HYDROGEN FUEL-CELLS: THE FUTURE OF CLEAN ENERGY TECHNOLOGY

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ABSTRACT

Fuel-cell technology, using hydrogen energy, is an advanced green energy technology for the future that is green, sustainable, clean and environment- friendly. Emission of Green-house gases from human activities has been proven beyond doubt as the main cause of global warming and climate-change. The finite world energy-supply, which consists nearly of 90% fossil-fuel, will be depleted in a short period of time precipitating an energy-crisis because of a widening gap between fossil-fuel production and demand. Many countries responded to the anticipated energy crisis by diversifying their fuel-resources to include renewable and alternative energy, and developing green-energy technology for the future. Despite political announcements on renewable energy, fossil-fuels will continue to dominate energy resources for some time in future, and carbon emission will increase; but global nuclear energy expansion is uncertain because of international tensions and general public fears of another Chernobyl disaster or a nuclear attack by terrorists. Biofuels too are plagued by the conflict between crops for fuel and crops for food, and there is a shift of interest towards crop-biomass waste. Further expansion of hydrogen energy is constrained by costs and by safety of hydrogen transport and storage. Fuel-cell R&D has shifted from older Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC) and Molten Carbonate Fuel Cell (MCFC), whose entry into the market was stalled by intractable operational and durability problems, to the more promising Polymer Electrolyte Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC) and Solid Oxid Fuel Cell (SOFC). A new type of fuel cell, the microbial fuel-cell (MFC), is also gaining attention because it provides a sustainable way of simultaneously reducing BOD & COD of waste-water and providing power: combined wastewater treatment and power (CWTP).

The main thrust in R&D of PEMFC is cost-reduction of membrane and electrocatalyst, by substitution with cheaper but more efficient organic/inorganic nanocomposite membranes and nano-inorganic electrocatalyst, as well as lower electrocatalyst loading, and by cost-reduction of bipolar plate by material reformulation with nanomaterials for injection or compression molding. In addition, cost-reduction can also be achieved by reduction of system complexity, using non-hydrated or self-hydrated membranes that eliminate water management sub-system and CO tolerant anodes that eliminate CO removal of reformate hydrogen feed. PEMFC system efficiency can be further enhanced by better designing of flow field in bipolar plates, fuel and air manifold in the stack as well as through process-optimization using process system engineering tools. The main thrust of R&D in SOFC is reduction of its operational temperature by replacement with low-temperature electrolytes, anodes and cathodes. Future DMFC R&D focuses on methanol crossover reduction, better water-management and lower manufacturing costs. Future R&D on MFC focuses on understanding the electron-transfer mechanism and redox reactions in cells and developing more efficient nanostructured electrodes and cell immobilization. The main thrusts of R&D in production of hydrogen from liquid fuels are in the development of low-temperature auto-thermal steam reforming catalysts, purification of reformate hydrogen through pressure-swing adsorption and membrane processes, as well as membrane reactors, and higher hydrogen-storage capacity in carbon nano-tubes and other nanostructures. The main focus of R&D for sustainable hydrogen production is using photolysis of water into hydrogen and oxygen in solar photovoltaic-electrolyzer system, direct solar photoelectrochemical reactors and solar photo-biological fermentors.

Keywords: *Hydrogen economy, green energy, fuel cell, nanomaterials, nanostructures, and solar hydrogen.*

1. INTRODUCTION

The worldwide annual consumption of energy was 474 exajoules (474×10^{18} J) in 2008, with 80 to 90 % of it derived from fossil-fuels [1]. The finite world energy-supply that consists of up to 90% fossil-fuel will peak during 2020-2030 and will be depleted in 30 to 40 years [2]. This will generate an energy crisis because of widening gap between fossil-fuel production and demand [2]. Green-house gases emission from human activities has been proven beyond doubt to be the main cause of global warming and climate change [3]. The Kyoto Protocol has forced governments to cut CO_2 emission but the post Kyoto-Protocol world has been facing problems.

Many countries responded to the threats of energy crisis and global warming by (i) diversifying their fuel-resources to include renewable and alternative energy; and (ii) developing green energy technology

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to replace conventional energy technologies. Fuel-cell technology, using hydrogen energy, is an advanced green energy technology that is green, sustainable, clean and environment-friendly. Hydrogen fuel-cells emit only water and their introduction in the energy-industry will reduce carbon emission significantly [4, 5].

2. HYDROGEN ENERGY

Hydrogen can be produced from fossil-fuels, and used alongside fossil-fuels in hybrid fuel systems in the transportation, electricity-generation, residential, commercial and industrial sectors. Subsequently, as solar hydrogen and other renewable hydrogen technologies mature and become more viable, hydrogen will be used in fuel-cells for all sectors of the energy market. Ultimately, both solar and hydrogen energy will merge to produce renewable hydrogen. This is considered the most likely path towards a fully commercial application of hydrogen-energy technologies, where solar energy and fuel-cell technologies play crucial roles [5, 6].

Research activities on hydrogen production and storage technologies were focused on (a) auto-thermal steam-reforming catalysts for both gas and liquid fossil-fuels, gasification/pyrolysis, thermochemical cycle, (b) solar photovoltaic-electrolyzer splitting of water, photo-electrochemical and photo-biological splitting of water and carbon nanotube hydrogen storage. The first three are improvements of current technologies, but the latter three are new technologies for hydrogen production and storage. Solar photo-electrochemical splitting of water – a one-step process of splitting water directly from solar energy by using a combination of photovoltaic electrode and electrolysis in one cell – is touted potentially as the ultimate renewable hydrogen-production technology of the future. Major barrier in commercializing this technology is the low efficiency (of about 8%), large energy-band gap for redox electrochemical reaction and electrode corrosion.

2.1 Fuel Processed Hydrogen

Hydrogen needed for operation of fuel-cells should ideally be produced by using renewable energy resources but, in order to introduce fuel-cells technology early, hydrogen should be produced from fossil-fuels using catalysts. The Fuel-processing Group at the Fuel Cell Institute (FCI), UKM, Malaysia, has developed catalysts for autothermal reforming of methanol for hydrogen-production based on CuZ_n [7, 8, 9]. The Group studied the effect of metal-loading in the alumina-supported catalyst on CO reduction [10] and multi-metal composition of ZSM-supported catalyst for hydrogen-production [11].

Hydrogen produced by autothermal reforming of methanol contains CO, which can poison the catalyst in membrane electrode assembly (MEA) and reduce PEMFC's performance. The group has developed a pressure swing adsorption (PSA) system, using activated carbon impregnated with SnCl that can remove CO to less than 10 ppm [12-16]. The group has also developed a four-stage compact PSA that can reduce CO level even further [17], using adsorption [18]. A membrane reactor, consisting of a Palladium (Pd) membrane on a ceramic tube surrounded by the catalysts in the shell, has been developed to produce and separate the hydrogen in one unit [19, 20]. Hydrogen storage, a critical issue in commercial applications of fuel-cells, was critically reviewed by the fuel-processing group at UKM [21].

2.2 Solar Hydrogen

Hydrogen was successfully produced by electrolysis of water, using power from a hybrid solar photovoltaic and wind-energy system [22]. Hydrogen can also be produced by direct photolysis of water by solar energy in photo-electrochemical cells. The Solar Hydrogen Group at the FCI, UKM, has successfully synthesized and characterized three forms of the tetraalkylammonium tetrathiotungstate, a precursor to a tungsten tris (1-acarboxyl-2-phenyl-1,2-ethylenodithiolenic-S,S') [23], – a dye photocatalyst complex, which was subsequently synthesized and characterized successfully [24]. The group has also successfully synthesized and studied the stability of the photocatalyst tungsten tris (1,2-bis(3,5-dimetoksifenil)-1,2-etilenodithiolenik-s,s') (MTDT) through four organic-steps. The photoelectron current produced from the photoelectrode, sensitized by MTDT in a homogenous photoelectrochemical test, was found to be larger than those produced without it [25].

Photoelectrochemical cell produces oxygen when the anode is illuminated and hydrogen at the cathode. The main issue in a photoelectrochemical cell is the availability of a stable anode, maximum light exposure to the anode, collection of hydrogen gas [26] and unimpeded ionic movement [27]. The Solar Hydrogen Group at UKM compared the performance of photoelectrochemical cells, using TiO_2, WO_3, Fe_2O_3 and combined TiO_2-WO_3-Fe_2O_3 electrodes, for water splitting and has shown that the photoelectrode WO_3 gave the highest current density [26, 28].

2.3 Biohydrogen

Renewable hydrogen could also be produced from photoautotrophic microorganisms, such as *cyanobacteria* and *microalga* in anaerobic condition using CO_2 with hydrogenase, which is cheaper, and by photoheterotrophic microorganism, such as nitrogen-fixing bacteria, using more costly organic carbon with nitrogenase. The first process is cheaper than the second one. The main weakness of biohydrogen is low efficiency (1–10%) and enzyme inhibition. The Biohydrogen Group at FCI, UKM, has recently produced hydrogen from *clostridium saccharoperbutylacetonicum* by glucose fermentation at the rate of 3.1 moles of hydrogen per mole of glucose at pH 4.0, 37°C, and initial glucose concentration of 10 g L^{-1} [29]. A second Biohydrogen Group at UKM has produced hydrogen from clostridium acetobutylicum by glucose fermentation at the rate of 391 mL hydrogen per gram of glucose at pH 7.0, 30°C and initial glucose concentration of 25 g L^{-1} [30, 31].

3. FUEL CELLS

Fuel cells play an important role in the renewable hydrogen economy, because it is the most efficient, sustainable, clean and environment-friendly energy-converter of hydrogen. A fuel cell is an electrochemical energy-conversion device that converts chemical energy of hydrogen and oxygen into electricity and heat, by means of electrochemical redox reactions at the anode and the cathode of the cell, respectively, with only water as its by-product.

The six common types of fuel-cell technologies are Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC), Polymer Electrolyte Membrane Fuel Cell (PEMFC), and Direct Methanol Fuel Cell (DMFC). The seventh less common type of fuel cell is the Microbial Fuel Cell (MFC). Although R&D activities on the first three fuel-cell types have been well-established, yet their niche commercial applications are still facing teething problems. Whereas, intense R&D activities on the latter four fuel-cell types are now being carried out all over the world [32].

The major areas of fuel science and technology, and research and development work include: efficient process-system engineering of fuel cells on more efficient fuel- cell systems; low Pt/non-Pt nanostructured electrodes and nanocomposite proton-exchange membranes, nanocomposite bipolar plates; μdirect methanol fuel-cells; low temperature SOFC and microbial fuel cells for power from waste-water.

3.1 Process System Engineering of Fuel Cells

The main problem of process system engineering of PEMFC is the lack of good engineering understanding of major components of a PEMFC system, such as the PEMFC stack, gas humidifier, pressure swing adsorbers, fuel-processing reactor and membrane gas-separation module, as well as water management. The Fuel-cell Process-system Engineering Group at FCI, UKM, has successfully developed models for pressure swing adsorbers [17, 18, 33], gas separation membrane modules [33, 34, 35, 36, 37, 38] and studied the interaction between the two technologies [39]. The Group has also modeled a 5 kW PEMFC system, with an on-board fuel-processing system [40, 41] and with various methods of hydrogen purification [42,43]. The failure of water-management in the PEMFC stack can lead to PEMFC failure, because of flooding and short-circuiting. The Group has successfully modeled a humidifier system for fuel cells [44] and has proposed a new model of water-flow in the PEMFC and a better way of managing water in the fuel cell [45]. The Group is also developing a better model for design of PEMFC [46], a better gas flow field design [47], as well as the effect of mechanical stress on the electrical contact resistance in PEMFC stacks [48].

The Group has also designed and built the PEMFC prototypes: (i) hydrogen-fueled, air-cooled, open cathode, 50-500W PEMFC system; and (ii) a water cooled, 1-5 kW PEMFC system have been developed. Two motorcycle prototypes powered by fuel cell called SERINDIT-I (50 W) and SERINDIT-II (200 W) have been designed, fabricated and tested. A 500W to 1kW portable fuel-cell power-module called LESTARI 1000 and 5 kW portable fuel-cell power-module, called LESTARI 5000, have also been designed, fabricated and tested.

3.2 Proton-Exchange Membranes and Membrane Electrode Assemblies

Currently available proton-exchange membrane fuel cells (PEMFC) that use Nafion from Dupont as its proton-exchange membrane cannot operate more efficiently at a temperature higher than 90°C because its proton-exchange membrane suffers from thermal instability above that temperature. The Fuel-cell Electrochemical Processes Research Group at the FCI, UKM, has successfully developed a new high-temperature composite Nafion-silicon oxide (SiO^2)-phosphotungstic acid (PWA) composite-membrane with lower resistance, higher proton-conductivity, higher current density and better thermal stability at 90°C than the Nafion membrane from Dupont [49, 50, 51] and the Aciplex membrane from ASAHI [51]. The research group has also started research on inorganic membrane that can operate at high temperature, without humidification-based cesium diphosphate (CDP) [52].

Membrane electrode assemblies loaded with costly Ptalimium (Pt), key component of the PEMFC, contribute to the high cost of PEMFC, which prevents the latter's early commercialization. The Group developed a local carbon-source for the electrode [53, 54]. The research group has successfully developed high-performance MEAs with low Pt loading and gas diffusion layers [56, 57]. The group has also developed a new dimensionless spray number for the manufacturing of improved MEAs, using a spraying machine [58].

3.3 Bipolar Plate Material and Manufacturing

The cost of manufacturing bipolar plates can be reduced by substituting the graphite material with polymer composite. Suitable polymers for the polymer composite are thermoplastic polymers, such as polyethylene, polypropylene and polivenylfluoride; and thermoset resins, such as phenolics, epoxy and venyl ester. The Fuel-cell Material and Manufacturing Group at the FCI, UKM, has successfully developed a polymer composite from polypropylene and graphite [59, 60, 61].

3.4 Micro Direct Methanol Fuel Cells

The main problems of micro direct methanol fuel-cells are: methanol crossover and electrode-degradation that diminishes the power of DMFC after a short time of operation; high cost of catalysts and electrolyte membrane; and heat and water management [62, 63]. The Micro Direct Methanol Fuel-cell Group at the FCI, UKM, has developed a design advisor tool, to help predict the performance and optimize the design of the direct methanol fuel-cell [64]. The Group began by developing a passive air-breathing single cell direct methanol fuel-cell, to study the effect of methanol concentration on direct methanol fuel cell performance [65]. It went on to develop a passive single-cell based on air-breathing polymethyl methacrylate (PMMA) and a multi-cell stack micro-direct methanol fuel cell (DMFC) with 1.0 cm^2 active area, and a novel cathode plate structure and assembly layer for better air-access and water removal by gravity [66]. A µDMFC, with low catalyst loading, was also developed by the Group [67]. The effect of methanol concentration and mass transport on the current density of unsteady- state operation of a direct methanol fuel cell was also studied by the Group [68, 69]. Hybrid membranes were also considered to replace Nafion [70]. The use of nanomaterials and nanostructures as nanocatalysts in DMFC was explored [71, 72]. The design of µDMFC was also optimized [73].

3.5 Solid Oxide Fuel Cells

Solid oxide fuel-cells research is primarily undertaken on low and intermediate temperatures (500–600°C). The Solid-oxide Fuel-cell Group of the FCI, UKM, is developing intermediate and low-temperature cells using ceria (CeO_{2-x}) doped with Gd, lanthanum gallate (Perovskite) doped with Sr and Mg (LSGM) and inter metallic bismuth oxide [74, 75], and cathodes from lanthanum cobaltite (perovskite) embedded with Fe, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF, typically $x \sim 0.2$, $y \sim 0.8$) [76].

3.6 Biofuel Cell

Palm Oil Mill-Effluent (POME) is a waste-water, reeking of very high chemical oxygen demand (COD) 50 g L^{-1} and very high biochemical oxygen demand (BOD) 20 mg L^{-1}. Biofuel Cell Group at the FCI, UKM, used the biohydrogen produced from anaerobic fermentation of POME, using mixed culture from POME at pH level 7 directly without combustion, to produce electricity in a dual chambered microbial fuel cell that could reach a current density of 500 mA cm^{-2} and power density of 250 mW m^{-2} [77]. The Group has also studied microbial fuel-cell, using pure culture *Clostridium butyricum* from POME at pH level 4, producing a current density 150 mA cm^{-2} and power density 56 mW cm^{-2} [78]. The open-circuit voltage obtained ranged from 0.3 to 0.5 volt [77-81]. The microorganisms used vary from mixed culture from POME [73,74]: *Clostridium butyricum* [74], *Pseudomonas putida, Lactobacillus, Escherida coli, Aspegillus niger* and *Saccharomyces cerevisia* [79, 80, 81]. The microbial fuel cell has been proven to produce power from waste-water and also reduce the COD and BOD of the wastewater.

A recent study on future hydrogen demand and supply network in Peninsular Malaysia concluded that liquefied hydrogen produced by natural gas steam-reforming and delivered via tanker trucks is the optimum hydrogen supply-chain method [82]. Eighteen new hydrogen plants of 50,000 tonne/year capacity are required for the optimum supply-chain, which is, therefore, more expensive than the future hydrogen infrastructure cost in the UK because the existing hydrogen infrastructure in the latter is better established.

4. CONCLUSION

Research and Development in hydrogen energy is focused on (a) catalyst- development for autothermal reforming of liquid fuels into hydrogen; (b) solar hydrogen by solar energy assisted water splitting using photoelectrochemical cells; and (c) biohydrogen by anaerobic fermentation of waste-water. On the other hand, research and development in fuel cells are centered around design and prototyping of PEM fuel cells, membrane electrode assemblies, bipolar plate materials, micro direct methanol fuel-cells, intermediate and low temperature solid oxide fuel-cell materials and microbial fuel-cells producing power from waste-water. Hydrogen is currently produced by steam reforming and electrolysis, and is used mainly in the petrochemical and oleochemical sectors, as well as in metal cutting. Renewable hydrogen will be produced by electrolysis, using excess capacity of hydropower or off-peak electricity and, ultimately, directly from solar energy by photoelectrochemical means.

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