Methanol Electrolysis for Hydrogen Production Using Polymer Electrolyte Membrane: A Mini-Review

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Abstract: Hydrogen (H_2) has attained significant benefits as an energy carrier due to its gross calorific value (GCV) and inherently clean operation. Thus, hydrogen as a fuel can lead to global sustainability. Conventional H_2 production is predominantly through fossil fuels, and electrolysis is now identified to be most promising for H_2 generation. This review describes the recent state of the art and challenges on ultra-pure H_2 production through methanol electrolysis that incorporate polymer electrolyte membrane (PEM). It also discusses about the methanol electrochemical reforming catalysts as well as the impact of this process via PEM. The efficiency of H_2 production depends on the different components of the PEM fuel cells, which are bipolar plates, current collector, and membrane electrode assembly. The efficiency also changes with the nature and type of the fuel, fuel/oxygen ratio, pressure, temperature, humidity, cell potential, and interfacial electronic level interaction between the redox levels of electrolyte and band gap edges of the semiconductor membranes. Diverse operating conditions such as concentration of methanol, cell temperature, catalyst loading, membrane thickness, and cell voltage that affect the performance are critically addressed. Comparison of various methanol electrolyzer systems are performed to validate the significance of methanol economy to match the future sustainable energy demands.

Keywords: hydrogen production; fuel cell; cell voltage; methanol; future energy

1. Introduction

The energy-related issues of the future, such as economic development, environmental friendliness, pollution free atmosphere, climate change, and wider availability, are complex and multi-dimensional [1]. A highly efficient and sustainable energy system produces only minimal harmful emissions [2,3]. Fuel cells are such clean alternatives to replace power production from fossil fuels [4], yet operating at high efficiency. H_2 is a clean energy source available from both renewable and non-renewable bases, and serves as input for the fuel cells [5,6]. It can also be regenerated by the fuel cell when connected in reverse mode (electrolyzer) through any hydrogen carrier such as water, methanol, etc. For instance, dark fermentation with anaerobic digestion of residual algae biomass is a significant method to generate H_2 and methane (bio-hythane) [7]. Such sustainable biofuel production can solve the energy issues in the modern technological world to a great extent.

According to the US Department of Energy (DOE), "Hydrogen is a leading candidate because it can be clean, efficient and capable of production from diverse domestic resources, both renewable and non-renewable". There are many technologies to produce hydrogen such as electrolysis or thermolysis of water, photoelectrochemical/photocatalytic splitting of water, hybrid fossil fuel/renewable technologies, reforming from fossil fuels, high-temperature ceramic membranes, biomass gasification, thermochemical processes and low-temperature techniques [8,9]. However, they are not efficient due to CO control issues. While the thermolysis of water faces the recombination issues of H_2 and O_2, difficulty to obtain heat sources, and heat exchange and corrosion problems, photoelectrolysis depends on the solar radiation intensity and the optimization of photocatalysts. Though electrolysis is the most widely adopted H_2 production method, it faces several limitations such as requirement of large space and external connections for monopolar electrolyzers, joining, and sealing of the cells in series for the bipolar electrolyzers, etc. Corrosion-related issues are also very common in alkali-based electrolysis process [10]. In recent years, there are many research activities towards aqueous methanol electrolysis due to its high-purity hydrogen production characteristics despite of lower operating voltage. Thus, the fuel cell and electrolyzers can contribute to sustainability by meeting the energy demand in a positive manner.

Polymer electrolyte membrane fuel cells (PEMFCs) with H_2 energy source are promising power solutions for numerous applications [11,12] due to their superior performance, light weight, and power density [13]. Fuel cell vehicles exhibit higher energy efficiency around 40–50% compared to conventional internal combustion (IC) engine vehicles (gasoline/battery hybrids), which provide 10–16% efficiency in current road tests [2]. However, the hydrogen storage units associated with the vehicles possess considerable challenges for the wider marketplace. On-site H_2 production from ethanol or methanol can solve the distribution and storage issues at the same time, and this is why polymer electrolyte membrane (PEM) fuel cells are gaining significant interest [14,15].

PEM-based electrolysis has numerous advantages compared to alkali-based electrolysis, such as the ability to operate at high current densities, high-level gas purity, safe and optimum H_2 compression possibility at high pressure, adaptability to transient electrical power variations, and lower mass/smaller dimensions [16,17]. However, the high investment cost and shorter lifetime of PEM electrolyzers require extensive studies to develop efficient materials with high H_2 production capacity [10]. Methanol fuel in PEM electrolysis is more interesting for hydrogen production as it is economical and has respective volumetric and gravimetric densities of 4.82 $kWhL^{-1}$ and 18.8% by weight [18,19] compared with pressurized hydrogen (0.18 $kWhL^{-1}$ at 1000 psi, 25 °C) [20–22]. In this review, we have summarized the recent literature focusing on PEM-based methanol electrolysis for ultra-pure and on-demand hydrogen production. However, there are many papers in the open literature for methanol oxidation, and the current study reports and compares the challenges and advantages in the field. The electrochemical reforming process is environmentally friendly as bioalcohol is the fuel and the plants can recapture the CO_2 byproduct. Other advantages such as H_2 production in the cathodic compartment is also discussed in this report. The current study also includes extensive critical discussion on the operating parameters to optimize the hydrogen production challenges and subsequently emphasizing its economic benefits.

Pure Hydrogen Production from Methanol by Electrochemical Method

Figure 1 schematically represents the various strategies of hydrogen production and the significance of fuel cells. Narayanan et al. (2001) from the California Institute of Technology, USA [23], first proposed the concept of H_2 production by electrolysis of aqueous organic solutions. He claimed that a methanol–water mixture could be electrolyzed through a PEM electrolyzer cell to produce high-purity hydrogen at a very low operating voltage (ca. one-third) compared to a water electrolyzer. In addition, the economics of H_2 production by this technique includes the cost of methanol. Thus, this technique could result in about 50% less cost compared to hydrogen produced by the electrolysis of water. Solar energy can be converted to mechanical and electrical energy that further used for the electrolysis process of H_2 generation. In addition, the solar radiation can be useful for the thermolysis, photolysis and

biomass conversion (photo fermentation) processes. Dark fermentation is another promising method of biomass degradation using anerobic bacteria in the absence of light [24].
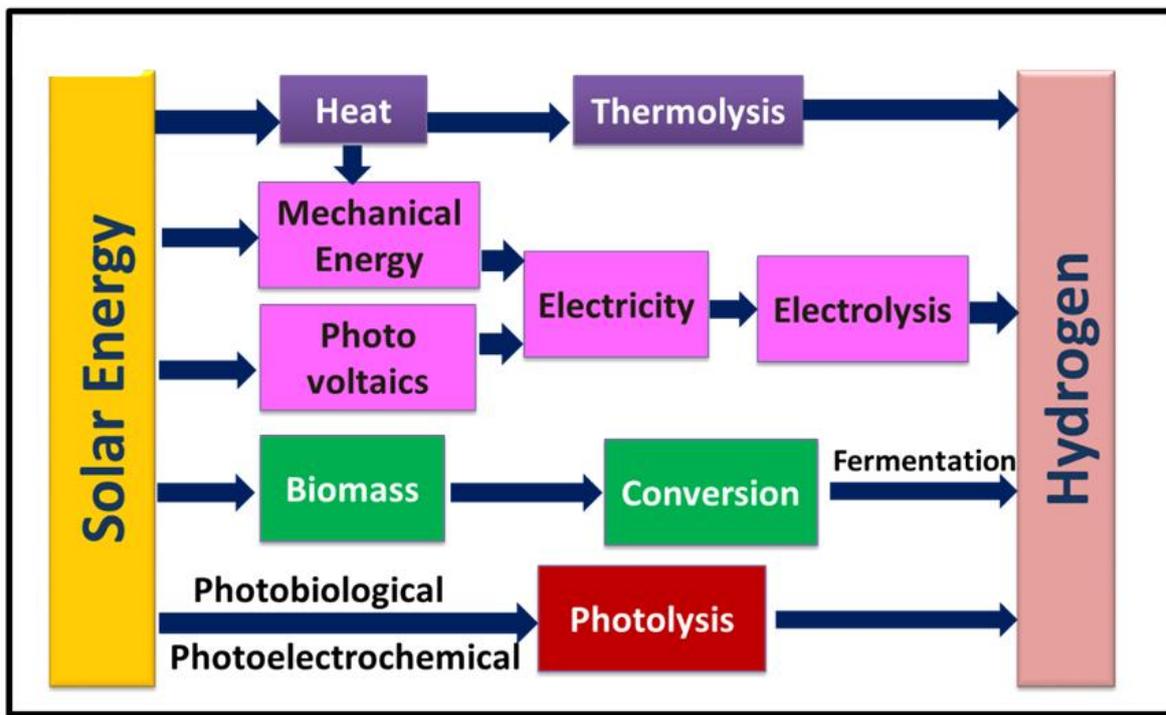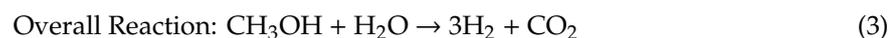

Figure 1. Schematic representation of various strategies of H_2 production from solar radiation.

PEM-based methanol electrolyzer has a structural configuration similar to a PEM fuel cell with a polymer electrolyte membrane (PEM) sandwiched between the gas diffusion electrodes (GDEs), anode, and cathode. A GDE has two layers, gas diffusion and catalyst, that are bonded with the membrane to form a membrane electrode assembly (MEA). Platinum or platinum alloys are used as electrocatalysts due to their reactivity, selectivity, and chemical stability [25,26]. Reactant gas is supplied to the electrode by flow field plates on either side of the MEA, and analogously to in an electrolyzer, water is fed to the anode and H_2 is formed at cathode. Figure 2 shows a line sketch of the PEM-based electrolyzer cell.

Generally, the MEA reduces the resistance to a minimum. The aqueous methanol solution at the anode liberates CO_2 by the following chemical reaction when current is applied:

$$\text{Anode Reaction: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1}$$

These electrons migrate externally to the cathode. The protons (H^+) liberated travel through the proton conducting membrane to the cathode, where it combines with the electrons, to generate H_2, as shown below:

$$\text{Cathode Reaction: } 6H^+ + 6e^- \rightarrow 3H_2 \tag{2}$$

$$\text{Overall Reaction: } CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \tag{3}$$

Carbon dioxide is also produced in this process, in addition to H_2 by steam, reforming methanol. However, during the electrolysis of methanol–water mixture, H_2 and CO_2 get separated, and are liberated in separate compartments (cathode and anode) and, thus, purification of hydrogen to remove CO_2 is not required in this process. Due to these potential advantages, in the recent year, many systematic investigations have been carried out on H_2 generation by methanol–water electrolysis using a PEM methanol electrolyzer (PEMME) [27,28]. In addition, hypothetically, electrolysis of

methanol occurs at about 0.02–0.03 V, which is much lower compared to the minimum theoretical voltage of 1.23 V for water electrolysis (Table 1).
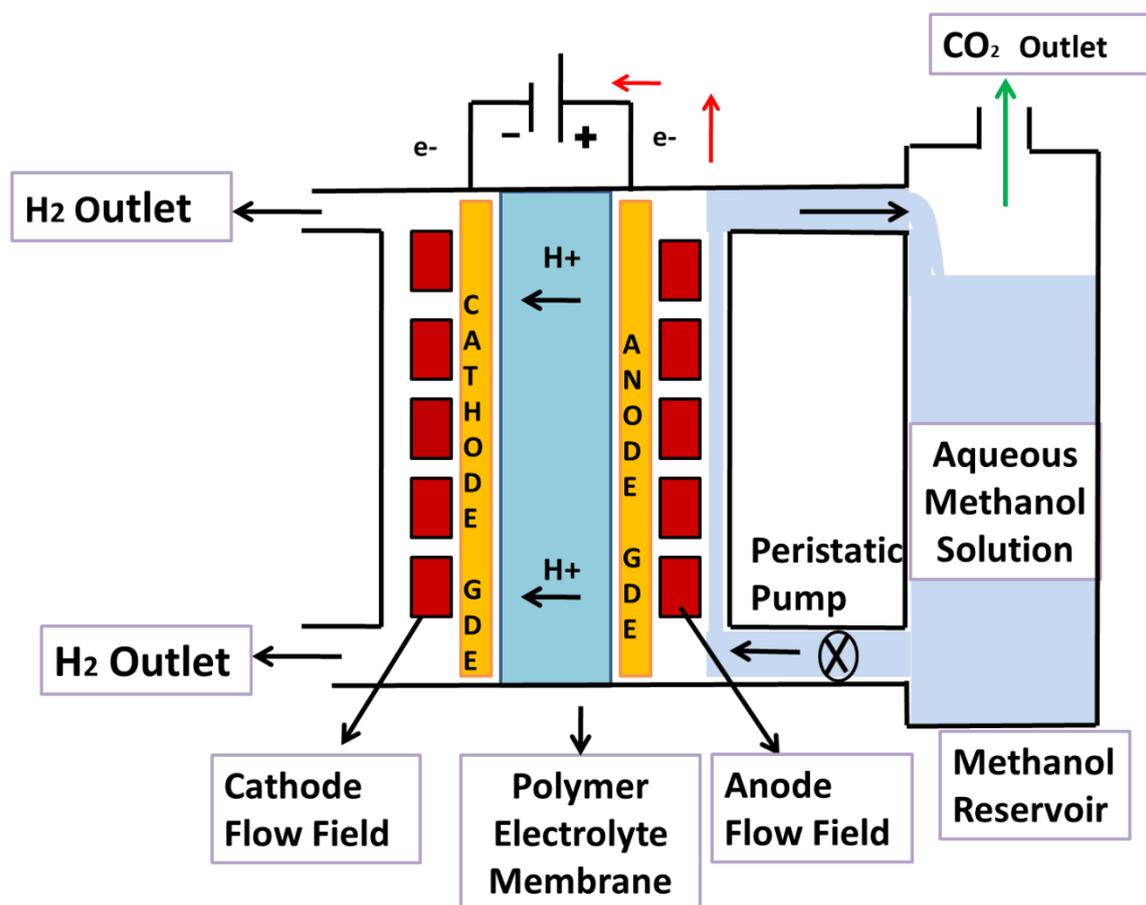

Figure 2. Schematic of polymer electrolyte membrane (PEM) methanol electrolyzer.

Table 1. Comparison of different energy parameters such as onset potential/efficient for different solvents to convert hydrogen.

Fuel	Electrical Potential for Electrolysis (V)	Energy Density (kWh/kg)
Water	1.23 V	–
Methanol	0.03 V	6.1
Ethanol	1.145 V	8.1
Ammonia	–	5.7

Since methanol electrolysis occurs at a very low voltage, there is scope for development of very low power consuming hydrogen generators based on methanol–water electrolysis [29]. The PEM technology for electrolysis was introduced in the 1960s by GE, USA, to overcome the limitations of the alkaline electrolysis technology [30]. The uniqueness of this technology is its potential to operate at high current densities [31] that can possibly result in reduced operational costs.

2. Components of PEM Methanol Electrolyzer

NASA first invented PEMFCs in the early 1960s; however, their high cost and difficulty in management prevented their commercial development until the 1990s. Further research resulted in the development of low-cost smart electrolyte membranes, and from the 1990s, PEMFCs are one of the priority areas of scientific attention. Their high efficiency, simplicity, flexibility, and low operation

temperature in addition to low cost are fundamental in designing a sustainable energy environment. Commercially viable designs are under investigation, with cheaper and lighter compact structures [32].

The major components of a polymer electrolyte membrane methanol electrolyzer (PEMME) are shown in Figure 3. MEA is placed between two Ti or graphite plates on which flow channels are grooved. Titanium mesh is placed on either side of the MEA for effective current collection, back support for MEA, and uniform methanol and gas distribution. To prevent electric shortage between the plates and for fluid sealing, suitable gaskets are placed around the electrode area on both sides of the MEA. The above set together with the grooved plates is finally clamped together between two end plates using nuts/bolts. Current is applied between the Ti fluid distribution plates. In the cells with graphite plates, used for fluid distribution, current is applied to the copper plates kept between the graphite plate and end plate. Major components of the PEM methanol electrolyzers such as electrode plates, membrane assembly, and current collector are discussed in this section.
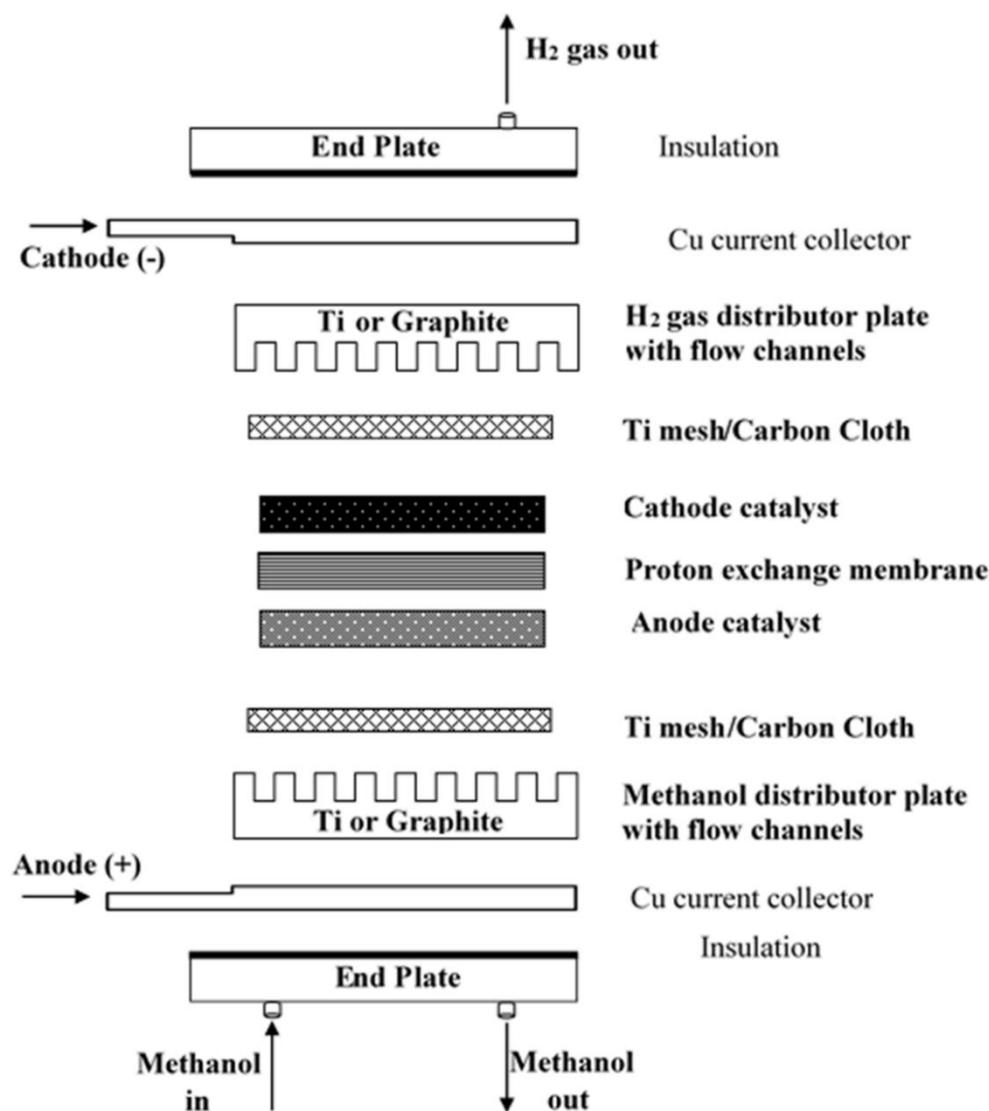

Figure 3. Components of PEM methanol electrolyzer.

2.1. Bipolar Plates

The bipolar plate is one of the main components of the electrolyzer and it should fulfill the following functional requirements [33–41]. The functional attributes of bipolar plates are good thermal/electrical conductivity, mechanical stability, corrosion resistance at low thickness, lightweight and low cost.

Since the theoretical value for the methanol–water electrolysis voltage is 0.02 V, much smaller than the 1.23 V required for water electrolysis, the theoretical energy consumption for aqueous methanol electrolysis is low [6]. Therefore, stainless steel and carbon-based materials are used as bipolar plates for PEM methanol electrolysis. However, due to its poor corrosion resistances, these materials cannot be used on the anode side of the PEM water electrolysis at high operating voltages [42].

Shudo et al. [43] studied porous flow field methanol electrolyzer made of sintered metal powder and reported significant improvement in hydrogen production by their bipolar plate compared to conventional grooved bipolar plates [43]. This is due to improved reactant supply and actual byproduct removal by the proposed porous bipolar plate. Moreover, porous structure increases the effective electrode area by the flow field. In another investigation by the same research group [44], the influence of grain diameter and porous metal flow field, as shown in Figure 4, is reported.
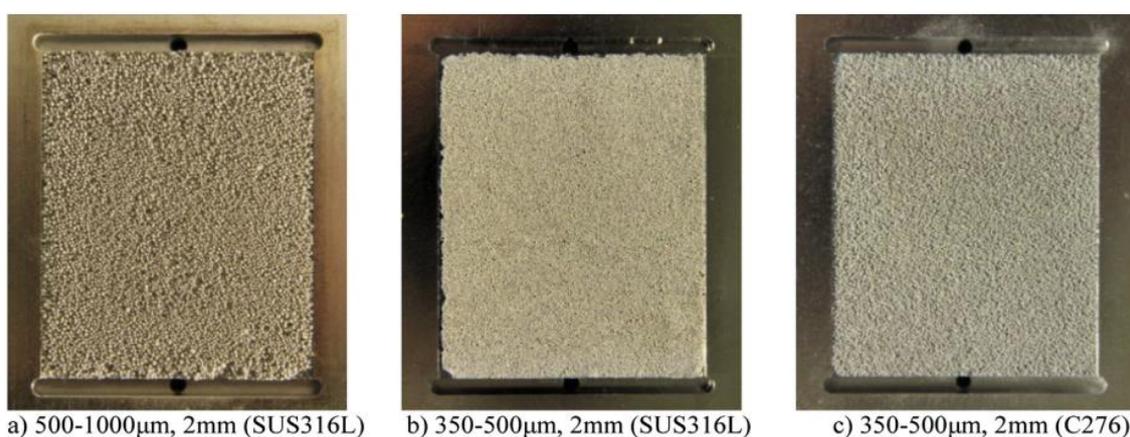

a) 500-1000μm, 2mm (SUS316L)   b) 350-500μm, 2mm (SUS316L)   c) 350-500μm, 2mm (C276)

Figure 4. Porous flow fields made of sintered spherical metal powder with different grain diameter (**a**) 500–1000 μm (**b**) 350–500 μm for SUS316L steel and (**c**) 350–500 μm for C276 steel. Adapted with permission from [44], copyright 2013.

From the investigation, it is clear that the reduced grain diameter and lower cell resistance (attributed to higher contacting spots in small area) enhanced the H_2 production performance of the electrolyzer. In our previous study [14], we used graphite as a bipolar plate for methanol electrolysis. Initially, a titanium plate was used and ironically, for the water electrolyzer the operating voltage was high. Consequently, we decided to fabricate PEMME using graphite plates, since the operating voltage is low, to reduce the capital cost and compare its performance with that of Ti-based cell.

2.2. Current Collector

The current collector efficiently distributes the current to the catalyst layer from the external circuit, leads the methanol flow to anode layers, and provides structural support to the MEA. An efficient current collector needs to fulfil several functional attributes, namely [45]:

1.   Strong corrosion resistance.
2.   Good electrical conductivities.
3.   Good mechanical support to the membrane.
4.   Effective removal of gases and efficient reaction pathways for fuel to reach catalyst layer.

Platinized titanium mesh (Figure 5) of thickness 0.1 to 0.25 mm is used as a current collector in most of the studies [6,46] due to its exceptional performance in water electrolysis. Titanium mesh is expensive, and its sharp corners damage the membrane unless it is properly placed. Consequently, in our studies [14,47], we used a pore-designed microporous-layer-coated gas diffusion layer as a current distributor in PEM methanol electrolyzer due to the low voltage operation of methanol electrolyzers. The pore design efficiently provides pathways to the fuel to easily reach the catalyst

layer similarly to conventional Ti mesh (shown in Figure 5a). However, the limited number of pores effectively control the methanol flow into the catalyst layer (B—shown in Figure 6). This reduces the initial cost of PEM methanol electrolyzer compared with PEM water electrolyzer that contains expensive Pt-coated titanium bipolar plate and Ti mesh current collector.
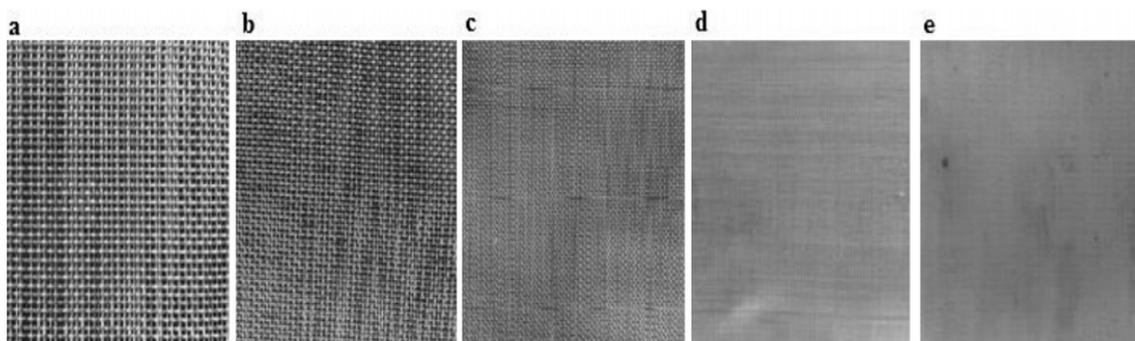

Figure 5. Five different types of the current collector with (**a**) 41%; (**b**) 39.4%; (**c**) 38.5%; (**d**) 27%; (**e**) 16% open ratios. Adapted with permission from [46], copyright 2015.
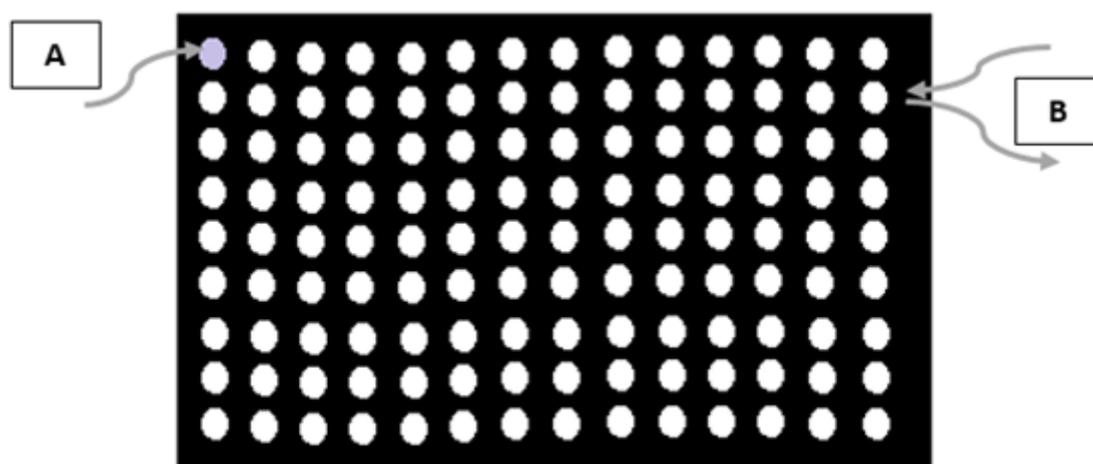

Figure 6. Gas diffusion layer with pore design (**A**) pore and (**B**) limited pore area. Adapted with permission from [14], copyright 2014.

2.3. Membrane Electrode Assembly

MEA includes anode and cathode with a membrane in between. Generally, MEA has been prepared by various techniques, and the following materials have been used for its fabrication [48,49]: electrocatalyst, ionomer solutions, proton exchange membranes, carbon cloth or polyimide film or Teflon film (as catalyst decal support), solvents like isopropyl alcohol (IPA), water, etc. Due to their important role and recent research focus, this section mainly elaborates on electrocatalyst and the development of proton exchange membranes for PEMME.

2.3.1. Electrocatalyst for Methanol Electrolysis

There are many reports on electrooxidation of methanol [50–59], but this paper principally focuses on methanol oxidation for hydrogen productions. Narayanan [23] et al. first described H_2 production by aqueous organic solution electrolysis using Pt–Ru catalyst. They reported that bimetallic powder of separate Pt particles and Ru particles produce better results than its alloy. To improve the electrolysis efficiency, they have added titanium oxide, rhodium, iridium, and osmium as an additive. They found the best performance was achieved with 60% Pt and 40% Ru. Few studies report aqueous methanol electrolysis and are predominantly on Pt–Ru-based alloy, due to its CO-tolerant nature. Table 2 shows

some of the recent studies based on Pt–Ru/C as anode catalyst for methanol electrolysis applications. For each system, the composition of Pt and Ru depends on the energy consumption value; however, no general trend is observed based on the specific concentration.

Table 2. Energy consumption of electrolysis based on Pt–Ru/C as an anode catalyst.

Anode Catalyst	Cathode Catalyst	Membrane	Energy Consumption kWh $(Nm^3)^{-1}$	Reference
40% Pt–Ru/C	20% Pt/C	Nafion-117	1.48–2.87	[23]
Pt–Ru (1:1)/C	Pt/C	Nafion-117	1–1.2	[60]
Pt–Ru (1:1) black	Pt black	Nafion-115	1.46	[61]
50% Pt–Ru/C	50% Pt/C	Nafion-117	1.38–1.78	[43]

Other than Pt–Ru, there are few more novel catalysts have been tested for hydrogen evolution reactions. Nei et al. [62] prepared Pd-modified Pt supported by tungsten carbide nanocrystals (PtPd–WC/C) by intermittent microwave heating. They reported PtPd–WC/C had better performances in H_2 evolution reactions compared to Pt–WC/C electrocatalyst, due to the specific function of Pd. Badwal et al. [63] investigated methanol electrolysis with Pt-based anode (methanol oxidation) catalysts (Pt/C, Pt/C–SnO_2, Pt/C–CeO_2, PtRu/C, PtRu/C–SnO_2, and PtSn/C) and reported the cell performance in the order of PtRu/C > Pt/C–SnO_2 > PtRu/C–SnO_2 > Pt/C > PtSn/C > Pt/C–CeO_2 as shown in Figure 7a. From the durability study, it is inferred that Pt/C–SnO_2 catalyst gives the lowest cell voltage with time, representing high stability due to SnO_2 addition.
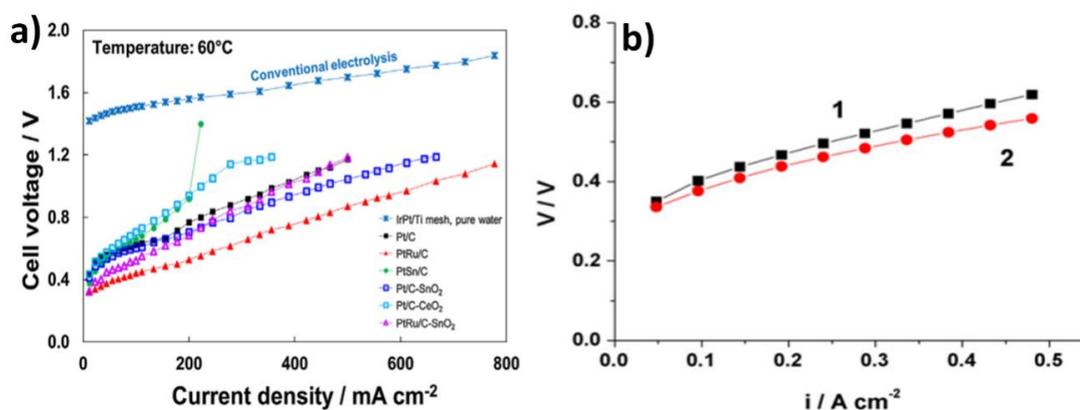

Figure 7. (**a**) Comparison of methanol assisted water electrolysis (2 M methanol at 60 °C) by 40 wt% Pt/C, 40 wt% PtRu/C, 20 wt% PtSn/C, 40 wt% Pt/C–SnO_2,40 wt% Pt/C–CeO_2, and 40 wt% PtRu/C–SnO_2 (**b**) Current–voltage curves of membrane electrode assemblies (MEAs) of (1) Pt/C and (2) Pt–WC/C cathode electrocatalysts in 2 mol dm^{-3} CH_3OH at 90 °C. Adapted with permission from [63], copyright 2017.

Cathode catalysts also play significant role in methanol electrolysis as alternative low-cost electrocatalysts can be developed in that directions. Shen et al. [64] prepared tungsten carbide-supported Pt/C (Pt–WC/C) as cathode electrocatalyst by intermittent microwave heating. The Pt-WC/C cathode electrolyzer performed better than the Pt/C cathode electrocatalyst (Figure 7b).

In an above similar study, Dhathathreyan et al. [65] used Pd nanoparticles as cathode catalyst and reported that the cell performance using MEA with Pd nanoparticles is similar to that of MEA based on C-supported Pt electrocatalyst, particularly at high voltage, where it performs better than commercial Pt/C catalyst as shown in Figure 8a. Pd nanoparticles prepared by hard template-assisted method could be a suitable alternative electrocatalyst to C-supported Pt for methanol electrolysis. The variation in current density with membrane thickness is represented in Figure 8b, which shows the significant variation in fuel cell performance.
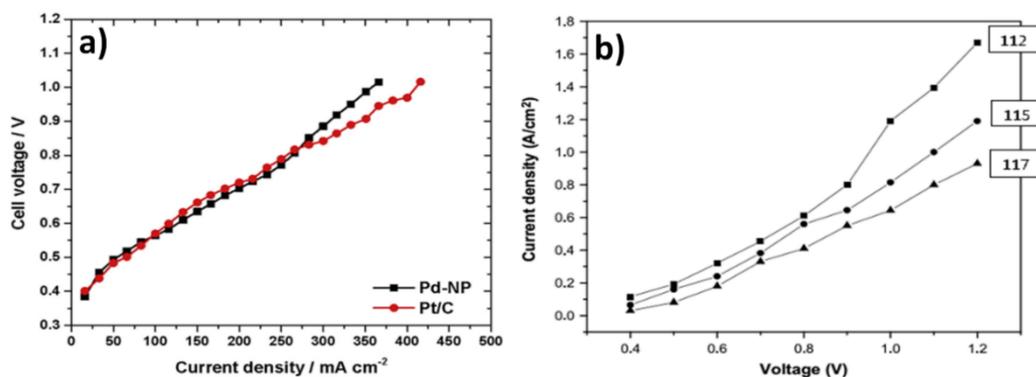
Figure 8. (**a**) Polarization curve of Pd nanoparticles and 20 wt% Pt/C. (**b**) Dependence of membrane electrolyte thickness on current the density of methanol electrolyzer. Adapted with permission from [65], copyright 2016.

The size of metal particles is highly dependent on the performance of metal-supported catalysts in methanol electrolyzers. A very recent study by Li et al. synthesized Pt nanoparticles (1 wt%) of variable sizes (2.5 and 7 nm) on porous CeO_2 supports [66]. The size effect causes better activity for H_2 production for the single-site Pt/CeO_2 catalyst than the nanoparticles of variable sizes (40 and 800 times respectively higher performance for 2.5 and 7 nm). The authors also proposed the capability of the single-site catalyst in liquid alcohol hydrogen production using alcohols other than the methanol. Karim and co-workers also demonstrated the significantly higher selectivity of Pt-supported TiO_2 subnanometer-sized particles compared to the larger particles for acetylene hydrogenation [67]. As the nuclearity of Pt decreases (from 2.1 nm to single atoms), the coordination decreases with Pt and increases with support, weakening the electronic properties. This causes electron deficiency at Pt and weaker CO and ethylene adsorption. The acetylene hydrogenation and H–D isotope exchange activity of Pt/TiO_2 catalysts show over two orders of magnitude difference between the single atoms and subnanometer clusters (-0.7 nm) and nanoparticles (2.1 nm), and this behavior improves with increased metal nuclearity, electron density, and metal–reactant binding energies.

Since Pt and other noble metals are rarely available and costly, non-noble-metal catalysts are being investigated based simply on available materials. Molybdenum carbide nanoparticles generated by modified carbothermal reduction on carbon catalysts is observed as good for H_2 evolution in an electrochemical cell at various pH and in a laboratory-scale electrolyzer. Such catalysts showed good efficiency at acidic environment and durability over a month. Nitrogen functionalized few-walled carbon nanotubes in acidic media are also reported for the H_2 evolution reaction and extensive durability [68]. However, this research is currently progressing to identify vast nanomaterials for highly efficient H_2 generation.

2.3.2. Proton Exchange Membrane

In most of the studies, a proton exchange membrane such as Nafion is used as an electrolyte for methanol electrolyzer, due to high proton conductivity and outstanding chemical, mechanical, and thermal stability. In our previous work [6], we have tested different thicknesses of Nafion membranes, viz. Nafion-117 (thickness of 7 mils), Nafion-115 (thickness of 5 mils), and Nafion-112 (thickness of 2 mils), and observed that the cell performance is in the order of Nafion-112 > Nafion-115 > Nafion-117 (Figure 8b). This trend is attributed to the low resistance of the membranes. However, Nafion-112 is not suitable for longer operation since its thinner nature enhances methanol crossover and leads to performance degradation and hydrogen contamination. The membranes not only conduct protons but also act as separators between anode and cathode and help to separate H_2 and CO. To circumvent that limitation, in our previous study, we developed Pt-nanocatalyzed membranes and Pt–Pd bimetallic/Nafion nanocomposite membranes for methanol electrolysis [14,47]. Both catalyzed membranes showed improved performance compared to conventional membranes due to better

catalytic activity and reduced methanol crossover. The continuous improvement of activity and durability is also impacted by the insight on the exact active sites [69].

However, there are few disadvantages, namely its cost and disposal, that make researchers move towards alternate membranes with bifunctionality. Nafion/silica composite membrane [70] serves the function of membrane along with self-humidification. Nagendran et al. [71] converted polyether sulfone (PES) into ionomer via sulfonation and used it in polymer electrolyte membranes for methanol electrolysis applications. They reported that the developed sulfonated polyether sulfone (SPES)-based membrane had similar conductivity of Nafion but was cheaper, potent, easily made, and immune to fuel crossover compared with Nafion membranes. From a quick overview, SPES membrane-based methanol electrolysis exhibits a peak current density of 0.802 A/cm^2 at a cell voltage of 1.2 V at 80 °C under suitable fabrication conditions.

Commercial applications of the PEMFCs depend on the durability and performance of the membrane. Catalyst layer/electrolyte membrane interfacial interaction is required to reduce the resistance, enhance proton transport, and improve performance. Accelerated stress tests are generally done to evaluate and mitigate the membrane degradation. Many methods are adopted to investigate membrane degradation pathways, starting from the beginning of the reaction to carefully deal with the degradation impact [72].

3. Optimizing Operating Parameters

Optimizing the experimental parameters is one of the key criteria to increase its efficiency and energy requirements, which includes operating temperature and methanol concentration.

Generally, the current density and H$_2$ gas production rate increase with temperature (Figure 9a) [6,42,71]. This is due to higher kinetic energy at high temperatures. At lower activation overvoltage, the catalytic activity is enhanced, and the Gibbs free energy difference between the reaction products and reactants decreases toward the negative side (i.e., the reaction spontaneously occurs). This causes the reduction in activation resistance and aqueous surface tension at high temperature [71]. Figure 9b shows the decrease in current efficiency with cell temperature, attributed to the methanol electrooxidation occurring on Pt-based catalysts [61].
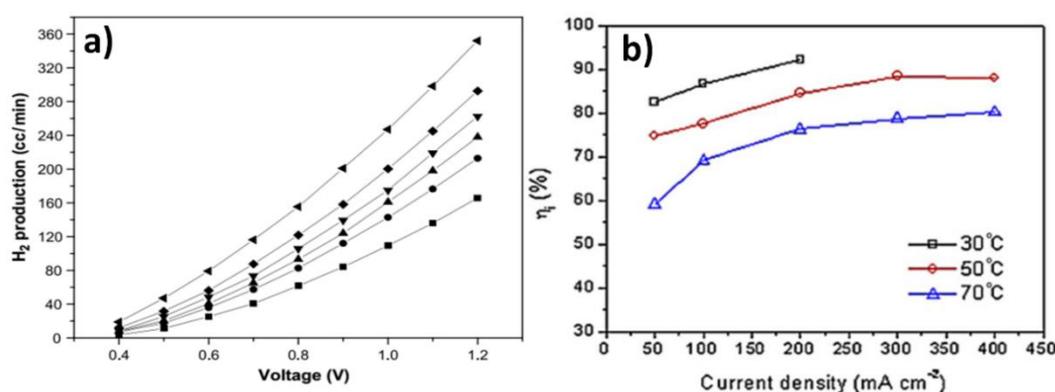

Figure 9. (**a**) Effect of operating temperature on methanol electrolysis for pure hydrogen production (■) 30 °C, (●) 40 °C, (▲) 50 °C, (▼) 60 °C, (♦) 70 °C and (◄) 80 °C. Adapted with permission from [6], copyright 2008. (**b**) Effect of operating temperature on corresponding current efficiency. Adapted with permission from [61], copyright 2012.

Nafion perfluorosulfonic acid polymers are commonly used as polymer electrolyte membranes due to their excellent thermal and chemical stability. These polymers also have certain limitations such as permeability to methanol [17,73,74], H$_2$ purity contamination, conversion loss in fuel, cathode poisoning by CO, and reduced cell performance [75]. Hence, optimizing methanol concentrations for methanol electrolysis is a very important step. In most of the studies, methanol concentration was changed from

1 to 20 M [47,76], and a sharp increase in current density and H_2 production was observed in the 4 to 12 M range, with the values decreasing beyond. The lower current density at higher methanol concentrations is due to the dissolution of Nafion ionomer present in the catalyst layer and change in membrane conductivity. Nafion membrane consists of interconnected clusters of narrow pores, and the less polar methanol increases the cluster size, especially at higher concentrations, and decreases the ionic conductivity [40]. Finally, artificial intelligence techniques, such as fuzzy logic [77], can also be used to optimize the operating parameters. The performance of direct methanol fule cell (DMFC) system varies with mass flow rate of methanol, mass flow rate of oxidant/air, pressure of methanol, pressure of oxidant, cell operating temperature, and current density, in addition to other parameters.

4. Methanol Electrolyzer Weight Comparison and Advantages of Methanol Economy

The approximate weight of methanol electrolyzer system for 1 Nm^3/h of hydrogen production (corresponding to 1 kW continuous electrical power from PEM fuel cells) was calculated based on our experimental work, and compared with commercially available water electrolyzer and methanol reformers [41–44,78]. Table 3 shows the weight comparisons of various hydrogen generators. From the information, though methanol steam reformer has reduced weight with attractive energy consumption [14], issues like long start-up time and meagre transient response are barriers that still impede its commercialization. Moreover, from the weight breakdown of the methanol electrolyzer (Figure 10) system, 38.46% of weight is occupied just by power supply unit; however, if it is replaced by a high-energy-density battery with improved methanol electrolyzer [45], then it could be a promising technology for commercial applications.

Table 3. Hydrogen generator weight comparisons.

Hydrogen Production Method	Weight of 1 Nm^3/h Hydrogen Generators (kg)	Hydrogen Purity (%)	Company	References
Methanol electrolyzer	65	99	Home made	[14]
Water electrolyzer	250	99.99%	Hydrogenics	
Methanol steam reformer	58	99.95%	Element 1 (S-Series)	
Methanol steam reformer	25	75%	WS FLOX (FPMC1)	

Methanol is a versatile fuel that can be used as a fuel for both the heat (IC) engines as well as fuel cells. Its unique characteristics such as high-octane number, allows it to be used as a fuel directly in IC engines, directly/indirectly in methanol fuel cells, or indirectly (after being converted to H_2) in PEM fuel cells. Generally, natural gas is the feedstock widely used for methanol production; however, methanol production from municipal solid waste (MSW) is also industrially mature. The MSW from human and animal activities threatens the environment, if not disposed of properly. Hence, in recent years, biomethanol from MSW is one of the most important subjects due to its economic and environmental advantages, specifically, in Singapore. Based on our calculations from the literature survey (shown below), it is possible to replace gasoline usage in Singapore by 51% volume (25% by energy) if the total MSW is taken as the base. However, the current practice is to recycle almost half of the total generated MSW and, hence, it can be concluded with reasonable confidence that 28.9% volume (14.2% by energy) of the gasoline usage can be easily replaced by disposable MSW in Singapore (Figure 11).
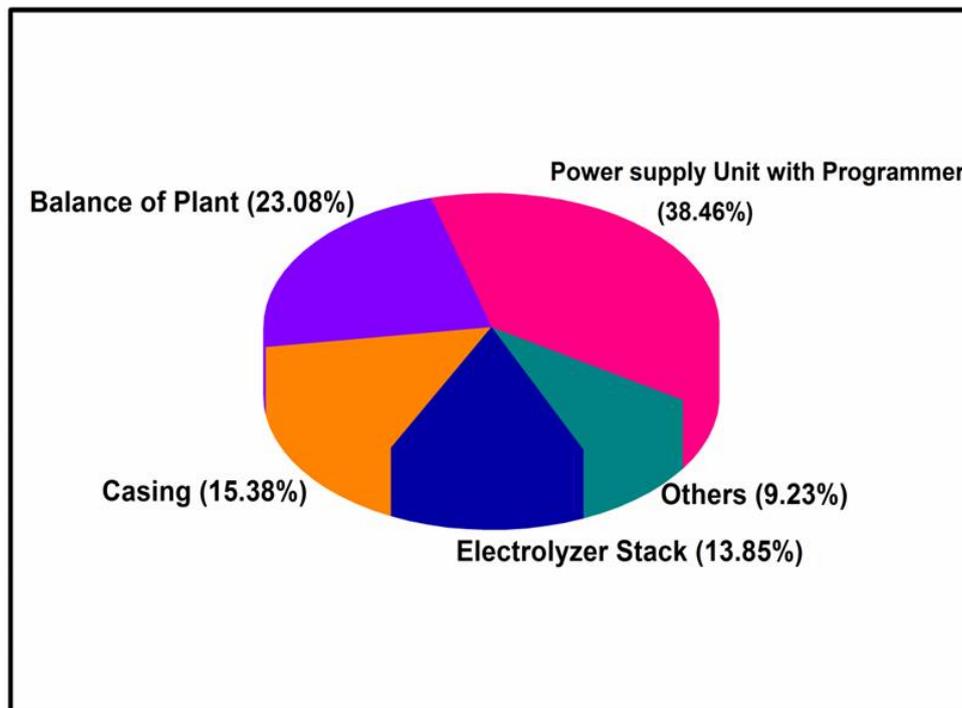
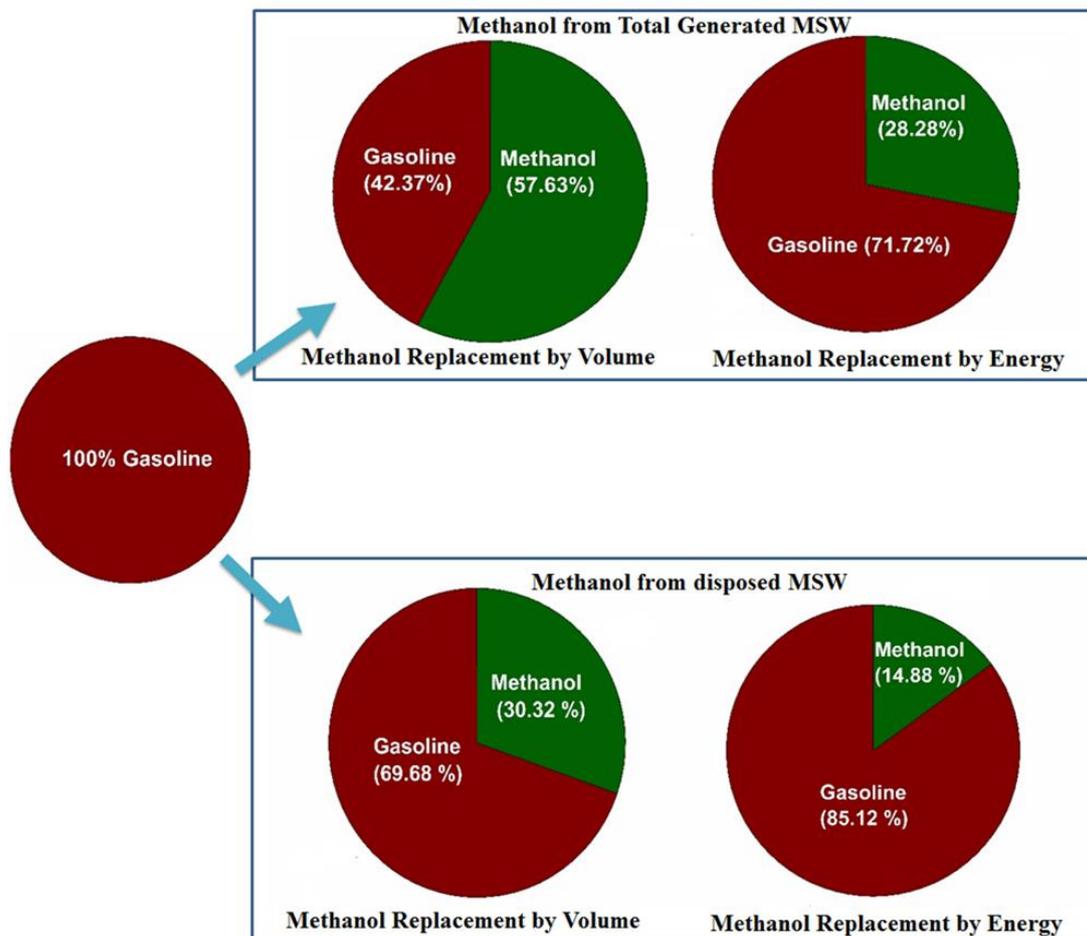**Figure 10.** Weight breakdown of the methanol electrolyzer system.

Figure 11. Replacement potential diagram of bio methanol from municipal solid waste.

Total MSW generated per year (wood, horticultural waste, paper/cardboard, and food) = 2.8253×10^9 kg [44]. Total MSW disposed = 1.4865×10^9 kg [44]. Total gasoline consumption in Singapore = 852,000 metric tons [46] = 852/0.745 megaliters (ML) = 1143.6 ML.

Methanol derived from total generated MSW [79]

185 kg of biomethanol per metric ton of MSW
2.8253×10^9 kg $\times$ 0.185/0.793 = 659.118 ML
Overall replacement of motor gasoline by methanol
659.118/1143.6 $\times$ 100 = 57.63% (by volume)
$(659.118 \times 15.8)/(1143.6 \times 32.2) \times 100$ = 28.28% (by energy)

Methanol derived from disposed MSW (185 kg of biomethanol per metric ton of MSW [46])

1.4865×109 kg $\times$ 0.185/0.793 = 346.79 ML
Overall replacement of gasoline by methanol
346.79/1143.6 $\times$ 100 = 30.32% (By volume)
$(346.79 \times 15.8)/(1143.6 \times 32.2)$ = 14.88% (By energy)

5. Future Research Perspectives

Renewable energy resources are in high demand in the present technical era as petrochemical products near extinction. Hydrogen is limited in its fuel applications, and it has huge potential for meeting the future energy demands. Utilizing methanol for H_2 production involves the use of an environmentally benign strategy for the next generation materials. In reading the current review, the authors believe readers will develop basic knowledge of future technologies based on PEMFCs and the application of H_2 fuel in various industrial and technological areas [80]. This kind of fuel cell can power households to small-scale industries if properly utilized. Zohuri described the major challenges in large-scale hydrogen production [81] and identified steam reforming as the most feasible method. Methanol electrolysis possesses many limitations for large-scale production and hydrocarbons are a better source in that case. In addition, there are various fuel cells utilizing microbial organisms to biomass, extending the possibility of recycling waste and energy generation.

6. Conclusions

Methanol steam reforming (MSR) reactions are widely practiced for H_2 production due to high purity and promising compactness. Radial MSR reactors are integrated in PEMFC using catalysts and the dense metal membranes produce high-purity gas. The main limitation involved in H_2 generation is attributed to electronic short circuiting occurring through the polymeric membranes. The current characteristics in a fuel cell depend on the features of the polymer electrolyte membrane. The interfacial electronic level interaction between the redox levels of electrolyte and band gap edges of the semiconductor membranes controls the efficiency. The efficiency also depends on the nature and type of fuel, fuel-to-oxygen ratio, flow rates, pressure, temperature, humidity, and cell potential. Moreover, high fuel concentration and flow rate loss also contribute to the fuel-to-energy conversion efficiency. A brief analysis of the strength, weakness, opportunity, and threat (SWOT) analysis can provide better insights into the commercialization of methanol energy system and its infrastructure.

References

1. Ni, W.; Chen, Z. Synergistic utilization of coal and other energy—Key to low carbon economy. *Front. Energy* **2011**, *5*, 1–19. [CrossRef]
2. Jayakumar, A.; Chalmers, A.; Lie, T.T. A Review of Prospects for Adoption of Fuel Cell Electric Vehicles in New Zealand. *IET Electr. Syst. Transp.* **2017**, *7*, 259–266. [CrossRef]
3. Jayakumar, A. An assessment on polymer electrolyte membrane fuel cell stack components. *Appl. Phys. Chem. Multidiscip. Approaches* **2018**, *3*, 23–49.
4. Cosnier, S.; Gross, A.J.; Le Goff, A.; Holzinger, M. Recent advances on enzymatic glucose/oxygen and hydrogen/oxygen biofuel cells: Achievements and limitations. *J. Power Sources* **2016**, *325*, 252–263. [CrossRef]
5. Ay, M.; Midilli, A.; Dincer, I. Exergetic performance analysis of a PEM fuel cell. *Int. J. Energy Res.* **2006**, *30*, 307–321. [CrossRef]
6. Sasikumar, G.; Muthumeenal, A.; Pethaiah, S.S.; Nachiappan, N.; Balaji, R. Aqueous methanol eletrolysis using proton conducting membrane for hydrogen production. *Int. J. Hydrogen Energy* **2008**, *33*, 5905–5910. [CrossRef]
7. Ghimire, A.; Kumar, G.; Sivagurunathan, P.; Shobana, S.; Saratale, G.D.; Kim, H.W.; Luongo, V.; Esposito, G.; Munoz, R. Bio-hythane production from microalgae biomass: Key challenges and potential opportunities for algal bio-refineries. *Bioresour. Technol.* **2017**, *241*, 525–536. [CrossRef]
8. Gu, W.; Shen, J.P.; Song, C. Hydrogen production from integrated methanol reforming over Cu-ZnO/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts for PEM fuel cells. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **2003**, *48*, 804.
9. Susastriawan, A.; Saptoadi, H. Small-scale downdraft gasifiers for biomass gasification: A review. *Renew. Sustain. Energy Rev.* **2017**, *76*, 989–1003. [CrossRef]
10. Ursua, A.; Gandia, L.M.; Sanchis, P. Hydrogen production from water electrolysis: Current status and future trends. *Proc. IEEE* **2011**, *100*, 410–426. [CrossRef]
11. Steele, B.C.; Heinzel, A. Materials for fuel-cell technologies. In *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific: Singapore, 2011; pp. 224–231.
12. Steele, B.C.; Heinzel, A. Materials for fuel-cell technologies. *Nature* **2001**, *414*, 345–352. [CrossRef] [PubMed]
13. Jayakumar, A.; Sethu, S.P.; Ramos, M.; Robertson, J.; Al-Jumaily, A. A technical review on gas diffusion, mechanism and medium of PEM fuel cell. *Ionics* **2015**, *21*, 1–18. [CrossRef]
14. Sethu, S.P.; Gangadharan, S.; Chan, S.H.; Stimming, U. Development of a novel cost effective methanol electrolyzer stack with Pt-catalyzed membrane. *J. Power Sources* **2014**, *254*, 161–167. [CrossRef]
15. Kumar, J.A.; Kalyani, P.; Saravanan, R. Studies on PEM fuel cells using various alcohols for low power applications. *Int. J. Electrochem. Sci.* **2008**, *3*, 961–969.
16. Atlam, O.; Kolhe, M. Equivalent electrical model for a proton exchange membrane (PEM) electrolyser. *Energy Convers. Manag.* **2011**, *52*, 2952–2957. [CrossRef]
17. Smith, A.; Newborough, M. *Low-Cost Polymer Electrolysers and Electrolyser Implementation Scenarios for Carbon Abatement*; Rep. Carbon Trust ITM Power: Sheffield, UK, 2006.
18. Lin, J.; Wu, P.H.; Wycisk, R.; Trivisonno, A.; Pintauro, P.N. Direct methanol fuel cell operation with pre-stretched recast Nafion®. *J. Power Sources* **2008**, *183*, 491–497. [CrossRef]
19. Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y.W.; et al. Low-temperature hydrogen production from water and methanol using Pt/α-MoC catalysts. *Nature* **2017**, *544*, 80. [CrossRef]
20. Zhang, J.; Liu, H. *Electrocatalysis of Direct Methanol Fuel Cells: From Fundamentals to Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2009.
21. Pethaiah, S.S.; Ulaganathan, M.; Viswanathan, M.R.; Chan, S.H. Fabrication and electrochemical characterization of Pt–Pd impregnated nanocomposite polymer electrolyte membranes for high concentration DMFCs. *RSC Adv.* **2015**, *5*, 981–987. [CrossRef]
22. Fujiwara, N.; Siroma, Z.; Ioroi, T.; Yasuda, K. Rapid evaluation of the electrooxidation of fuel compounds with a multiple-electrode setup for direct polymer electrolyte fuel cells. *J. Power Sources* **2007**, *164*, 457–463. [CrossRef]
23. Narayanan, S.R.; Chun, W.; Jeffries-nakamura, B.; Valdez, T.I. Hydrogen Generation by Electrolysis of Aqueous Organic Solutions. U.S. Patent 6,299,744, 9 October 2001.

24. Mishra, P.; Krishnan, S.; Rana, S.; Singh, L.; Sakinah, M.; Ab Wahid, Z. Outlook of fermentative hydrogen production techniques: An overview of dark, photo and integrated dark-photo fermentative approach to biomass. *Energy Strategy Rev.* **2019**, *24*, 27–37. [CrossRef]

25. Holton, O.T.; Stevenson, J.W. The role of platinum in proton exchange membrane fuel cells. *Platin. Met. Rev.* **2013**, *57*, 259–271. [CrossRef]

26. Pethaiah, S.S.; Paruthimal Kalaignan, G.; Sasikumar, G.; Ulaganathan, M.; Swaminathan, V. Development of nano-catalyzed membrane for PEM fuel cell applications. *J. Solid State Electrochem.* **2013**, *17*, 2917–2925. [CrossRef]

27. Budak, Y.; Devrim, Y. Comparative study of PV/PEM fuel cell hybrid energy system based on methanol and water electrolysis. *Energy Convers. Manag.* **2019**, *179*, 46–57. [CrossRef]

28. Lonis, F.; Tola, V.; Cau, G. Assessment of integrated energy systems for the production and use of renewable methanol by water electrolysis and CO_2 hydrogenation. *Fuel* **2021**, *285*, 119160. [CrossRef]

29. Gurau, V.; Ogunleke, A.; Strickland, F. Design of a methanol reformer for on-board production of hydrogen as fuel for a 3 kW High-Temperature Proton Exchange Membrane Fuel Cell power system. *Int. J. Hydrogen Energy* **2020**, *45*, 31745–31759. [CrossRef]

30. Russell, J.H.; Nuttall, L.J.; Ficket, A. Hydrogen generation by solid polymer electrolyte water electrolysis. *Hydrogen Energy* **1975**, 441–455. [CrossRef]

31. Ferreira-Aparicio, P.; Chaparro, A.M. *Portable Hydrogen Energy Systems*; Elsevier Academic Press: Cambridge, MA, USA, 2018; ISBN 978-0-12-813128-2.

32. Ren, H.; Chae, J. Fuel cells technologies for wireless MEMS. In *Wireless MEMS Networks and Applications*; Woodhead Publishing: Cambridge, UK, 2017; pp. 35–51.

33. Dicks, A.L. The role of carbon in fuel cells. *J. Power Sources* **2006**, *156*, 128–141. [CrossRef]

34. Peng, L.; Yi, P.; Lai, X. Design and manufacturing of stainless steel bipolar plates for proton exchange membrane fuel cells. *Int. J. Hydrogen Energy* **2014**, *39*, 21127–21153. [CrossRef]

35. Fu, Y.; Lin, G.; Hou, M.; Wu, B.; Li, H.; Hao, L.; Shao, Z.; Yi, B. Optimized Cr-nitride film on 316L stainless steel as proton exchange membrane fuel cell bipolar plate. *Int. J. Hydrogen Energy* **2009**, *34*, 453–458. [CrossRef]

36. Tang, Y.; Yuan, W.; Pan, M.; Li, Z.; Chen, G.; Li, Y. Experimental investigation of dynamic performance and transient responses of a kW-class PEM fuel cell stack under various load changes. *Appl. Energy* **2010**, *87*, 1410–1417. [CrossRef]

37. Yoon, W.; Huang, X.; Fazzino, P.; Reifsnider, K.L.; Akkaoui, M.A. Evaluation of coated metallic bipolar plates for polymer electrolyte membrane fuel cells. *J. Power Sources* **2008**, *179*, 265–273. [CrossRef]

38. Wang, J.; Sun, J.; Li, S.; Wen, Z.; Ji, S. Surface diffusion modification AISI 304SS stainless steel as bipolar plate material for proton exchange membrane fuel cell. *Int. J. Hydrogen Energy* **2012**, *37*, 1140–1144. [CrossRef]

39. Hermann, A.; Chaudhuri, T.; Spagnol, P. Bipolar plates for PEM fuel cells, a review. *Int. J. Hydrogen Energy* **2005**, *30*, 1297–1302. [CrossRef]

40. Li, X.; Sabir, I. Review of bipolar plates in PEM fuel cells, Flow-field designs. *Int. J. Hydrogen Energy* **2005**, *30*, 359–371. [CrossRef]

41. Antunes, R.A.; Oliveira, M.C.L.; Ett, G.; Ett, V. Corrosion of metal bipolar plates for PEM fuel cells: A review. *Int. J. Hydrogen Energy* **2010**, *35*, 3632–3647. [CrossRef]

42. Pham, A.T.; Baba, T.; Sugiyama, T.; Shudo, T. Efficient hydrogen production from aqueous methanol in a PEM electrolyzer with porous metal flow field, Influence of PTFE treatment of the anode gas diffusion layer. *Int. J. Hydrogen Energy* **2013**, *38*, 73–81. [CrossRef]

43. Tuan, A.; Shudo, T. Efficient hydrogen production from aqueous methanol in a proton exchange membrane electrolyzer with porous metal flow fields. *Int. J. Automot. Eng.* **2012**, *3*, 125–130. [CrossRef]

44. Pham, A.T.; Baba, T.; Shudo, T. Efficient hydrogen production from aqueous methanol in a PEM electrolyzer with porous metal flow field: Influence of change in grain diameter and material of porous metal flow field. *Int. J. Hydrog. Energy* **2013**, *38*, 9945–9953. [CrossRef]

45. Carmo, M.; Fritz, D.L.; Mergel, J.; Stolten, D. A comprehensive review on PEM water electrolysis. *Int. J. Hydrogen Energy* **2013**, *38*, 4901–4934. [CrossRef]

46. Mallick, R.K.; Thombre, S.B.; Shrivastava, N.K. A critical review of the current collector for passive direct methanol fuel cells. *J. Power Sources* **2015**, *285*, 510–529. [CrossRef]

47. Sethu, S.; Viswanathan, M.R.; Mani, U.; Chan, S.H. Evaluation of impregnated nanocomposite membranes for aqueous methanol electrochemical reforming. *Solid State Ion.* **2015**, *283*, 16–20. [CrossRef]

48. Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. In *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific: Singapore, 2011; pp. 265–270.

49. Tang, H.; Wang, S.; Pan, M. A comparative study of CCM and hot-pressed MEAs for PEM fuel cells. *J. Power Sources* **2007**, *170*, 140–144. [CrossRef]

50. Huang, T.; Mao, S.; Zhou, G.; Zhang, Z.; Wen, Z.; Huang, X.; Ci, S.; Chen, J. A high-performance catalyst support for methanol oxidation with graphene and vanadium carbonitride. *Nanoscale* **2015**, *7*, 1301–1307. [CrossRef] [PubMed]

51. Kakati, N.; Maiti, J.; Lee, S.H.; Jee, S.H.; Viswanathan, B.; Yoon, Y.S. Anode catalysts for direct methanol fuel cells in acidic media, do we have any alternative for Pt or Pt–Ru? *Chem. Rev.* **2014**, *114*, 12397–12429. [CrossRef]

52. Brookes, C.; Bowker, M.; Wells, P. Catalysts for the selective oxidation of methanol. *Catalysts* **2016**, *6*, 92. [CrossRef]

53. Alia, S.M.; Pylypenko, S.; Neyerlin, K.C.; Kocha, S.S.; Pivovar, B.S. Platinum Nickel Nanowires as Methanol Oxidation Electrocatalysts. *J. Electrochem. Soc.* **2015**, *162*, F1299–F1304. [CrossRef]

54. Garbarino, S.; Ponrouch, A.; Pronovost, S.; Guay, D. Enhanced stability and activity of PtRu nanotubes for methanol electrooxidation. *Electrochem. Commun.* **2009**, *11*, 1449–1452. [CrossRef]

55. Liu, Z.; Zhang, X.; Hong, L. Physical and electrochemical characterizations of nanostructured Pd/C and PdNi/C catalysts for methanol oxidation. *Electrochem. Commun.* **2009**, *11*, 925–928. [CrossRef]

56. Liu, H.; Song, C.; Zhang, L.; Zhang, J.; Wang, H.; Wilkinson, D.P. A review of anode catalysis in the direct methanol fuel cell. *J. Power Sources* **2006**, *155*, 95–110. [CrossRef]

57. Liu, J.; Sun, G.; Zhao, F.; Wang, G.; Zhao, G.; Chen, L.; Yi, B.; Xin, Q. Study of sintered stainless steel fiber felt as gas diffusion backing in air-breathing DMFC. *J. Power Sources* **2004**, *133*, 175–180. [CrossRef]

58. Sapountzi, F.M.; Gracia, J.M.; Fredriksson, H.O.; Niemantsverdriet, J.H. Electrocatalysts for the generation of hydrogen, oxygen and synthesis gas. *Prog. Energy Combust. Sci.* **2017**, *58*, 1–35. [CrossRef]

59. Uhm, S.; Lee, J. Accelerated durability test of DMFC electrodes by electrochemical potential cycling. *J. Ind. Eng. Chem.* **2009**, *15*, 661–664. [CrossRef]

60. Guenot, B.; Cretin, M.; Lamy, C. Clean hydrogen generation from the electrocatalytic oxidation of methanol inside a proton exchange membrane electrolysis cell (PEMEC), effect of methanol concentration and working temperature. *J. Appl. Electrochem.* **2015**, *45*, 973–981. [CrossRef]

61. Uhm, S.; Jeon, H.; Kim, T.J.; Lee, J. Clean hydrogen production from methanol–water solutions via power-saved electrolytic reforming process. *J. Power Sources* **2012**, *198*, 218–222. [CrossRef]

62. Wu, M.; Shen, P.K.; Wei, Z.; Song, S.; Nie, M. High activity PtPd-WC/C electrocatalyst for hydrogen evolution reaction. *J. Power Sources* **2007**, *166*, 310–316. [CrossRef]

63. Ju, H.; Giddey, S.; Badwal, S. The role of nanosized SnO_2 in Pt-based electrocatalysts for hydrogen production in methanol assisted water electrolysis. *Electrochimica Acta* **2017**, *229*, 39–47. [CrossRef]

64. Hu, Z.; Wu, M.; Wei, Z.; Song, S.; Shen, P.K. Pt-WC/C as a cathode electrocatalyst for hydrogen production by methanol electrolysis. *J. Power Sources* **2007**, *166*, 458–461. [CrossRef]

65. Mahesh, K.N.; Balaji, R.; Dhathathreyan, K.S. Palladium nanoparticles as hydrogen evolution reaction (HER) electrocatalyst in electrochemical methanol reformer. *Int. J. Hydrog. Energy* **2016**, *41*, 46–51. [CrossRef]

66. Chen, L.N.; Hou, K.P.; Liu, Y.S.; Qi, Z.Y.; Zheng, Q.; Lu, Y.H.; Chen, J.Y.; Chen, J.L.; Pao, C.W.; Wang, S.B.; et al. Efficient hydrogen production from methanol using a single-site Pt1/CeO2 catalyst. *J. Am. Chem. Soc.* **2019**, *141*, 17995–17999. [CrossRef]

67. Kuo, C.T.; Lu, Y.; Kovarik, L.; Engelhard, M.; Karim, A.M. Structure sensitivity of acetylene semi-hydrogenation on Pt single atoms and subnanometer clusters. *ACS Catal.* **2019**, *9*, 11030–11041. [CrossRef]

68. Tuomi, S. Hydrogen Evolution Research with non-Noble Metal Catalysts and Methanol Electrolysis. Ph.D. Dissertation, Aalto University, Helsinki, Finland, 2019.

69. Wu, G. Current challenge and perspective of PGM-free cathode catalysts for PEM fuel cells. *Front. Energy* **2017**, *11*, 286–298. [CrossRef]

70. Xu, G.; Wu, Z.; Wei, Z.; Zhang, W.; Wu, J.; Li, Y.; Li, J.; Qu, K.; Cai, W. Non-destructive fabrication of Nafion/silica composite membrane via swelling-filling modification strategy for high temperature and low humidity PEM fuel cell. *Renew. Energy* **2020**, *153*, 935–939. [CrossRef]

71. Muthumeenal, A.; Pethaiah, S.S.; Nagendran, A. Investigation of SPES as PEM for hydrogen production through electrochemical reforming of aqueous methanol. *Renew. Energy* **2016**, *91*, 75–82. [CrossRef]

72. Meyer, Q.; Zeng, Y.; Zhao, C. In situ and operando characterization of proton exchange membrane fuel cells. *Adv. Mater.* **2019**, *31*, 1901900. [CrossRef]

73. Sun, H.; Sun, G.; Wang, S.; Liu, J.; Zhao, X.; Wang, G.; Xu, H.; Hou, S.; Xin, Q. Pd electroless plated Nafion® membrane for high concentration DMFCs. *J. Membr. Sci.* **2005**, *259*, 27–33. [CrossRef]

74. Hogarth, M.; Hards, G. Direct methanol fuel cells. *Platin. Met. Rev.* **1996**, *40*, 150–159.

75. Palo, D.R.; Dagle, R.A.; Holladay, J.D. Methanol steam reforming for hydrogen production. *Chem. Rev.* **2007**, *107*, 3992–4021. [CrossRef]

76. Take, T.; Tsurutani, K.; Umeda, M. Hydrogen production by methanol–water solution electrolysis. *J. Power Sources* **2007**, *164*, 9–16. [CrossRef]

77. Jayakumar, A.; Ramos, M.; Al-Jumaily, A. A Novel Fuzzy Schema to Control the Temperature and Humidification of PEM Fuel Cell System. In Proceedings of the ASME 2015 13th International Conference on Fuel Cell Science, Engineering and Technology, San Diego, CA, USA, 28 June–2 July 2015.

78. Sunahiro, S.; Matsui, M.; Takeda, Y.; Yamamoto, O.; Imanishi, N. Rechargeable aqueous lithium–air batteries with an auxiliary electrode for the oxygen evolution. *J. Power Sources* **2014**, *262*, 338–343. [CrossRef]

79. Shamsul, N.; Kamarudin, S.K.; Rahman, N.A.; Kofli, N.T. An overview on the production of bio-methanol as potential renewable energy. *Renew. Sustain. Energy Rev.* **2014**, *33*, 578–588. [CrossRef]

80. Abdalla, A.M.; Hossain, S.; Petra, M.; Ghasemi, M.; Azad, A.K. Achievements and trends of solid oxide fuel cells in clean energy field: A perspective review. *Front. Energy* **2018**, *14*, 359–382. [CrossRef]

81. Zohuri, B. Large-Scale Hydrogen Production. *Hydrog. Energy* **2019**, 229–255. [CrossRef]