

Electrochemical Water Splitting Coupled with Solar Cells

Katsushi Fujii

Abstract The simplest method for solar to chemical energy conversion is water splitting using electrochemical cells operated by solar cells. Both two devices have been established and well-studied, however, their coupling is difficult due to the variability of the solar radiation. In this chapter, the coupling technique and efficiency improvement of the combination of the electrochemical cell and solar cell are discussed based on the basic principles of both devices.

1 Introduction

Electrochemical water splitting has a long history, starting with William Nicholson and Anthony Carlisle who in 1800 used the voltaic pile (battery) invented a few weeks before by Alessandro Volta [1]. The industrial water splitting method to hydrogen and oxygen was developed by Dmitry Lachinov in 1888 [2]. Today, electrochemical water splitting is one of the major water splitting methods alongside photoelectrochemical, photochemical, photobiological, and thermochemical water splitting.

Solar cells also have a long history. The first demonstration of photovoltaic effect was performed by Alexandre Edmond Becquerel via an electrode in a conductive solution exposed to light. In 1887, James Moser introduced the dye sensitized photoelectrochemical cell. The first solid state photovoltaic cell was built by Charles Fritts in 1883, which consisted of semiconductor selenium with an extremely thin layer of gold to form junctions [3]. The first practical photovoltaic cell with a diffused silicon p-n junction was developed by Daryl Chapin, Calvin Souther Fuller, and Gerald Pearson in 1954 at Bell Laboratories [4]. After that solar cells

K. Fujii (✉)

Global Solar Plus Initiative, The University of Tokyo, 4-6-1 Komaba, Meguro-Ku,
Tokyo 153-8904, Japan
e-mail: k.fujii@rcast.u-tokyo.ac.jp

based on the p-n junction concept spread widely to become a representative means of creating renewable energy.

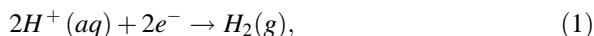
The combined use of electrochemical water splitting and solar cells began in 1970s in order to produce hydrogen energy in a sustainable way [5]. The system is the combination of two well-known technologies, however, electrochemical cell operated by solar cells was accompanied with many technical difficulties. This chapter discusses electrochemical water splitting coupled with solar cells.

2 Electrochemical Water Splitting

Electrochemical water splitting is the method of decomposing water (H_2O) into hydrogen (H_2) and oxygen (O_2) using a current path through the water (electrolyte) [6]. The most simple electrochemical water splitting can be performed as shown in Fig. 1. In this case, the water includes some acid or salt, which is not oxidized/reduced by the water splitting (adding NaCl usually produces Cl_2 instead of O_2 from the anode.) The electrode must also not be oxidized/reduced by water splitting like carbon.

In water splitting, the chemical reactions in acidic solutions are basically;

Cathode (reduction):



Anode (oxidation):

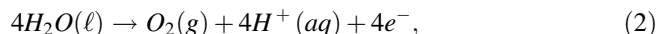
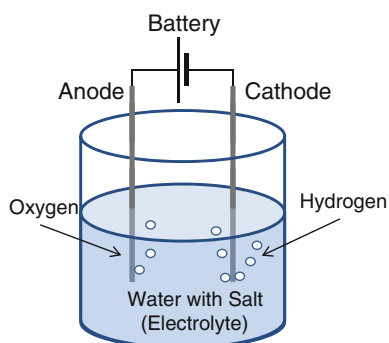
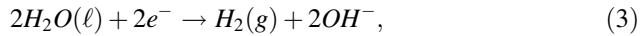


Fig. 1 Schematic electrochemical water splitting

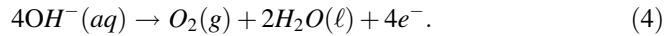


in basic solution are;

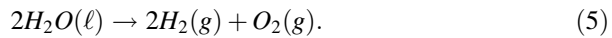
Cathode (reduction):



Anode (oxidation):



The reduction occurs at the cathode surface to produce hydrogen gas with the electrons in the cathode supplied to the hydrogen ions (protons) in the electrolyte. At the anode surface, water is oxidized to produce oxygen with electrons transferred from water molecules to the anode. Thus, the total reaction is;



In neutral solution, both half reactions occur.

The thermodynamics of the electrochemical reactions is defined by the Gibbs energy difference (ΔG) as shown in Fig. 2. The standard formation of Gibbs energy (under 25 °C, 1 atm) changes in the Eq. (5) as follows;

$$\Delta_f G^0 = +237.13 \text{ [kJ/mol]}. \tag{6}$$

This Gibbs energy change shows the form of water is the stable state, i.e., hydrogen can storage energy. The Gibbs energy change includes not only the enthalpy change (ΔH : Enthalpy changes with chemical reaction and phase change for example.) but also the entropy change ($-\Delta TS$: Entropy changes with the state of the materials using the S of the entropy); $\Delta G = \Delta H - T\Delta S$. In Eq. (5), the state of materials change (the change of the entropy) at 25 °C is;

$$\Delta S^0 = 163.34 \text{ [J/molK]}, -T\Delta S^0 = -48.70 \text{ [kJ/molK]}, \tag{7}$$

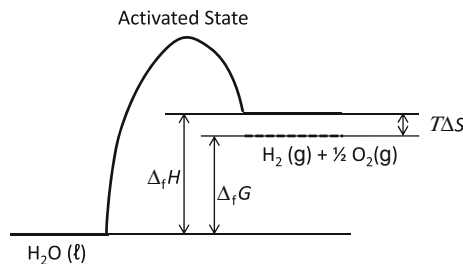


Fig. 2 Schematic thermodynamics for water splitting

and the enthalpy change is;

$$\Delta_f H^0 = +285.83[\text{kJ/mol}]. \quad (8)$$

When the closed cell is used for the electrolysis (the total volume; V and temperature; T are constant), the Helmholtz energy ($\Delta F = \Delta H - T\Delta S - p\Delta V = \Delta U - T\Delta S$) has to be used because the pressure changes. For the open cell (the pressure; P and temperature; T are constant), the Gibbs energy change is enough for the consideration because the pressure does not change.

For the electrolysis, the $\Delta_f G$ of the reaction;



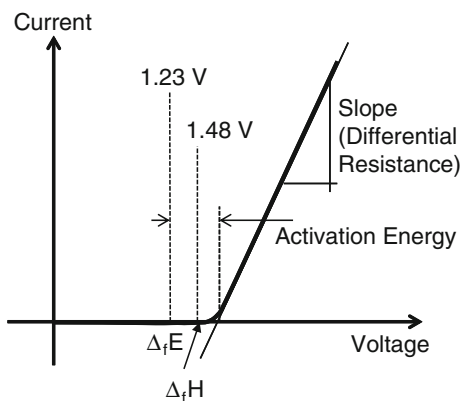
is zero at pH 0 with standard condition. The required voltage for water splitting when using Faraday constant F ; $\Delta G = -nF\Delta E$ (n : the number of electrons transferred, F : Faraday constant 96485 C/mol, ΔE : potential difference) from $\Delta_f G$ in Eq. (6);

$$\Delta_f E = -1.23 [\text{V}] \quad (10)$$

The negative value of the required voltage shows that energy must be added for water splitting.

The current—voltage (I - V) characteristics are shown in Fig. 3 schematically. The turn on voltage is higher than 1.23 V even using open cell due to the existence of the activation energy for the chemical reaction of water splitting. The slope after the turn on the current shows the series resistance of the overall of the electrolysis circuit. The reductions of the overpotential and resistance improve the electrochemical performance of water splitting.

Fig. 3 Schematic current—voltage characteristics for water splitting. $\Delta_f E$ and $\Delta_f H$ show the required voltage calculated from Gibbs free energy change and enthalpy change



3 Solar Cells

In order to perform electrochemical water splitting by solar power, solar energy has to be converted to electric energy using solar cells. Solar cell is a device which converts light to electricity usually using semiconductor p-n junction [7]. When a photon hits a piece of semiconductor, one of three things happens;

1. the photon passes through the semiconductor when the photon energy is lower than that of semiconductor band gap,
2. the photon reflects the semiconductor surface,
3. the photon is absorbed by the semiconductor when the energy is higher than that of the semiconductor band gap. In this case, the electron-hole pair (and heat) generates in the semiconductor.

This generated electron-hole pair is the source of the electricity. The generated electron-hole pair usually recombines and emits light or heat at the position. For carrier separation, there are two main mechanisms;

1. drift of carriers driven by an electric field established across the device,
2. diffusion of carriers due to their random thermal motion.

In thick solar cells, there are no electric fields in the active region, thus the dominant mode of carrier separation is diffusion. In order to realize effective carrier separation, the diffusion length of minority carrier must be larger than the cell thickness. This condition is achieved only when the semiconductor is almost perfect and very few defects exist in the semiconductor. Usually, the diffusion length of minority carrier is very short due to the existence of defects and high probability of the recombination with majority carrier. Thus, the semiconductor p-n junction, which extends to the whole thickness of the cell, is used in order to separate the electron-hole pair. The schematic view of solar cell is shown in Fig. 4.

In order to understand the electronic behavior of solar cell, the electrically equivalent model is important. The equivalent circuit model of a solar cell is shown in Fig. 5. An ideal solar cell consists of a current source and a diode (due to the existence of p-n junction or Schottky junction), which is parallel to the current source. In practice, a solar cell has a shunt resistance (R_{SH}) and a series resistance (R_S) with the components of current source and diode.

Using this equivalent circuit, the output current produced by the solar cell (I) is defined as;

$$I = I_L - I_D - I_{SH}, \quad (11)$$

where, I_L is photogenerated current, I_D is diode current, and I_{SH} is shunt current. The output voltage (V) is defined using the voltage across the diode and shunt resistance (V_j) and the series resistance;

Fig. 4 Band diagram of a semiconductor solar cell under short circuit condition

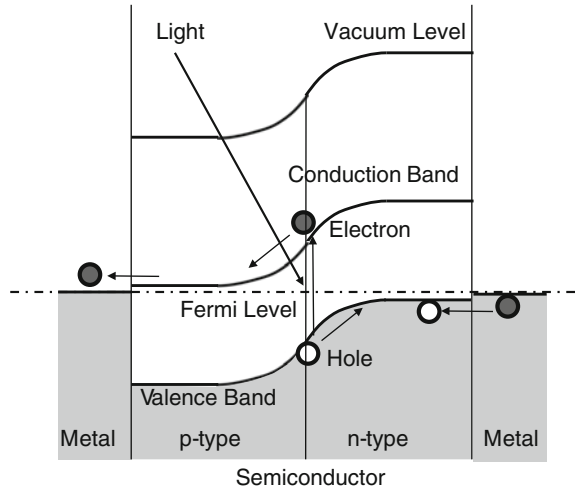
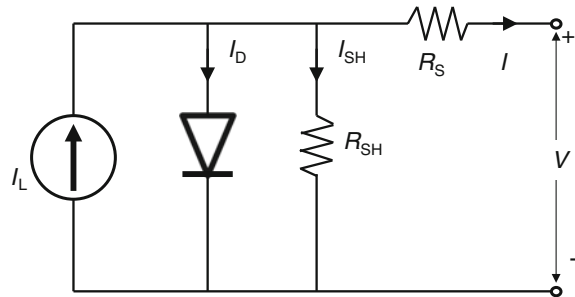


Fig. 5 Equivalent circuit of a solar cell



$$V_j = V + IR_s. \tag{12}$$

The current path through the diode is defined by the Shockley diode equation;

$$I_D = I_0 \left\{ \exp \left[\frac{qV_j}{nkT} \right] - 1 \right\}, \tag{13}$$

where, I_0 is the reverse saturation current, n is diode ideality factor (usually n is in-between 1 to 2, and 1 for an ideal diode), q is elementary charge, k is Boltzmann's constant, and T is absolute temperature. The current passing through the shunt diode is defined by Ohm's law;

$$I_{SH} = \frac{V_j}{R_{SH}}. \tag{14}$$

Substituting Eq. (12–14) into Eq. (11), the characteristic equation of a solar cell is obtained;

$$I = I_L - I_0 \left\{ \exp \left[\frac{q(V + IR_s)}{nkT} \right] - 1 \right\} - \frac{V + IR_s}{R_{SH}}. \tag{15}$$

From Eq. (15), open circuit voltage (V_{OC}) at the output terminals which is defined as $I = 0$ with the assumption of the shunt resistance being high enough to neglect the final term of Eq. (15);

$$V_{OC} \approx \frac{nkT}{q} \ln \left(\frac{I_L}{I_0} + 1 \right). \tag{16}$$

Similarly, short circuit current (I_{SC}) at $V = 0$ for high-quality solar cell (low R_s and I_0 and high R_{SH});

$$I_{SC} \approx I_L. \tag{17}$$

Typical I–V characteristics are shown in Fig. 6. The maximum power conversion point is shown as P_{max} with the current and voltage being I_{max} and V_{max} , respectively. The fill factor (FF) is defined as;

$$FF = \frac{P_{max}}{V_{OC}I_{SC}}. \tag{18}$$

This FF is the key parameter of the performance of solar cell. Solar cell with high FF shows low R_s and high R_{SH} , that is, high-quality solar cell.

Temperature affects the solar cell characteristics Eq. (15) directly via T in the exponential term and I_0 of the reverse saturation current. The net effect is linear

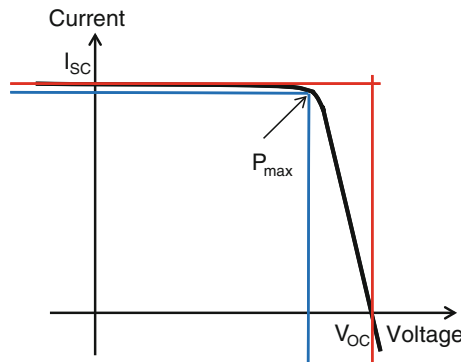


Fig. 6 Schematic current –voltage characteristics for solar cell. I_{SC} , V_{OC} , and P_{max} are short-circuit currents, open-circuit voltage, and maximum power point with current I_{max} and voltage V_{max} , respectively

reduction of V_{OC} with increasing temperature. In addition, I_{SC} increases slightly with temperature due to the bandgap shrinkage in the solar cell material induced by temperature.

4 Electrochemical Cells

Electrochemical cell is a device for the water splitting reaction. Although the wider meaning of electrochemical cell is a device which either derives electrical energy from chemical reaction or facilitates chemical reaction by electrical energy, the device discussed here is the latter definition [8]. The typical structure of the electrochemical cell for water splitting is shown in Fig. 7. It consists of an ion exchange materials in-between an anodic and a cathodic electrode. Proton exchange polymer is usually used as the ion exchange materials for water splitting. The smallest required applied voltage to operate this device for water splitting is the $\Delta_f E$ as defined in Eq. (10) due to the requirement of the chemical reaction.

The simplest equivalent circuit for an electrochemical cell is usually shown as Fig. 8a. The R_{ser} , C_p , and R_p are series resistance of the cell, capacitance and parallel resistance at the electrode-electrolyte interface, respectively. This equivalent circuit is useful for the impedance analysis at a certain voltage V , however, this model is not appropriate for the current–voltage characteristics in DC operations. The equivalent circuit for electrochemical cells in DC operations can be described as Fig. 8b when we discuss the optimal connection between solar cells and electrochemical cells. An electrochemical cell can be used as a fuel cell at its reverse bias region under the existence of hydrogen and oxygen in the electrolyte. For this regime of fuel-cell operation, the equivalent circuit is completely different from the one for electrochemical-cell operation and this is not discussed here.

Using this equivalent circuit, the current flowing the electrochemical cell (I) is defined as;

$$I = I_{Dfwd} + I_{prt}, \quad (19)$$

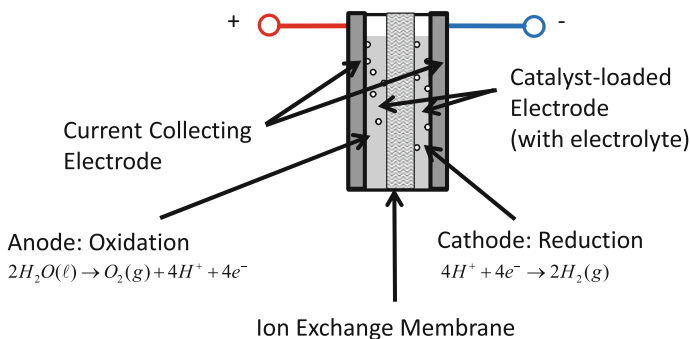


Fig. 7 Schematic electrochemical cell structure for water splitting

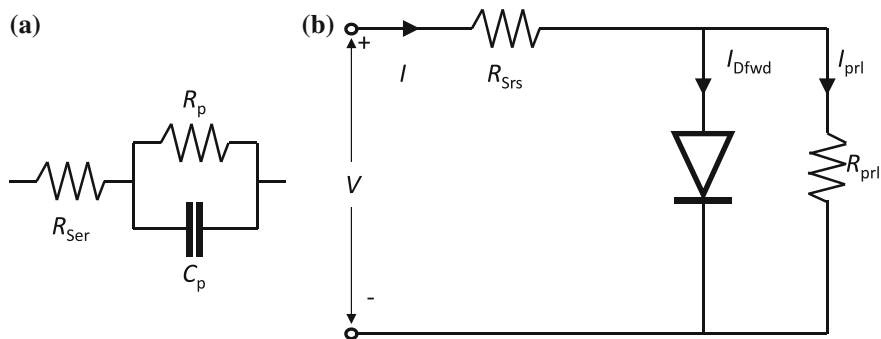


Fig. 8 Equivalent circuit for electrochemical cell **a** for impedance analysis and **b** for DC current circuit

where I_{Dfwd} is the forward diode current and I_{prl} is the parallel resistance current. The current path through the diodes are defined by the Shockley diode equation;

$$I_{Dfwd} = I_{0fwd} \left\{ \exp \left[\frac{q(V - IR_{srs})}{nkT} \right] - 1 \right\}, \quad (20)$$

where, I_{0fwd} is the reverse saturation current for forward diode and I_{0rev} is the reverse saturation current for the reverse diode. The current passing through the parallel diode is defined by Ohm's law;

$$I_{prl} = \frac{(V - IR_{srs})}{R_{prl}}. \quad (21)$$

Substituting Eq. (20) and Eq. (21) into Eq. (19), the characteristic equation of an electrochemical cell is obtained;

$$I = I_{0fwd} \left\{ \exp \left[\frac{q(V - IR_{srs})}{nkT} \right] - 1 \right\} + \frac{V - IR_{srs}}{R_{prl}}. \quad (22)$$

5 Electrochemical Cell Operated by Solar Cells

In order to convert solar energy to chemical energy like hydrogen generated from water splitting, electrochemical cells have to be operated by solar cells. In order to maximize the energy conversion efficiency in both solar cells and electrochemical cells, it is mandatory to employ an appropriate operation point (voltage and current) for both devices. When a solar cell and an electrochemical cell are connected directly in a series, the electric circuit requires the current and voltage under operation to be the same for the two devices. Therefore, the crossing point between

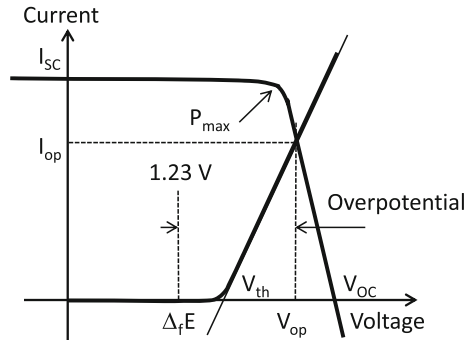


Fig. 9 Schematic current–voltage characteristics of the electrochemical cell operated by solar cell. I_{op} and V_{op} indicate the operating current and voltage, respectively. Overvoltage at the operating current is also shown in the graph

the current – voltage curves for the two devices determines the current (I_{op}) and the voltage (V_{op}) under operation as shown in Fig. 9.

The energy transfer efficiency from sunlight to the chemical free energy of hydrogen is usually defined as solar to hydrogen (STH) efficiency, which is the ratio of the free energy of the produced hydrogen to the input energy of the sun during a unit time;

$$STH = \frac{n_r m F \Delta_f E}{P_{sun}}, \quad (23)$$

where, n_r is the number of electrons transferred for the chemical reaction (2 for hydrogen generation as shown in Eq. (1) or (3)), m is the production rate of the hydrogen (mol/s), F is the Faraday constant (C/mol), $\Delta_f E$ is the minimum required voltage to produce hydrogen from water calculated from standard formation Gibbs energy (1.23 V for the standard condition), and P_{sun} is the energy of the sun light. STH can be decomposed into several elements to analyze the origin of the loss.

1. Conversion efficiency of solar cell (η_{sc}) at the power maximum point

$$\eta_{sc} = \frac{P_{max}}{P_{sun}} = \frac{I_{max} V_{max}}{P_{sun}}. \quad (24)$$

2. Matching efficiency (η_{op}) between the operation point and the power maximum point of solar cell

$$\eta_{op} = \frac{I_{op} V_{op}}{I_{max} V_{max}}. \quad (25)$$

3. The efficiency due to overpotential (η_{ov}), which is the ratio between the operation point voltage and the free energy stored as hydrogen ($\Delta_f E$)

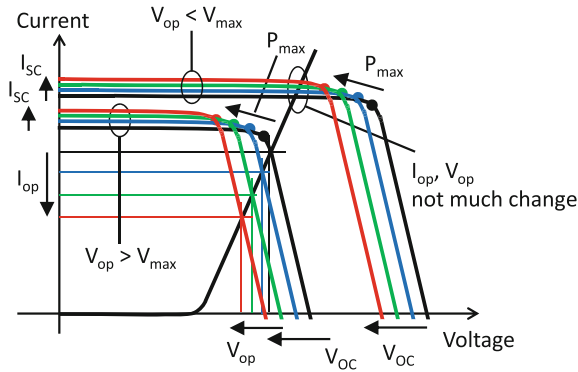


Fig. 10 Schematic current–voltage characteristics of the electrochemical cell operated by solar cell. I_{op} and V_{op} decrease with increasing solar cell operating temperature when $V_{max} < V_{op} < V_{oc}$

$$\eta_{ov} = \frac{\Delta_f E}{V_{op}} = \frac{\Delta_f E}{\Delta_f E + V_{ov}}, \tag{26}$$

where, V_{ov} is the overpotential. In order to improve η_{ov} , overvoltage must be reduced.

4. Faradic efficiency (η_{Fa})

$$\eta_{Fa} = \frac{n_r m F}{I_{op}}. \tag{27}$$

This Faradic efficiency describes the efficiency with the charge transferred into a system where an electrochemical reaction is facilitated. That is the ratio of the produced hydrogen and transferred electron. For the *STH* of Eq. (23) is described with using Eqs. (24)–(27);

$$STH = \eta_{sc} \eta_{op} \eta_{ov} \eta_{Fa}. \tag{28}$$

Each efficiency has to be improved in order to obtain the high *STH* from Eq. (28).

The temperature dependence of the solar cell affects the operation for the direct connection of the solar cell and electrochemical cell. Since the V_{oc} reduces linearly with increasing operating temperature, the operation efficiency is drastically influenced by the operating temperature of solar cell when the operating voltage V_{op} between V_{max} and V_{oc} is as shown in Fig. 10. The operation is relatively stable when the operating voltage V_{op} is smaller than V_{max} . This indicates that the operating voltage V_{op} should be smaller than V_{max} when the electrochemical cell is operated by solar cells with direct connection.

6 Water Electrolysis by Conventional Solar Cells

The practical way of water electrolysis by solar cell is the connection of the planer-type conventional solar cell and polymer-electrolyte electrochemical cell (PEEC). This connection was first reported in 1977 [5], and the usage of the concentrated photo voltaic cell (CPV) to improve the performance was proposed in 1982 [9]. The idea at the beginning was to directly couple the solar cell and electrochemical cell. Voltage and current matching was considered by controlling the number of solar cells and electrochemical cells [5, 9, 10]. The next proposal was the usage of maximum power point tracking (MPPT) to operate solar cells in order to increase hydrogen production [11–13]. The solar cell output voltage was adjusted to the electrochemical cell using a DC/DC converter after that [14]. This connection of the solar cell and electrochemical cell was applied to the polymer electrolyte electrochemical cell and fuel cell system to store and use the renewable energy as chemical energy [15].

Due to the variability of solar radiation, efficient coupling is not easy. The solar cell output voltage adjustment by DC/DC converter with a specific algorithm was proposed in 2008 [16]. The efficiency of electricity to hydrogen with DC/DC converter was greater than 90 % for most voltages [17]. The exception was 87 % when solar cell input power was low because the converter operated near the open-circuit voltage. When a DC/DC converter is used, the efficiency of the converter is also an important parameter for enhancing the total efficiency of the system. Thus, direct coupling of solar cell and electrochemical cell has been also studied [18]. The relative sizing between the solar cell and electrochemical cell was proposed based on the simple modeling of both current–voltage curves [19]. The estimated overall annual energy loss due to direct coupling compared with that using MPPT was estimated to be only a few % [20]. Direct coupling by controlling the number of solar cells and electrochemical cells was also demonstrated [21].

Problems faced in the improvement of the connection of the planer-type solar cell and electrochemical cell are system integration and control. Although the optimized system of the coupling increased the hydrogen generation efficiency, the solar to hydrogen energy conversion efficiency (*STH*) was reported to be 12.4 % [22], which is close to the efficiency of solar cells.

7 Water Electrolysis by Concentrated Solar Cells

In order to improve solar to hydrogen energy conversion efficiency using water splitting, the efficiency of solar cells is the largest bottleneck. The approach of using highly efficient solar cells was gradually applied to the concentrator-array design of solar cell in 1982 [9]. The efficiency of the concentrated-array solar cell made by Si was 11 %, thus, the overall solar to hydrogen conversion efficiency (*STH*) was reported to be 7 %.

The first approach from photoelectrochemical water splitting was to be used for multiple-junction type photoelectrochemical electrodes [23]. The electrode was similar to the multiple-junction solar cell and had the structure of p-In_{0.5}Ga_{0.5}P/n-GaAs/p-GaAs connecting to a metal electrode. The light to hydrogen conversion efficiency under tungsten-halogen white light with 3.0 mol/L H₂SO₄ aqueous solution was reported to be 12.4 %. A photohydrolysis system was proposed in 2000 to be an Al_xGa_{1-x}As/Si double-junction solar cell directly attached to Pt black and RuO₂ electrodes dipped into 1.0 mol/L HClO₄ aqueous solution [24]. The energy conversion efficiency from sunlight to hydrogen was 18.3 % under AM0 (130 mW/cm²).

These two ideas of concentrated solar cell (CPV) and multiple-junction solar cell were combined and used for water splitting as reported in 2007 [25]. The hydrogen generation was performed by a Ga_xIn_{1-x}P/Ga_yIn_{1-y}As double-junction solar cell system and a polymer electrolyte electrochemical cell (PEEC) using Pt-cathode and Ir-anode under 500-times solar light concentration. Unique characteristics include direct attachment of the electrochemical cell under the double junction solar cell and the usage of PEEC. The electrolyte for PEEC is a proton exchanging polymer membrane, thus the system does not require conductive aqueous electrolytes and pure water is used as the source of hydrogen. The energy conversion efficiency from real sunlight to hydrogen was 15.1 % from the recalculation used with the hydrogen Gibbs energy of 1.23 V, which is commonly reported value. The efficiency was reported to be 18.1 % with hydrogen Helmholtz energy of 1.48 V. Since the electrochemical water splitting structure was located just underneath of the tandem type solar cell, the device was specially designed for solar to hydrogen energy conversion.

To establish a “stand-alone total natural energy” system for not only energy generation but also energy usage, a high-efficiency and simple device is suitable for converting sunlight into storage energy. In addition, the separation of electricity and hydrogen generation is indispensable because the energy storage device must be used in conjunction with other energy sources like water and/or wind power generation. Therefore, a much simpler water-splitting hydrogen generation system, combining a PEEC and a concentrated photovoltaic cell (CPV) [26] was proposed. Since the PEEC and CPV can be set separately, the system provides much more flexibility from the design point of view. The energy conversion efficiency under 10-times solar simulator light to hydrogen was 15.3 % with the operating voltage matching EC and CPV.

The typical systems of highly efficient solar cells and electrochemical cell for water splitting are shown in Fig. 11 schematically. The structures, especially those for the solar cells, are complicated. Even though, it is clear that applying high efficiency solar cell to water splitting hydrogen generation is effective for improving conversion efficiency compared to the combination of the planer solar cell and electrochemical cell.

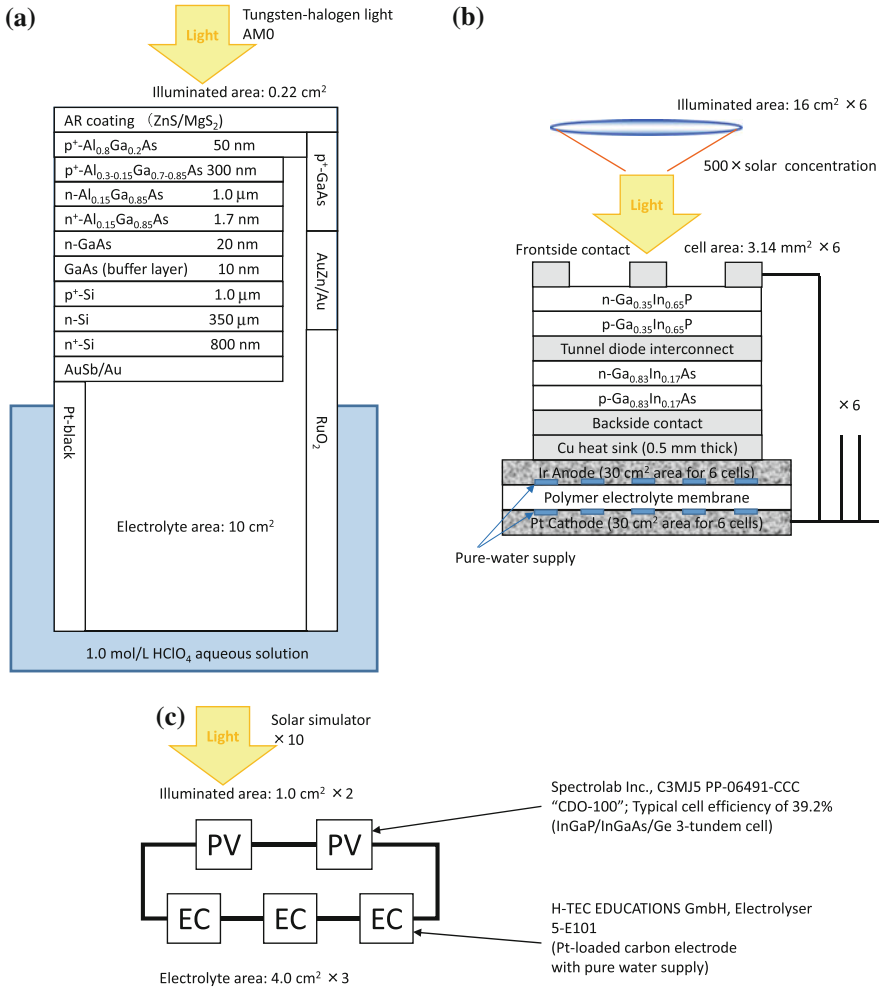


Fig. 11 Schematic diagrams for water electrolysis by concentrated solar cells. **a** Proposed by Licht et al. [24]. **b** Proposed by Peharz et al. [25], and **c** Proposed by Fujii et al. [26]

8 Future Improvements

Keypoints in the improvement of solar to hydrogen conversion efficiency (*STH*) include conversion efficiency improvement of solar cell, voltage and current of electrochemical cell matching the maximum power point of solar cell, electrochemical cell overpotential reduction, and Faradic efficiency improvement. They are discussed with Eq. (28).

The improvement of the conversion efficiency of solar cell affects the increase of *STH* as discussed in the previous section. Another important aspect for the design of

the solar cell is the open circuit voltage or the voltage for the maximum power point. It is clear from the discussion of current matching of Eq. (25), that the operating point for an electrochemical cell should match the maximum power point of a solar cell to reduce loss. This means that the design of the solar cell, when it is coupled with a water electrolyzer, must take into account not only the efficiency of the solar cell itself at its power maximum point but also how the voltage at the power maximum match the operation voltage of an electrolyzer.

For the purpose of water splitting, it is therefore necessary to employ a solar cell whose maximum power point voltage locates around 1.7 V, which is a typical operating voltage of an electrochemical cell at a typical current density such as 0.1 to 1.0 A/cm². An alternative way is to connect plural solar cells and electrochemical cells in series so that the sum of the operation voltages is controlled to well match the solar cell and the electrochemical cells.

The reduction of the overvoltage of electrochemical cell is also important. The hydrogen evolution overvoltage is not so high (<0.05 V for 1 mA/cm²) when appropriate water-reduced electrochemical catalyst is used, however, the oxygen evolution overvoltage is still high (about 0.15 V for 1 mA/cm²) even when a water-oxidized electrochemical catalyst is used [27]. This shows that the development of oxygen evolution electrochemical catalyst is important to improve electrochemical cell performance.

Faradic efficiency was reported to be affected by the current density of the electrochemical cell [26], that is, there exists an optimized current density. This can be explained by the fact that parasitic reaction becomes dominant at low current densities, and the product blocks the reaction at high current density. The keypoint for the improvement is to find the factor for increasing the optimized current density.

9 Conclusion

Electrochemical water splitting by solar cells is the most practical solar to chemical energy conversion technique. Both solar cells and electrochemical cells used for generating hydrogen with splitting water have a long history and are well-studied. However, the optimized coupling of the two devices is not easy and is still under discussion. Conversion efficiency is defined by the conversion efficiency of the solar cell, voltage and current matching of solar cell and electrochemical cell, overpotential of the electrochemical cell, and Faradic efficiency. The usage of high efficiency solar cell like concentrated photo voltaic cell improves solar to hydrogen conversion efficiency. Since both solar cells and electrochemical cells are not suitable for solar to chemical energy conversion, there are many problems even at the device level that have to be resolved.

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