium Titanite and InGaP [9].

Researchers found that the STH efficiency of a PV-EC system could also be improved by using a polymer electrolytic film in combination with an InGaP/GaAs/GaInNASSb triple junction solar cell. This combination allows the PV section to generate a large enough current to drive the EC section. And by precisely controlling the power output, the device can achieve an average STH efficiency of 30% over 48 hours. This is one of the more STH-efficient units available at this stage of our technology. This significant improvement in STH efficiency will make the PV-EC system more commercially viable [10].

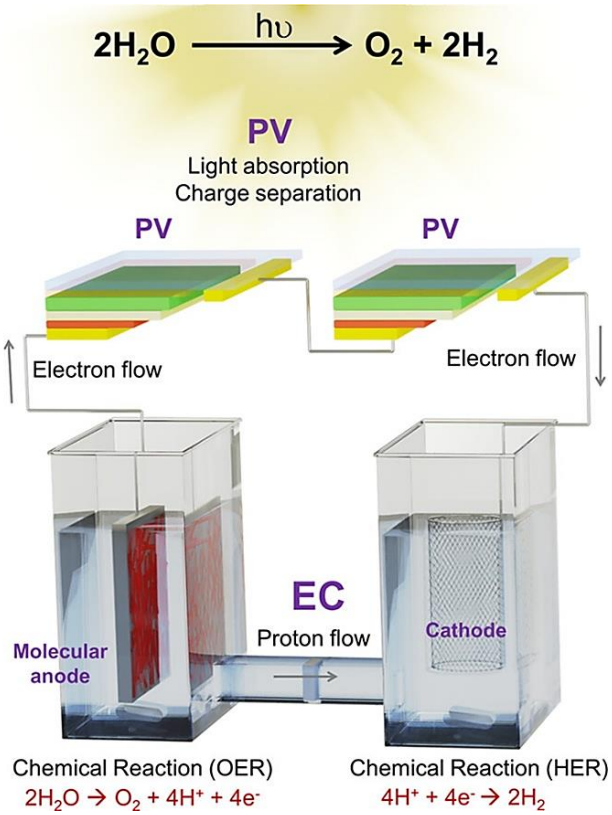


Figure 3 The principle of the developed PV-EC [9].

The PV-EC system is an ideal energy generation device for residential and commercial buildings, where it is desired to make each building an energy production unit that is self-sufficient and can deliver energy to the outside [11]. As we mentioned earlier, the PV-EC system is made up of two separate components, which makes it possible to arrange the system flexibly in commercial complexes or residential areas. A research study in 2018 showed that the combination of the PV-EC system with residential and commercial buildings will facilitate the goal of moving towards distributed production of zero-carbon energy. The PV-EC is a fully autonomous and zero-emissions-based module, where each pair of PV-ECs can be controlled as a stand-alone unit, flexibly and precisely regulating the efficiency of the hydrogen production in the EC section or calling on reserves of hydrogen for power generation by means of the power input to the solar cells, in order to adequately cope with fluctuating power load profiles throughout the year. By integrating the electrolysers, hydrogen storage, solar cells and fuel cells into the system, one can achieve a targeted analysis of the power load level and thus precisely control the power supply and the process of converting, storing and converting hydrogen, increasing the capacity efficiency.

In addition, when a building is located far from the city's electricity network or is disconnected from the external power supply, it usually uses UPS or diesel generators for power supply, which is often heavy and has a short operating life and do not have a satisfactory output. If this system is applied to the above building scenario, it can supply electricity to such buildings for a considerable period of time. As hydrogen has an energy density of approximately 2.7 times that of diesel and petrol, the same mass of hydrogen can produce more electricity in a fuel cell and the system has a higher output power than conventional UPS and diesel generators. Figure 4 shows the principle diagram of this system [12].

In order to make the modular PV-EC technology more efficient as soon as possible, some researchers have developed a scaled-up PV-EC device in 2020. This scalable device consists of a triple-junction thin-film silicon solar cell as a light collection system and a hydrogen production unit using electrodeposited bifunctional nickel-iron-molybdenum as a hydrolysis catalyst. In the framework of the device, the thin film used to separate the gas is produced using 3D printing technology, an initiative that increases the productivity of the device and reduces production costs. When one uses single-junction or double-junction solar cells in a light harvesting system, additional connection systems are required, which leads to a waste of part of the area of the light harvesting system as a dead zone. The device is an innovative use of triple-junction solar cells made from thin silicon-based films in the light collection system, where each cell can operate independently without the use of a connection system, which will increase the effective light collection area of each cell. The device also uses a bifunctional nickel-iron-molybdenum catalyst prepared by electrodeposition in a hydrogen production system, which eliminates the need for different catalytic materials at the anode and cathode. The device worked for a total of 30 minutes without special assistance, achieving an STH efficiency of 4.67% in the active region of 5.33% and a hydrogen production efficiency of 1.26 μmol/s. This study not only accelerates the commercialisation of PV-EC, but also explores the idea of gas management in hydrogen production by hydrolysis in a PV-EC system, a modular PV-EC device could provide a more flexible energy deployment option for zero-carbon energy and is a foreseeable development towards flexible zero-carbon energy production in the future [13].

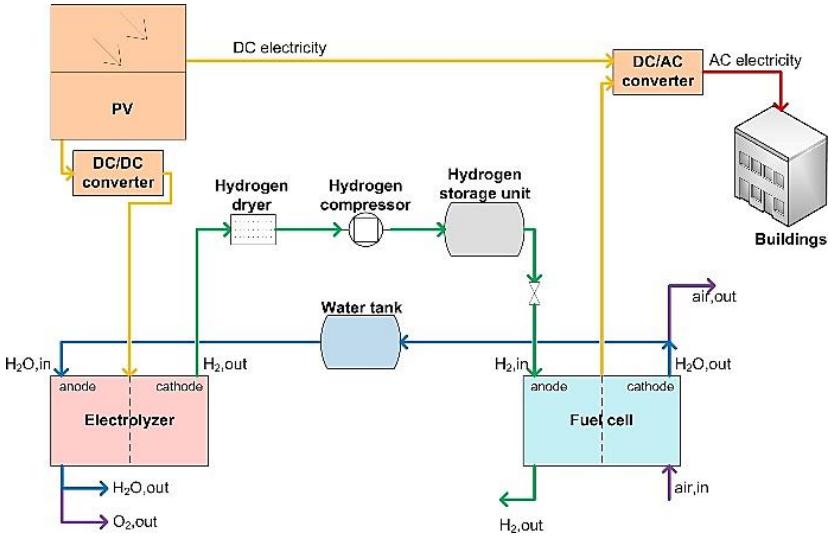


Figure 4 The principle of the designed PV-EC-FC system [12].

In addition to research into STH efficiency, many countries have started to build their own large-scale PV-EC systems to transport light energy from remote areas to energy-hungry cities in an environmentally friendly way. This proactive approach to transforming research results into commercial projects will provide a good example of how PV-EC can be used in the future to develop and popularise zero carbon energy.

In Texas, construction is underway on the world's largest environmentally friendly hydrogen centre, which they are calling hydrogen city, with the first phase due to open in 2026. Hydrogen city will eventually harness 60 gigawatts of solar and wind energy and use it to produce more than 2.5 billion kilograms (2.4 million tonnes) of green hydrogen per year, which will be stored in underground caves located in the salt domes of Piedras Pintas before being transported. These caves are an important part of the development and they will act as a buffer zone for intermittent energy production. When conditions are favourable, the solar arrays will use photovoltaic power to power the hydrogen electrolysers and this buffer storage, will ensure continuity of power for customers. The hydrogen will be piped to nearby Corpus Christi and Brownsville to be converted into green ammonia, sustainable jet fuel and other products.

In 2020, Germany's Thyssenkrupp was awarded a technical study contract for the project. the planned facility will integrate ThyssenKrupp's green hydrogen and green ammonia technologies. The overall project will include an 800 MW solar photovoltaic plant to power hydrogen-to-ammonia production. The plant is expected to produce 200,000 tonnes of green ammonia for export annually once completed. The project's initial phase entails a 300 MW solar PV plant and an estimated 35,000 tonne-a-year ammonia production facility. However, final specifications and capacity for phase 1 are still under discussion. The green ammonia production facility will target regional and international markets. Close to $60bn-worth of green hydrogen and ammonia schemes have been announced in the Middle East and North Africa (Mena) region since July 2020.

4. Conclusion

In summary, by comparing the operational mechanism and construction economics of PEC and PV-EC, the author believes that PEC systems will gradually lose their dominant position as the price of high-performance PV panels decreases, and PV-EC systems will become the backbone of the future zero carbon PV industry. By digging into the development of PV-EC technology, the author found that the research of PV-EC now all aims at improving the STH efficiency of the system, realising distributed power generation unit networking, etc. The solutions are mainly focused on the following directions: (1) Use metal oxides combined with organic matter in framework molecular materials to make catalysts with high catalytic efficiency and good stability for hydrolysis, and try to avoid the solution of electrolytic tank. (2) The use of triple-junction thin-film silicon-based solar cells

to improve the photovoltaic conversion efficiency per unit area while reducing the weight of the structure. (3) The use of advanced manufacturing technologies such as 3D printing to reduce manufacturing costs and improve production efficiency, and to a certain extent to promote the distributed commercial deployment of zero-carbon power units. All of these solutions are contributing to the practical application of zero-carbon power generation units, and some countries are beginning to plan for the commercial deployment of PV-EC systems in packages.

For the future development of humanity, reducing carbon emissions is one of the pressing needs in the field of environmental protection today, but with current energy technologies, reducing carbon emissions often means that we need to reduce the supply of energy, which is not a difficult task for developed countries with more than 2 kilowatts of installed power generation per capita, and which have more than enough funds to make the transition, but in developing countries with less than one kilowatt of installed power generation per capita This is particularly difficult to achieve in developing countries with less than one kilowatt per capita, which need to build up their national infrastructure and take on a lot of low value-added industrial manufacturing, and therefore need more energy supplies. In this context, it is important to develop a power generation technology with very low carbon emissions and low constraints, and the PV-EC system is a good solution to the conflict between carbon emissions and energy supply. It should aim to reduce carbon emissions without sacrificing the path of human development and minimising the quality of life, and at the same time strive to develop zero-carbon energy technologies as a solution to reduce carbon emissions.

When PV-EC systems become widespread, one can deploy PV-EC systems in urban complexes and residential areas, with each building providing a reliable energy supply solution, while PV power arrays in remote areas can deliver power to urban complexes for supplementing power gaps at peak electricity consumption or providing green power for EC systems. In Africa, there are large areas of high-quality light sources where we can deploy PV systems and then transmit the electricity to the Middle East, Europe and other regions that use a lot of electricity through extra high voltage transmission technology. This distributed deployment solution can solve the regional limitations of energy and also alleviate the economic problems of developing countries in Africa.

At this stage, the main constraint to the commercialisation of PV-EC is the STH efficiency, which researchers are now working on by improving the materials of photovoltaic panels, electrodes and catalysts, and have already achieved some results. Modular PV-EC systems have also been demonstrated in the laboratory in order to achieve distributed deployment.

Authors' Contributions

Junming Fu completed the work design and article writing.

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