CHAPTER I

INTRODUCTION

1.1 Hydrogen Energy

Since last two centuries, energy consumption worldwide has mainly relied on fossil fuels, such as coal, crude oil, and natural gas. Via burning fossil fuels, especially in the combustion vehicles, air pollution due to the releases of CO_2, CO, SO_x, NO_x, etc. impacts detrimentally both environment and living quality. Moreover, the high energy consumption has resulted in the reduction of the crude oil supply, which is a critical obstacle for the future developments. For decades, renewable energy resources including solar, wind, geothermal, hydropower, biomass, and hydrogen have been of interest to replace fossil fuels. Since hydrogen offers many advantages of high energy density (142 MJ kg^{-1}) (Jain, I. P., Lal, and Jain, A., 2010), great varieties of sources (e.g., water, biomass, and organic matters (Figure 1.1)) and low environmental impact, usage of hydrogen in fuel cell for several applications of stationary powers, portable devices, and transportations has been widely proposed.

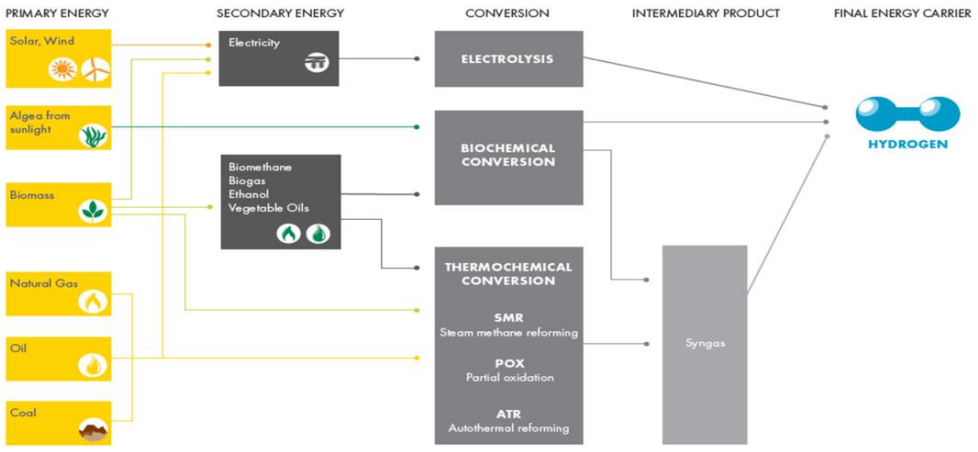

Figure 1.1 Processes of hydrogen productions (Shell Deutschland Oil GmbH 22284 Hamburg, 2017).

Hydrogen can be produced by steam methane reforming, partial oxidation, auto thermal reforming, or electrolysis methods, but the cost of these processes are quite high and they require energy in the production process. Therefore, scientists are turning to hydrogen production by biological methods or bio-hydrogen (Figure 1.2).

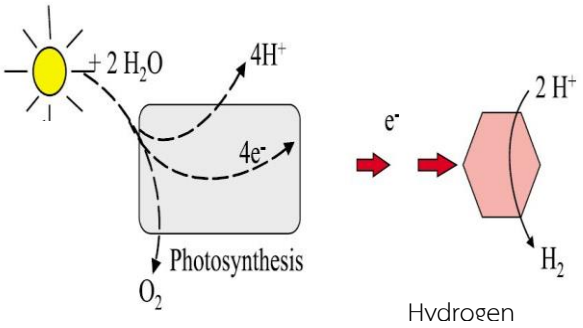

Figure 1.2 Bio-hydrogen processing cycle (Microbial Redox Metalloenzyme Research Group, 2005).

Figure 1.2 shows the bio-hydrogen processing cycle. This process is the production of hydrogen using solar energy. In this process, solar energy is captured by the photosynthetic apparatus, afterward, water is decomposed into oxygen (O_2), protons (H^+), and electrons (e^-). Electrons are delivered to hydrogenase enzyme to created hydrogen (Microbial Redox Metalloenzyme Research Group, 2005). The first commercial fuel cell vehicle (FCV) from Toyota, named Mirai was launched in Japan (2016) and planned to sale worldwide in the following years. In 2021, two hydrogen cars named Toyota Mirai and Hyundai Nexo have been released in selected markets (IHS Inc, 2016). Moreover, hydrogen fuel-cell vehicle name Honda Clarity was produced from 2016-2021 (Haymarket Media Group, 2021).

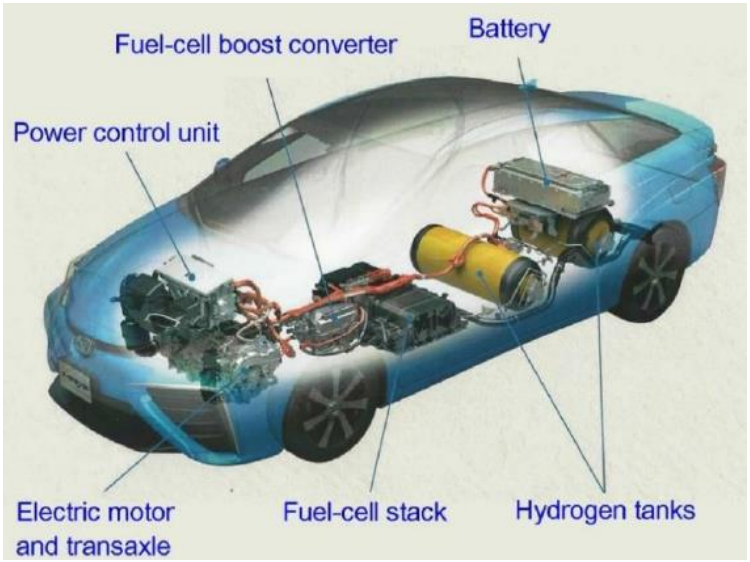

Figure 1.3 Components of Toyota Mirai (Tuan, Karpukhin, Terenchenko, and Kolbasov, 2018).

From Figure 1.3, the major components of Toyota Mirai are proton exchange membrane fuel cell (PEMFC) stack, compressed hydrogen storage tanks, nickel-metal hydride battery, power control unit, and motor. PEMFC stack consisting of 370 single cells (37.74 kg) provides maximum output of 114 kW (Yoshida and Kojima, 2015). For compressed hydrogen storage tank ($p(H_2)$= 70 MPa), volumetric and gravimetric hydrogen capacities are 40 gH_2/L and 5.7 wt. % H_2, respectively. Up to 5 kgH_2, required for 480 km driving distance can be filled in two compressed hydrogen gas tanks with total weight and volume of 87.5 kg and 122.4 L, respectively (Millikin, 2014).

1.2 Fuel Cells

There are several types of fuel cells, each of which is suited for different applications. Fuel cells are typically grouped according to their operating temperatures and types of electrolyte used (Table 1.1). The amount of power generated by a fuel cell is determined by several factors including fuel cell type, size, operating temperature, and pressure. The most common type of fuel cell used in FCVs is the polymer electrolyte membrane fuel cells (PEMFCs).

Table 1.1 Types of fuel cells (Larminie, 2003; U.S. Department of Energy, 2023).

Fuel cell types	**Electrolytes**	**Operating temperature (°C)**	**Applications**
Proton exchange membrane fuel cells (PEMFCs)	Polymers	50-90	- Transportation - Specialty vehicles - Portable power - Backup power - Distributed generation
Alkaline fuel cell (AFC)	Solution of KOH in water	60-90	- Transportation - Military - Submarine - Backup power
Direct methanol fuel cells (DMFCs)	CH_3OH/CO_2	80-110	- Portable power - Vehicles - Military - Man-portable tactical equipment
Phosphoric acid (PAFC)	H_3PO_4	160-220	- Distributed generation
Molten carbonate fuel cell (MCFC)	molten Na_2CO_3	600-700	- Military - Electrical utility - Power plants
Solid oxide fuel cell (SOFC)	ZrO_2	700-1,000	- Auxiliary power - Electric utility - Distributed generation

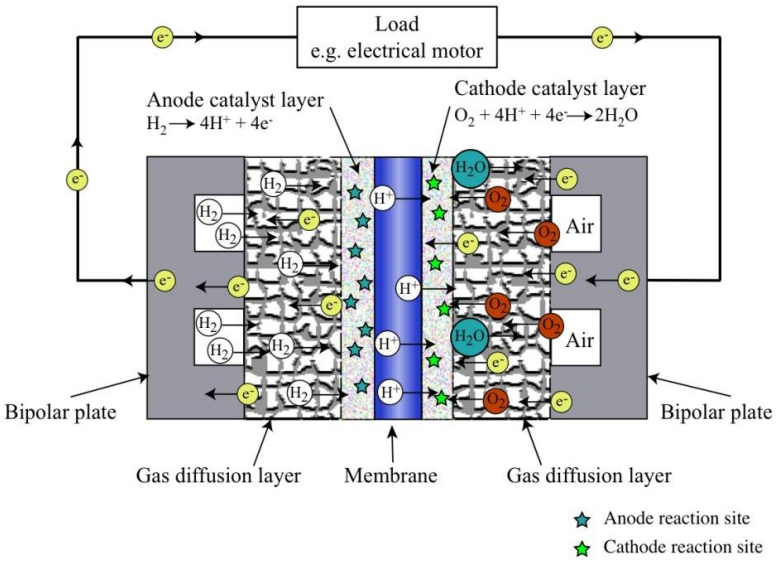

Figure 1.4 Polymer electrolyte membrane fuel cells (PEMFCs).
(http://www.mece.ualberta.ca/groups/energysystemsdesign/research.html)

PEMFCs consist of polymer electrolyte membrane (PEM), electrodes, bipolar plates, and gas diffusion layers (Figure 1.4). The PEM placed between anode (negative electrode) and cathode (positive electrode) by pressure/temperature compression is denoted as a membrane electrode assembly (MEA). Hydrogen gas supplied to anode performs oxidation reaction (equation (1.1)) to produce protons (H^+) and electrons (e^-).

$$2H_2 \rightarrow 4H^+ + 4e^- \quad (1.1)$$

The PEM allows only protons passing through to cathode, while the electrons travel through an external circuit to the anode. The flow of electrons through this circuit creates the electric current. At cathode, oxygen gas reacts with protons and electrons to produce water and heat (equation (1.2)). Overall redox reaction of PEMFC is shown in equation (1.3).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O + \text{Heat} \quad (1.2)$$

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Heat} \quad (1.3)$$

Although redox reaction rate in PEMFCs can be improved by increasing operating temperature (> 100 °C), evaporation of water molecules acting as proton carriers in PEM (e.g., Nafion membrane) results in significant reduction of proton conductivity. Therefore,

research and developments on the enhancement of operating temperature of PEM by preparation of polymer-inorganic composites and syntheses of thermally stable polymers have been intensively focused. Besides operating temperature, purity of hydrogen gas supplied to PEMFC is another concern. For example, carbon monoxide (CO) impurity in hydrogen gas produced from steam natural gas reforming process can seriously poison the platinum (Pt) catalyst at electrodes. The other factor affecting the performance of on-board PEMFCs in transportation is hydrogen storage systems with high hydrogen capacity, operating at moderate temperature and pressure condition, fast hydrogen charging and discharging, and low cost.

Table 1.2 Competing technologies for hydrogen storage systems (Varin, Czujko, and Wronski, 2009; Hirscher, 2009).

Storage systems	Volumetric hydrogen capacity ($kgH_2\ m^{-3}$)	Drawbacks
Compressed hydrogen gas under 80 MPa pressure	~40	-Safety problem -Cost of pressurization -Large pressure drop during use hydrogen
Liquefied hydrogen at cryogenic temperature (-252 ºC or 21 K)	~71	-Large thermal losses -Safety -Cost of liquefaction
Cryo-compressed hydrogen (350 bar, 63 K)	~80	-Large thermal losses -Safety problem
Solid state hydrides	80-160	-High hydrogen desorption/ absorption temperature -Slow hydrogen desorption/ absorption kinetics -Release of toxic gases during operation (e.g., B_2H_6 from decomposition of $LiBH_4$

Considering compressed hydrogen gas system used in the car (Toyota Mirai, Figure 1.3), not only materials and technology for tank fabrication are expensive to resist high hydrogen pressure (80 MPa) and impact in the case of accident, but also cost of pressurization. Moreover, low storage capacity (40 kgH_2 m^{-3}) is obtained despite compression under high pressure. For liquefied hydrogen, although hydrogen can be stored at lower pressure than compressed hydrogen system, remarkable cost of insulation for storage tank and refilling station to keep hydrogen in liquid form (at 20 K) hampers its use in practical application. Thus, further development of cryo-compressed system has been proposed. In this system, hydrogen can be stored in the form of liquid-gas mixture at higher temperature than liquefied hydrogen (63 K) and lower pressure than compressed gas (35 MPa). In addition, cryo-compressed system provides superior hydrogen storage capacity (80 kgH_2 m^{-3}) to compressed and liquefied hydrogen. However, hydrogen stores at nearly cryogenic temperature and high pressure in cryo-compressed system, therefore, hydrogen storage tank with good thermal insulation and high pressure tolerance cannot be avoided. In the case of solid state hydrides, high theoretical volumetric and gravimetric capacities of 80-160 kgH_2 m^{-3} and 5-18 wt. %, respectively (Züttel, Remhof, Borgschulte, and Friedrichs, 2010) are attractive for hydrogen storage applications. However, hydride materials still have some obstacles based on severe temperature and pressure conditions for hydrogen desorption/absorption (e.g., above 400 °C and 600 °C (under 35 MPa H_2) (Orimoa, Nakamoria, and Kitaharaa, 2005) for hydrogen desorption and absorption, respectively, for $LiBH_4$), slow hydrogen desorption/absorption kinetics (rehydrogenation of $LiBH_4$ at ~600 °C, 35 MPa H_2, for >12 h) (Züttel, Wenger, and Rentsch, 2003), and release of toxic gases during operation (e.g., B_2H_6 from $LiBH_4$). With respect to the targets of hydrogen storage system for fuel cell vehicles (Table 1.3), in this wok we aim to improve the performances of hydride materials focusing on high hydrogen content released and reproduced, fast hydrogen exchange reaction rate, and low temperature and pressure for de/rehydrogenation.

Table 1.3 US DOE Freedom CAR hydrogen storage system targets (U.S. Department of Energy, 2023).

Targeted factors	2020	2025	Ultimate
Compressed automotive hydrogen storage systems			
Gravimetric density			
kWh/kg system	1.5	1.8	2.2
(kg H_2/kg system)	(0.045)	(0.055)	(0.065)
Volumetric density			
kWh/L system	1.0	1.3	1.7
(kg H_2/L system)	(0.030)	(0.040)	(0.050)
Cost			
$/kWh	10	9	8
($/kg H_2)	(333)	(300)	(226)
Durability/Operability			
Operating ambient temperature (°C)	-40/60	-40/60	-40/60
Min/max delivery temperature from storage system (°C)	-40/85	-40/85	-40/85
Operational cycle life (1/4 tank to full) (cycles)	1,500	1,500	1,500
Min/max delivery pressure from storage system (bar)	5/12	5/12	5/12
System fill time (min)	3-5	3-5	3-5

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