World Journal of Engineering 12(6) (2015) 591-606

World Journal of
Engineering

Review on challenges of direct liquid fuel cells for portable application

Venkateswarlu Velisala[*], **G. Naga Srinivasulu, B. Srinivasa Reddy and K. Venkata Koteswara Rao**
Department of Mechanical Engineering, National Institute of Technology, Warangal, 506004, India
**E-mail: 2venkee@gmail.com*

(Received 29 June 2015; Accepted 29 September 2015)

Abstract

Fuel cells technologies are the most promising green energy technologies for diverse applications. One of the fastest growing areas is the portable electronic applications where the power range is the order of 1–100 W. For most of the portable electronic devices, rechargeable battery is the major energy source. Due to limitations like limited capacity, requirement of external power for recharge have led many researchers to look for alternative power sources to power portable electronic devices. The high energy density of fuel cells makes them very attractive alternative to batteries for portable power applications. There are a variety of fuel cell technologies being considered to replace batteries in portable electronic equipment. Direct Liquid Fuel Cells (DLFCs) have attracted much attention due to their potential applications as a power source for portable electronic devices. The advantages of DLFCs over hydrogen fed PEM fuel cells include a higher theoretical energy density and efficiency, a more convenient handling of the streams, and enhanced safety. Unlike batteries, fuel cells need not be recharged, merely refueled. This paper provides an overview on challenges of DLFCs (Direct Liquid Fuel Cells), like fuel crossover, cost, durability, water management, weight and size along with approaches being investigated to solve these challenges. Portable Fuel Cell Commercialization Targets for future and producers of portable fuel cells across the globe are also discussed in this paper.

Keywords: *Green energy, Portable electronic devices, Battery, Direct Liquid fuel cell, Challenges*

1. Introduction

Energy needs for portable electronic devices such as laptop, smartphone, and other broadband mobile computing are rising rapidly in the past few years due to the increasing their functionalities. The major energy source for most of portable electronic devices is the rechargeable battery. The disadvantage of using a rechargeable battery as a power source is the battery needs an external electrical power source to recharge, and this is a limitation to the mobility of the device because it can only be used with an electrical power source and has limited battery capacity. In remote areas, where no availability of electric power, charging for battery is a problem. These disadvantages of rechargeable batteries have led many researchers to look for alternative power sources to replace the battery technology. As an alternative to battery, fuel cell

ISSN:1708-5284

may be considered as best suited power source for powering portable electronic devices due to practical advantages such as high-energy density, light weight, compactness, simplicity as well as easy and fast recharging via a replacement or a refilled fuel cartridge. The ability of the fuel cell is to provide more energy from the same volume over battery power systems. Small fuel cells normally produce power between 0.5 and 100 W, which is sufficient for portable electronic devices. Fuel cells working with liquid fuels, like methanol, ethanol or formic acid, are closer to practical application in the range of 1–100W. Table 1 gives the Properties of some state of the art portable systems, including size, power requirement, power supply characteristics and autonomy.

For portable applications, Direct Liquid fed Fuel Cell (DLFC) is the most promising fuel cell technology (Klaus *et al*., 2003). Liquid fuels such as Methanol, Ethanol, Formic Acid and Borohydride solutions can be used as fuels for DLFCs without reforming process. DMFCs have 5–10 times higher energy densities than batteries, can operate for a longer time. But the problems with DMFCs are fuel crossover, slower anode electrochemical oxidation of methanol and cost of the components of fuel cell (Kamarudin *et al*., 2009).

Ethanol is also an attractive and promising fuel in DLFCs for portable fuel cell applications due to its: (i) non-toxicity, (ii) natural availability, (iii) renewability and (iv) higher power density. The current direct ethanol fuel cell (DEFC) technologies are able to meet the two important features: efficiency and total operation cost in order to realize the DEFC into commercialization. The well-known sluggish anode electro catalyst activities are at relatively low temperature (20°C – 120°C) due to problem in C-C bond breaking which lead to the low performance remains as the major technological problem. Another major issues facing by DEFC is ethanol permeated through membrane caused mixed potential effects at cathode which lead to reduce cathode performance and fuel utilizations. Another critical obstacle that limits the wide application of acid DEFCs is the cost:

Table 1.
Properties of some state-of-the-art portable systems, including size, power consumption, power supply characteristics and autonomy (Fernandez *et al*., 2013)

Class	Device	Device dimensions (cm^3)	Power requirements	Battery characteristics	Battery dimensions (cm^3)	Power density (Whl^{-1})	Autonomy
Medical implantable	Pace maker	5 × 5 × 0.6	25 μJ/pulse	Lithium iodine 2 Ah @ 2.2 V 0.15 Wh	0.5	300	5–7 years
	Defibrillator	6 × 5 × 1.5	15–40J/ pulse	Lithium silver vanadium oxide 1 Ah @ 2.8 V	0.5	600	3–5 years
	Cochlear implant	5	8 mA DC + 24 mA (pulse 100 ms)	Zn air 0.49 Ah @ 1.05 V	0.56	920	45 h
Medical	Hearing aid	2	5 mA cc + 15 mA (100 ms)	Zn air 0.6 Ah @ 1.05 V	0.5	1260	300 h
	Insulin pump	70	10 mW	Zn/MnO^2 (alkal ine) 2.5 Ah@1.5 V	8	470	400 h
Portable electronics	Smart phone	10 × 7 × 0.7	2 W	Li-ion 1.2 Ah @ 3.7 V	5 × 5 × 0.3	600	6 h
	Video camera	10 × 4 × 5	7 W	Li-ion 1.8 Ah @ 3.6 V	2 × 3 × 4	270	1 h
	Laptop	20 × 20 × 2	40 W	Li-ion 1.4 Ah @ 3.7 V	20 × 5 × 2	235	6 h
Toys	Car	20 × 20 × 5	5–15 W	Ni mh (× 6) 1.2 Ah @ 1.2 V	5 × 14 × 2	30	0.5 h
	Airplane	20 × 20 × 5 (1 kg)	110 W/kg	Ni mh, Ni Cd 1.7 Ah @ 1.2 V	5 × 14 × 2	15	0.3 h

acid electrolyte membranes (typically Nafion® material) are expensive; and a considerable amount of precious Pt is needed to achieve decent performance in acid DEFCs (Li *et al*., 2009).

Direct Formic Acid fuel cells (DFAFCs) are also promising alternative to hydrogen fed PEMFCs. Very high-power densities have been achieved in direct formic acid fuel cell (DFAFC) systems. DFAFCs also faces several challenges, the most important of these challenges are poor anodic reaction kinetics compared to hydrogen, and fuel crossover. The primary challenge is the tendency for formic acid oxidation to proceed through a –CO-type intermediate, a species that poisons Pt-based catalyst matervials. The second challenge is crossover of fuel, formic acid diffuses from the anode, through the membrane to the cathode. At the cathode, the fuel can react directly with oxygen, creating unwanted heat without producing electricity, thus reducing the overall fuel efficiency of the system.

Sodium borohydride aqueous solution also an interesting alternative as a liquid fuel for fuel cells. Direct borohydride fuel cell (DBFC) uses a sodium borohydride ($NaBH_4$) solution as fuel, and electricity is produced. A direct borohydride fuel cell (DBFC) is a device that converts chemical energy stored in borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. DBFC is similar to PEMFC and DMFC according to the usage of membrane electrolyte, similar to AFC because of its alkaline media, and similar to DMFC according to the usage of liquid fuel. Compared with other fuel cells, a DBFC has many advantageous features such as high open circuit potential, ease of electro-oxidation of BH_4^- on non-precious metals such as nickel, low operational temperature, high power density, low fuel crossover, and safety because it eliminates hydrogen storage problem (Celik *et al*., 2008). Hydrogen evolution due to the hydrolysis reaction during operation not only decreases the fuel utilization but also causes some problems in the system designing. In addition to this, BH_4^- crossover, NaOH accumulation at the cathode and $NaBO_2$ accumulation at the anode are other problems that need to be solved (Park *et al*., 2006).

2. Challenges

2.1. Fuel crossover

A common challenge for any direct liquid fuel cell is fuel crossover. In order to encourage the development of DLFC system this challenge need to be solved. For any type of PEM-based fuel cell, the fuel fed to the anode, can permeate to the cathode through membrane. To examine and quantify the fuel crossover behavior in DLFCs a number of studies were conducted (Rhee *et al*., 2003; Wang *et al*., 2004; Song *et al*., 2005;Liu *et al*.,2006; Jeong *et al*., 2007). High concentration of liquid fuel provides higher achievable energy density, but it also causes severe fuel crossover to the electrolyte membrane, it is a very serious problem that severely reduces cell voltage, current density, fuel utilization, and hence cell performance. The rate of crossover decreases with increasing current density, due to higher rate of fuel consumption at the anode (Yu *et al*., 2008). Several approaches have been proposed to reduce fuel crossover in DLFCs during the last decade. One common approach to reduce fuel crossover is the development of new proton conducting membranes with low fuel permeability and high proton conductivity, e.g. the acid-doped polybenzimidazole (PBI), sulfonated-poly (arylene ether ketone)s (SPAEKs), sulfonated-poly(ether sulfone)s (SPES), polyamides, sulfonated-polyimide (SPI), etc (Kerres., 2001; Wan and Lin., 2013). Another approach is the modification of Nafion membranes to make them suitable for DLFC utilization. Another approach is forming hybrid membranes by blending different types of polymers, such as the one being done with zirconium and phosphate, it is shown that the inorganic compound reduces the methanol permeability while the phosphate layer allows for more water to permeate rather than methanol (Bauer and Porada, 2004). Chien *et al*. (2013) developed a low methanol-crossover sulfonated graphene oxide (SGO)/Nafion composite membrane by simply blending well-exfoliated $SGO_{(aq)}$ and Nafion. In the DMFCs test, the SGO/ Nafion composite membrane exhibited performance superior to the commercial membrane Nafion 115 in 1 M and 5 M methanol solutions. SGO is a promising material for reducing methanol crossover and shows great potential for commercial applications. SPEEK is considered one of the most promising candidates for replacing Nafion because it offers lower cost, easier preparation, controllable conductivity, excellent chemical-thermal stability and low methanol crossover (Zhong *et al*., 2008; Tirupathi and Shahi, 2009; Gosalawit *et al*., 2009; Ismail *et al*., 2009; Lin *et al*., 2009). The assembly of Palladium nano-particles onto the Nafion membrane surface yields a good result in reducing methanol crossover up to 8 orders of magnitude compared to the unmodified membrane, and with no reduction in its ionic conductivity. The results demonstrate the promises of the application of such Pd-PDDA nanoparticle self-assembled Nafion^{TM} membrane in DMFC (Tang *et al*., 2005). Thiam *et al* (2013) adopted Palladium–silica nanofibres (Pd–SiO_2 fibre) as an additive to Nafion recast membranes in order to reduce methanol crossover and improve the cell performance. PVA has a good resistance to methanol permeability, but has low conductivity (Bhat *et al*., 2009; Yang *et al*., 2009; Huang *et al*., 2009). The performance of cells with double-layer membranes suggests they have promising applications in DMFCs when compared to SPEEK and PVA in single membrane cells (Yang *et al*., 2008; Maab *et al*., 2009). Abdelkareem and Nakagawa (2006) employed a hydrophobic porous carbon plate and a 2 mm gap between the fuel reservoir and the MEA as a methanol barrier layer and significantly reduced methanol crossover. Zhang and Hsing (2007) adopted a flexible graphite plate between the flow channel and the MEA in an active liquid feed DMFC to decrease the methanol crossover. Yuan *et al*. (2014) developed a novel methanol-blocking membrane prepared by layer-by-layer assembly of poly (diallyldimethylammonium chloride) (PDDA) and graphene oxide (GO) nanosheets onto the surface of Nafion® membrane. This PDDA-GO multilayer onto the Nafion film not only reduces the methanol crossover but also enhances the membrane strength. Yuan *et al*. (2013) fabricated a porous metal fiber sintered felt (PMFSF) as the anodic methanol barrier to control methanol crossover (MCO) in order to feed the fuel cell with a higher concentration of methanol fuel for a passive air-breathing direct methanol fuel cell (PAB-DMFC). This PMFSF helps greatly reduce the effects of methanol crossover. Wan and Lin (2013) proposed a new approach to mitigate methanol crossover, they prepared a composite membrane with a 5 bi-layers of poly (allylamine hydrochloride) (PAH)/polystyrene sulfonic acid sodium salt (PSS) containing Pt_{35}–Ru_{65} catalyst are self-assembled on the Nafion membrane surface through the layer-by-layer technique. A layer of Pt_{35}–Ru_{65} with a thickness of 87.5 nm deposited on Nafion acts as a methanol barrier. MEA with self-assembled Pt_{35}–Ru_{65} layers suppresses methanol crossover by 22% and improves power density by 48% (at 0.30 V) at 80°C.

Ethanol crossover remains the main issue that impedes the widespread use and application of DEFCs. Ethanol is well known for having a lower crossover rate and affecting cathode performance less severely than methanol because of its lower permeability through the Nafion membrane and its slower electrochemical oxidation kinetics on the Pt/C cathode (Song *et al*., 2005). The negative effects of ethanol crossover include decreasing the cathode potential and cathode depolarization (Kamarudin *et al*., 2013). The overall efficiency of direct ethanol fuel cells will decrease due to ethanol crossover. It also results in wasting fuel while in operation (Xu *et al*., 2011; Thiam *et al*., 2011). At the same time, the permeated ethanol and its oxidation intermediate products have the potential to poison the cathode catalyst (Song *et al*., 2007). Ethanol crossover rate is affected by temperature, current densities and feed concentration. The ethanol crossover rate increases with temperature, current densities and feed concentrations. Ethanol crossover occurs when ethanol passes through the membrane and reacts with oxygen at the cathode to produce acetic acid, which is eventually delivered back to the anode (James and Pickup, 2010). The main approach to solve this problem is through modification of the membrane as the core of the DEFC. The rate of ethanol crossover depends on the ethanol concentration in the anode catalyst layer (CL). Thus, feeding a diluted ethanol solution may help prevent ethanol crossover, but this may result in specific energy losses in the DEFC system. Andreadis *et al*. (2006) developed a mathematical model to describe ethanol behavior and its influencing factors in the DEFC. The model showed that the crossover rate increased linearly with the inlet ethanol concentration up to the maximum value of 10.0 M. The parasitic current formation at the cathode depended on the ethanol crossover and was greater at low current density. Another factor was that increasing the porosity of the diffusion and catalyst layers also increased the ethanol crossover rate as well as parasitic formation. Kontou *et al*. (2007) done experiments using a Nafion 115-based MEA received same findings for the ethanol permeation rate at various ethanol concentrations. A mathematical model developed by Suresh and Jayanti (2011) to examine the effect of operating current density on ethanol crossover for various ethanol feed concentrations. Maab and Nunes (2010) have used modified (sulfoneated poly (ether ether ketone)) SPEEK membranes. They suggested two methods to prepare effective SPEEK membranes that may reduce the crossover problem. The first method is coating the SPEEK with a carbon molecular sieves (CMS) layer, and the second is making SPEEK/PI (polyimide) blends. They compared the results of CMS-coated SPEEK and the SPEEK/PI blends, the SPEEK/PI blends have exhibited better performance. Wan and Chen (2009) prepared a composite anode containing a thin layer of Pt_{50}–Sn_{50} nanoparticles on Nafion membrane surface does suppress the ethanol crossover up to 17% and improve the performance up to 6% (average value) at 80°C. Battirola *et al.* reduced ethanol crossover by using doped-Nafion® 117 membranes with Pt and Pt-Ru nanoparticles. Rhee *et al.* (2003) studied the permeation of formic acid through Nafion 112 and Nafion 117 membranes at room temperature, the permeation of formic acid is higher through Nafion® 112 (50 μm) than through the thicker 180 μm Nafion® 117.

Crossover of BH_4^- can be solved by developing membrane electrolytes with high BH_4^- resistivity and cathode catalysts with high selectivity for electro-reduction of oxidant and high tolerance towards borohydride electro-oxidation (Ma *et al.*, 2010). Raman and Shukla (2007) used Nafion 961 membrane to reduce borohydride crossover, from anodic to cathodic compartments of the cell, instead of Nafion 117. Li *et al.* (2003) developed a DBFC anode made of a Zr-Ni alloy, a cathode made of Pt/C, Nafion 117 as membrane and compared with Nafion 112 membrane, Nafion 117 membrane demonstrated a considerable resistance to borohydride crossover and resulted in acceptable cell performance. Suda (2002) mitigated the BH_4^- crossover problem by adopting a fuel cell structure using Nafion membrane as electrolyte to separate the fuel from the cathode. Ma *et al.* (2012) modified a cost-effective and eco-friendly chitosan membrane by phosphate or triphosphate salt, chitosan triphosphate (CsTP) membrane demonstrates lower BH_4^- crossover rate than chitosan phosphate (CsP) membrane.

2.2. Cost

The cost of fuel cell system must be reduced before they can be competitive with conventional technologies. Fuel cell costs can be broken into three areas: the material and component costs, labor (i.e. design, fabrication, and transport), and capital cost of the manufacturing equipment (Marcinkoski *et al.*, 2011). Only labor and capital costs can be reduced through mass-manufacturing. Material and component costs, such as catalysts, membrane and bipolar plates are dependent on technological innovations and the market (Sun *et al.*, 2011; Odeh *et al.*, 2013). The manufacturers of fuel cells have to continue to collect subsidies from governments to scale these units up for commercial applications with limited success because of the challenges of cost, durability, robustness or reliability. One method of reducing costs is to develop Low cost, high-performance membranes, high-performance catalysts enabling ultra-low precious metal loading, and lower cost, lighter, corrosion-resistant bipolar plates to make fuel cell stacks competitive. As a result, research and development of fuel cells has been directed to solve the issues of materials, chemistry, water and hotspots (Houchins *et al.*, 2012; DOE Annual merit review proceedings, 2013). Electrolyte membranes are a major cost component of Fuel Cell stacks at low production volumes. These membranes also impose limitations on fuel cell system operating conditions that add system complexity and cost. Reactant gas and fuel permeation through the membrane leads to decreased fuel cell performance, loss of efficiency, and reduced durability in both PEMFCs and DMFCs. To address these challenges, the U.S. Department of Energy (DOE) Fuel Cell Technologies Program, in the Office of Energy Efficiency and Renewable Energy, supports research and development aimed at improving ion exchange membranes for fuel cells (Houchins *et al.*, 2012). Matos *et al.* (2015) performed electro-oxidation of formic acid on Pd-based catalysts supported on hybrid TiO_2-C materials prepared from different carbon origins by solvothermal and slurry synthesis, which will allow to reduce considerably the amount of expensive noble metal at the anode of DFAFC. Ma *et al.* (2012) prepared a cost-effective and eco-friendly chitosan membrane and modified by phosphate or triphosphate salt for DBFC and achieved a peak power density of 685 mW cm^{-2} at 60°C, which is over 50% higher than the power performance of a DBFC using commercial Nafion® materials. Ma and Sahai (2012) employed Chitosan, a cost-effective and eco-friendly material to prepare both electrode binder and polymer electrolyte and anode consisting of Ni-based composite electrocatalysts loaded on Ni foam substrate was developed and employed to reduce the cost and Chitosan membrane gave more than 50 % higher power performance than the commercial Nafion® membranes in DBFCs and costs less than 10% of the cost of Nafion®. Choudhury *et al.* (2012) developed a DBFC employing Na_2HPO_4-based ionically crosslinked CS hydrogel membrane electrolytes (ICCSHMEs) to reduce the cost of fuel cell by replacing commercial Nafion® membrane. Baglio *et al.* (2010) investigated a low-cost fluorine-free proton conducting polymer electrolyte, consists of a sulfonated polystyrene grafted onto a polyethylene backbone for DMFC mini-stacks. Its performance is compared with Nafion 117 membrane, despite the lower performance, the fluorine-free membrane showed good characteristics for application in portable DMFCs especially with regard to the perspectives of significant cost reduction. Huang *et al.* (2014) provided a promising way for the decrease of noble metal loadings for DMFCs. Added magnesium oxide (MgO) nanoparticles as a sacrificial pore-former into the catalytic layer (CL) and micro-porous layer (MPL) in the anode of a membrane electrode assembly (MEA) leads to a significant increase in catalyst utilization and a decrease in charge-transfer resistance of the anodic reaction, which results in reduction of noble metal loading and performance improvement.

2.3. Durability and stability

One of the major concerns in the commercialization of Fuel Cells is the stability of the cell during long-term operation. Portable fuel cell systems may operate up to 2000 h. For the same weight and volume, fuel cells can achieve much longer lifetimes than the traditional Li-ion battery. The lifetime of a fuel cell system is primarily determined by its durability, which is often evaluated in terms of platinum catalyst degradation, carbon catalyst support corrosion, membrane chemical attack and ageing of specific components. Durability affects other design criteria such as efficiency and cost. Improvements in nafion-based membranes due to the addition of inorganic compounds (SiO_2, silanes, Zr, MoPha, etc.) and acidic-basic composites (e.g., polyaryl) decrease methanol crossover but do not reduce cost. Hydrocarbon membranes are cheaper and more technically effective for DMFCs than Nafion membranes. They have lower methanol crossover and higher conductivity and stability (Neburchilov *et al.*, 2007). The durability of fuel cell systems has not been established. The degradation mechanisms and failure modes within the fuel cell components and the mitigation measures that could be taken to prevent failure need to be examined and tested. Contamination mechanisms in fuel cells due to air pollutants and fuel impurities need to be carefully addressed to resolve the fuel cell durability issue.

Peng *et al.* (2010) improved durability and more stable current output of a μDMFCs equipped with a water/air management device (WAMD). The system yielded a water removal rate of 5.1μl s^{-1} cm^{-2}, which is about 20 times much faster than the water generation rate of a μDMFC operated at 400 $mAcm^{-2}$. Jiang *et al.* (2005) carried out a 60 h life-time test of a direct ethanol fuel cell (DEFC) at a current density of 20 mA cm^{-2} (the beginning 38 h) and 40 mA cm^{-2} (the last 22 h). The home-made 50% Pt/C and 20% Pt–4% Sn/C were employed as the cathode and anode of a DEFC, respectively. Fifteen percent of the original maximum power density of the DEFC was lost after a 60 h life-time test. The agglomeration of the electrocatlaysts, the destruction of the anode PtSn/C catalyst, and the cathode flooded accelerated the degradation of the DEFC performance. However, in another experiment, they studied a 10 h lifetime test of DEFCs based on commercially available PtRu black catalyst to find a better MEA fabrication process in order to control the degradation problem. Their group concluded that the decal transfer method or delamination resulted in better cell performance than the brushing method of MEA fabrication because it made better contact between the catalyst layer and the electrolyte membrane, resulting in higher catalyst utilitzation. Their efforts may help increase the durability of DEFCs in the future. Hou *et al.* (2011) prepared a polymer electrolyte membrane for alkaline direct ethanol fuel cell (ADEFC) by dipping Nafion112 membrane into KOH solution for some time at room temperature. This single cell active ADEFC with Nafion112/KOH membrane delivered a peak power density of 58.87 mW/cm^2 at 90°C, meanwhile, it can stably run for at least 12 h above 0.2 V. On the other hand, Pt-free air breathing ADEFC with Nafion112/KOH can output a peak power density of 11.5 mW/cm^2 at 60°C, and the corresponding lifetime was as long as 473 h above 0.3 V. Hou *et al.* (2011) prepared KOH doped polybenzimidazole (PBI/KOH) membrane as polymer electrolyte membrane for alkaline direct alcohol fuel cell (ADAFC) and its durability is evaluated by means of ex situ and in situ tests. The results showed that the system could operate stably for 336 h above 0.3 V. Hong *et al.* (2010) designed a miniature air breathing compact direct formic acid fuel cell (DFAFC), with gold covered printed circuit board (PCB) as current collectors and back boards and this DFAFC showed long-term stability at constant current density. Cai *et al*. (2012) developed a 10-cell DFAFC stack, which can stably operate for about 50 h by one fuelling with 1.5 L of 10 mol L^{-1} formic acid solution. Four refueling procedures can bring a discharge time of about 240 h for the DFAFC stack. Wu *et al*. (2013) demonstrated a passive, air-breathing 4-cell micro direct methanol fuel cell (μDMFC) stack featured by a fuel delivery structure for a long-term stable power supply. The stack is operated for 100 h and observed a 3% performance decrease. A key to commercialization of DBFC is to demonstrate its reliability and long-term operation. Li *et al*. (2003) showed that a DBFC using surface-treated Zr–Ni Laves phase AB_2 alloy as anode and Pt/C as cathode was able to operate stably for 29 h at 200 mA cm^{-2}. Ma *et al*. (2012) prepared a cost-effective and eco-friendly chitosan membrane and modified by phosphate or triphosphate salt for DBFC and received a stable performance over the test period of more than 100 h at discharge of 120 mA cm^{-2} at 30°C. Choudhury *et al*. (2012) developed a DBFC employing Na_2HPO_4-based ionically crosslinked CS hydrogel membrane electrolytes (ICCSHMEs) and received a stable cell performance with a cell voltage loss of only 100 mV during an operation period of 100 h. Li *et al*. (2013) developed a DBFCs using Ni-Pd/C as the anode catalyst and polypyrrole-modified carbon-supported $Co(OH)_2$ [$Co(OH)_2$-PPy/BP] as the cathode catalyst to depress hydrogen evolution resulted in high performance stability. However, lifetime of fuel cells could be extended by controlling the flow conditions (i.e. humidity, flow rates and temperature) without any other alterations (i.e. materials or catalyst), and an optimized design can significantly reduce the impact of these flow conditions (Knights *et al*., 2004; Jang *et al*., 2008).

2.4. Size and weight

For portable applications, the size and weight of the fuel cell system should be comparable with the size and weight of the technology that it replaces, e.g., a battery. The presently high weight and volume of hydrogen and liquid fuels (methanol, ethanol, formic acid, Borohydride solution) storage is one of the main challenges for commercialization of fuel cell systems. Use of a portable hydrogen generating device (e.g., portable electrolysers) will solve the above issue. However, this increases the cost of the system. The size and weight of current fuel cell systems must be further reduced ,this applies not only to the fuel cell stack, but also to the ancillary components and major subsystems (i.e., fuel processor, compressor/expander, and sensors) making up the balance of power system.

Kim *et al*. (2008) investigated the possibility of the portable application of a direct borohydride fuel cell (DBFC), For weight reduction, carbon graphite is adopted as the bipolar plate material with this weight reduced by 4.2 times with 12% of performance degradation caused by insufficient contact between the end-plate and MEA from a lack of stacking force. For volume reduction Hong *et al*. (2011) designed a miniature air-breathing twin-cell stack consists of two face-to-face single cells with one shared fuel reservoir for direct formic acid fuel cell (DFAFC) applications.

2.5. Water management

Ineffective water management leads to liquid-phase water blockage and mass-transport-limited performance or decreased proton conductivity as a result of dehumidification of the ionomer. The portable fuel cells must be able to operate in environments where ambient temperatures fall below 0°C, a challenge for low-temperature fuel cells. R&D is needed to improve the designs of the gas diffusion layers, gas flow fields in bipolar plates, catalyst layers and membranes to enable effective water management and operation in subfreezing environments**.** Both low durability and reliability are caused by accumulated degradation of materials and catalyst due to water and heat issues. The degradation of materials and catalyst are mainly because of poor water management, fuel and oxidant starvation, corrosion and chemical reactions of cell components that cause dehydration or flooding. The dehydration can damage the membrane and flooding can facilitate corrosion of the electrodes, the catalyst layers, the gas diffusion media and the membrane (Schmittinger and Vahidi, 2008). Effective management of the water produced in low-temperature fuel cells is needed to alleviate flooding and/or drying out of the membrane over the full operating temperature range. So Water management is a very important parameter for the performance of a small portable fuel cell. The water level in a fuel cell affects the electrode kinetics, membrane properties, and transport of reactant. In the case of DMFC, methanol is oxidized at the anode producing hydrogen, which is transported through proton exchange membrane. Without water, the PEM will resist for the transport of hydrogen and hence each proton requires 2.5 water molecules to diffuse through the membrane. This proton in turn combines with oxygen at the cathode and produces water. Too much water accumulation in the cathode leads to the poor performance not only due to the flooding resulting in unavailability of the catalyst layer for the reaction but also poor diffusion of oxygen toward cathode. To achieve good performance optimal water balance is required in the anode and cathode. Although the excess water in the cathode can be removed by active water control, this is difficult due to the space constraints as well as the requirement of part of the produced energy to run the pump. The present use of carbon support does not work at high power load due to high flooding and thereby difficulty in the oxygen transport. Tsujiguchi *et al*. (2013) investigated the effect of the flooding on the power generation characteristics of the DFAFC. A hydrophobic filter inserted to the cathode surface to inhibit the flooding, this hydrophobic filter decreased the cathode over-potential significantly and improved the performance. For DEFC Li *et al*. (2010) experimented with using a water trap connected to the exit of the cathode channel and filled with anhydrous $CaSO_4$ (Dryerite®) to collect the water effluent. Peng *et al*. (2010) designed and fabricated successfully an effective water/air management device (WAMD) for μDMFCs by SU-8 molding and selective surface modification processes. The system yielded a water removal rate of $5.1 \mu l s^{-1} cm^{-2}$, which is about 20 times much faster than the water generation rate of a μDMFC operated at 400 $mAcm^{-2}$. Deng *et al*. (2013) designed and fabricated a novel micro-direct methanol fuel cell (μ-DMFC) with a CNT-MEA compound structure using MEMS technology for water management. Water produced by the electrochemical reaction can be captured by CNT layer and transported outside to prevent flooding and humidify dry oxygen which due to capillary action of carbon nanotube. This results in improvement in the cell performance. Liu and Wang (2008) studied the effectiveness of an anode WML on water crossover in a DMFC. It was reported that the wettability of the anode WML is important in controlling the water crossover. Shaffer and Wang (2009) employed a one dimensional, two-phase model to investigate the importance of using an anode WML to decrease the water for MEAs using the high concentration solutions of methanol. Wu *et al*. (2013) proposed a multi-layered membrane, consisting of an ultra-thin reaction layer composed of well-dispersed PtRu catalysts, SiO_2 nanoparticles and Nafion ionomers sandwiched between two thin membranes for DMFCs operating with neat methanol. This membrane offers better water management for DMFCs operating with neat methanol and enables improvements in cell performance. Peled *et al*. (2003) and Blum *et al*. (2003) reported that the use of a highly hydrophobic cathode WML makes it possible to have water-neutral operating conditions for a DMFC with low methanol feed concentration. Xu *et al*. (2010) added two additional layers of MPL-coated carbon cloth at the cathode of the DMFC worked as the water management layer (WML). It lowered the water and methanol crossover and increased the fuel efficiency. Yang and Zhao (2009) investigated the water transport in a DMFC by incorporating both anode and cathode WML, simultaneously. It was reported that optimum design of the anode porous structure reduces the diffusion flux of water to the cathode, while optimum design in the cathode is more effective in the convective back-flow of water to the anode. Research is needed to investigate the effectiveness of the anode WML compared to the cathode WML, or vice versa. Jewet *et al*. (2007) proposed two additional gas diffusion layer (GDL) and with the addition of air filter to increase the hydraulic pressure at the cathode which eventually will drive water created from the reaction back across the membrane to the anode. The addition of air filter is to block small airborne particle, create heat insulation and reducing water evaporation and lower methanol crossover. Guo and Faghri (2009) also developed a DMFC with air filter that functions as a water proof layer for the fuel cell cathode as water management. They had specifically developed a DMFC system characterized in passive technology for methanol fuel delivery, water recirculation, air and thermal management. For a superior performance of a fuel cell, proper distribution of the reactants and water management is necessary.

2.6. Hydrogen evolution

The hydrogen evolution was one of the most critical problems to the performance improvement of the DBFC stack and commercial DBFC development. The stacking loss of the DBFC was mainly caused by hydrogen evolution, which resulted in an uneven fuel distribution between the cells of the stack. Higher initial concentrations of borohydride lead to faster rates of hydrogen evolution. This hydrogen evolution would decrease not only the DBFC performance but also fuel utilization. A great deal of effort has been directed towards curtailing the main route to hydrogen evolution, namely, borohydride hydrolysis. One of the ways to overcome this limitation is to add some materials that are known for their inhibiting effect on hydrogen evolution to the BH_4^- solution. Another way is finding some anode catalysts on which BH_4^- can be completely electro-oxidized but no hydrolysis reaction occurs. On the other hand, more efforts should be made in optimization of flow field design and improvements of anode structure such as forming hydrophobic pore. Li *et al*. (2006) proposed two ways to reduce hydrogen evolution in DBFC, one is adding Pd, Ag and Au catalysts in the anode and another effective way is Coating a thin Nafion film on the catalyst surfaces. If the Nafion loading is too high, on the other hand, ingress of the fuel to the active sites is hindered; the optimal content was found, therefore, to be less than 25 wt. %. The hydrogen generation rate was also reduced by decreasing the temperature, which carried a penalty in terms of the cell performance. To depress hydrogen evolution Suda and co-workers employed Nickel based hydrogen storage alloys as the anode materials (Liu and Suda, 2008) and added Pd/C catalyst to FMH-Ni anode (Liu *et al*., 2008). Martins *et al*. (2007) proposed Thiuorea (TU) and tetraethyl ammonium hydroxide (TEAH) as inhibitors for the borohydride hydrolysis reaction. Celik *et al*. (2010) used thiourea (TU) as the additive in the sodium borohydride solution for minimizing the anodic hydrogen evolution on Pd, results in increase the performance of a direct borohydride fuel cell. Kim and co-workers (2008) tried to improve stack performance by decrease of hydrogen evolution influence through suitable anode shape design.

3. Portable fuel cell developing companies

Many companies and research groups work on developing different types of Portable Fuel Cell technologies to make them more advantageous than their competing technologies, i.e. batteries. Such fuel cells are especially crucial for the devices where high power density and long operation time are needed. Their application areas include consumer electronics, laptops, battery chargers, external power units and military applications. Lilliputian Systems received $5 million to help buy equipment for its Wilmington facility, which will produce USB charging systems, and Intel Capital took an equity stake in Lilliputian. Horizon Fuel Cell Technologies began shipments of the world's first miniaturized hydrogen fuel cells and refueling stations for use in model hobby radio controlled vehicles. The company also launched its new pocket-size fuel cell battery charger for the portable consumer electronics markets. Panasonic became an approved partner of SFC Energy, which includes the certification of Panasonic's Toughbook products for operation with SFC's fuel cells. Neah Power Systems announced that it will produce a hybrid fuel cell technology that recharges lithium ion batteries in consumer electronics. The Table 2 gives the list of portable fuel cell manufacturing companies across the globe.

4. Future targets for portable fuel cells

The U.S. Department of Energy has established targets for fuel cell cost, durability, power, energy and Mean time between failures for portable fuel cells commercialization.

Table 3 shows the DOE technical targets for portable fuel cell systems. The cost is based on production volumes of 50,000, 25,000, and 10,000 units per year for < 2 W, 10–50 W, and 100–250 W systems, respectively. The specific and volumetric energy densities of liquid methanol are 5.53 Wh g^{-1} and 4.35 Wh cm^{-3}, respectively, based on the LHV of 638.1 kJ mol^{-1}. If the electrical efficiency of a DMFC is 30%, then the effective specific and volumetric energy densities of methanol itself will be 1600 Wh kg^{-1} and 1300 Wh L^{-1}, respectively, which are 2.5 (1600/650) and 1.4 (1300/900) times those of the 2015 targets. Obviously, a system carrying more methanol will more easily meet those targets. For example, the energy density target of 900 Wh L^{-1} can be easily met when the volume of liquid methanol is around 70% of the total system volume (900/1300). Based on this fact, targets for the specific energy and energy density are met easily by carrying more liquid fuels. The specific power and the power density, however, are more crucial.

5. Conclusion

In this paper the challenges of DLFCs (Direct Liquid Fuel Cells), like fuel crossover, cost, durability, water management, weight and size are reviewed along with approaches being investigated to overcome these challenges. Progress in solving these technical challenges will certainly play a large role in commercialization of fuel cells. The

Table 2.
Major fuel cell system solutions development companies (Sharaf *et al*., 2014)

Country	#	Company	FC type(s)	Market(s)
United States	1	Motorola	DMFCs	Consumer electronics
	2	MTI Micro	DMFCs	Consumer electronics Battery chargers
	3	Neah Power	DMFCs	Consumer electronics Portable power generators Portable military equipment
	4	Protonex	PEMFCs SOFCs	Portable military equipment UAVs Battery chargers APUs Portable power generators EPS RAPS
	5	Ultra Electronics AMI	SOFCs	Consumer electronics APUs Battery chargers Portable military equipment Portable power generators
	6	UltraCell	RMFCs	Consumer electronics Portable power generators Portable military equipment
Japan	1	Canon	PEMFCs	Consumer electronics
	2	Hitachi	SOFCs DMFCs	Residential distributed CHP generation Consumer electronics Portable power generators
	3	NEC	DMFCs	Consumer electronics
	4	Panasonic[a]	PEMFCs DMFCs	Residential distributed CHP generation Portable power generators Consumer electronics
	5	Sony	Microbial FCs DMFCs	Consumer electronics Battery chargers
	6	Toshiba	DMFCs PEMFCs PAFCs	Consumer electronics Battery chargers Residential distributed CHP generation EPS
Germany	1	Heliocentris	PEMFCs	Toys and educational kits RAPS EPS
	2	Schunk	PEMFCs	Battery chargers General-purpose stacks and systems
	3	SFC Energy	DMFCs	Battery chargers RAPS EPS Portable power generators Portable military equipment
	4	Siemens	DMFCs PEMFCs SOFCs	Consumer electronics Marine propulsion Industrial distributed CHP generation
United Kingdom	1	Intelligent Energy	PEMFCs	L-FCEVs LTVs EPS Residential and commercial distributed CHP generation Consumer electronics

(*Continued*)

Table 2.
Continued

Country	#	Company	FC type(s)	Market(s)
South Korea	1	LG[b]	DMFCs SOFCs	Consumer electronics Industrial and commercial distributed CHP generation
	2	Samsung	DMFCs PEMFCs SOFCs	Consumer electronics Portable power generators Portable military equipment Distributed power generation
Sweden	1	Cellkraft	PEMFCs	RAPS EPS Portable military equipment
	2	myFC	PEMFCs SOFCs	Consumer electronics Battery chargers
Taiwan	1	Antig	DMFCs	Consumer electronics Battery chargers Portable power generators
Denmark	1	Serenergy	PEMFCs RMFCs	EPS APUs Material handling L-FCEVs Battery chargers Portable power generators
France	1	BIC[c]	N/A	Consumer electronics Battery chargers
Singapore	1	Horizon	PEMFCs DMFCs	UAVs Consumer electronics Battery chargers Portable power generators Toys and educational kits RAPS EPS L-FCEVs

[a] And its subsidiary Sanyo.

[b] In June2012,LG acquired Rolls-Royce Fuel Cell Systems.

[c] On November 2011,BiC acquired Angstrom Power.

Table 3.
Fuel Cell Commercialization Targets (Fuel cell technologies office: multi-year research, development, and demonstration plan. US Department of Energy, 2012)

Market	Characteristics	Unit	Current Status	Future Target
< 2 W Micro Portable[a]	Specific Power	$W\text{-}kg^{-1}$	5	10
	Power Density	$W\text{-}L^{-1}$	7	13
	Specific energy	$Wh\text{-}kg^{-1}$	110	230
	Energy Density	$Wh\text{-}L^{-1}$	150	300
	Cost[b]	$\$\text{-}system^{-1}$	150	70
	Durability[c]	h	1,500	5,000
	MTBF[d]	h	500	5,000
10–50 W Small Portable[a]	Specific Power	$W\text{-}kg^{-1}$	15	45
	Power Density	$W\text{-}L^{-1}$	20	55
	Specific energy	$Wh\text{-}kg^{-1}$	150	650
	Energy Density	$Wh\text{-}L^{-1}$	200	800
	Cost[e]	$\$\text{-}system^{-1}$	15	7
	Durability[c]	h	1,500	5,000
	MTBF[d]	h	500	5,000

(*Continued*)

Table 3.
Continued

Market	Characteristics	Unit	Current Status	Future Target
100–250 W Medium Portable[a]	Specific Power	W-kg^{-1}	25	50
	Power Density	W-L^{-1}	30	70
	Specific energy	Wh-kg^{-1}	250	640
	Energy Density	Wh-L^{-1}	300	900
	Costf	\$-system^{-1}	15	5
	Durability[c]	h	2,000	5,000
	MTBF[d]	h	500	5,000

importance of weight, volume, and lifetime in portable power applications provides a potential advantage to fuel cells with their high energy densities and the lack of a need for lengthy recharging cycles. Economically, it is reasonable to expect small-scale fuel cells for portable power applications to be the first to achieve widespread market penetration, likely in the very near future. To achieve that, different cost-effective materials have been recently explored as current collectors, membrane, and diffusion and catalyst layers both for the anode and cathode side. In this paper the list of portable fuel cells making companies across the globe and the targets for commercialization of fuel cells for portable power applications were also discussed.

References

Abdelkareem M.A., Nakagawa N., 2006. DMFC employing a porous plate for an efficient operation at high methanol concentrations. *Journal of Power Sources* **162**, Pp. 114–123.

Andreadis G., Song S., Tsiakaras P., 2006. Direct Ethanol Fuel Cell Anode Simulation Model. *Journal of Power Sources* **157(2)**, Pp. 657–665.

Andreadis G., Tsiakaras P., 2006. Ethanol Crossover and Direct Ethanol PEM Fuel Cell Performance Modeling and Experimental Validation. *Chem. Eng. Sci.* **61(22)**, Pp. 7497–7508.

Andreadis G.M., Podias A.K.M., Tsiakaras P.E., 2008. The Effect of the Parasitic Current on the Direct Ethanol PEM Fuel Cell Operation. *Journal of Power Sources* **181(2)**, Pp. 214–227.

Baglioa V., Stassi A., Modica E., Antonucci V., Aricò A.S., Caracinob P., Ballabio O., Colombo M., Kopnin E., 2010. Performance comparison of portable direct methanol fuel cell mini-stacks based on a low-cost fluorine-free polymer electrolyte and Nafion membrane. *Electrochimica Acta* **55**, Pp. 6022–6027.

Bauer F., Willert-Porada M., 2004. Microstructural characterization of Zr-phosphate–Nafion® membranes for direct methanol fuel cell (DMFC) applications. *Journal of Membrane Science* **233**, Pp. 141–149.

Bhat S.D., Sahu A.K., George C., Pitchumani S., Sridhar P., Chandrakumar N., Singh K.K., Krishna N., Shukla A.K., 2009. Mordenite-incorporated PVA-PSSA membranes as electrolytes for DMFCs. *J. Membr. Sci.* **340**, Pp. 783–83.

Blum A., Duvdevani T., Philosoph M., Rudoy N., Peled E., 2003. Water-neutral micro direct-methanol fuel cell (DMFC) for portable applications. *Journal of Power Sources* **117**, Pp. 22–25.

Cai W., Yan L., Li C., Liang L., Xing W., Liu C., 2012. Development of a 30 W class direct formic acid fuel cell stack with high stability and durability. *International Journal of Hydrogen Energy* **37**, Pp. 3425–3432.

Cassidy Houchins., Greg J. Kleen., Jacob S. Spendelow., John Kopasz., David Peterson., Nancy L. Garland., Donna Lee Ho., Jason Marcinkoski., Kathi Epping Martin., Reginald Tyler, Dimitrios C. Papageorgopoulos, 2012. U.S. DOE Progress Towards Developing Low-Cost, High Performance, Durable Polymer Electrolyte Membranes for Fuel Cell Applications. *Membranes* **2**, Pp. 855–878.

Cenk Celik., Fatma Gul Boyaci San., Halil Ibrahim Sarac., 2010. Improving the direct borohydride fuel cell performance with thiourea as the additive in the sodium borohydride solution. *International Journal of Hydrogen Energy* **35**, Pp. 8678–8682.

Cenk Celika., Fatma Gul Boyaci San., Halil Ibrahim Sarac., 2008. Effects of operation conditions on direct borohydride fuel cell performance. *Journal of Power Sources* **185**, Pp. 197–201.

Chien H.C., Tsai L.D., Huang C.P., Kang C.Y., Lin J.N., Chang F.C. 2013. Sulfonated graphene oxide/Nafion composite membranes for high-performance direct methanol fuel cells. *International Journal of Hydrogen Energy* **38**, Pp. 13792–13801.

Deng H., Zhang Y., Li Y., Zhang X., Liu X. 2013. A CNT-MEA compound structure of micro-direct methanol fuel cell for water management. *Microelectronic Engineering* **110**, Pp. 288–291.

DOE Annual merit review proceedings, 2013. In: http://www.hydrogen.energy.gov/annual_review13_proceedings.html

Fernández-Moreno J., Guelbenzu G., Martín A.J., Folgado M.A., Ferreira-Aparicio P., Chaparro A.M., 2013. A portable system powered with hydrogen and one single air-breathing PEM fuel cell. *Applied Energy* **109**, Pp. 60–66.

Fuel cell technologies office, 2012. multi-year research, development, and demonstration plan. US Department of Energy.

Gosalawit R., Chirachanchai S., Basile A., 2009. A Thermo and electrochemical characterization of sulfonated PEEK-WC membranes and Krytox-Si-Nafion composite membranes. *Desalination* **235**, Pp. 293–305.

Guo Z., Faghri A., 2009. Development of a 1W passive DMFC. International Communications in Heat and Mass Transfer 35, Pp. 225–39.

Hong P., Liao S., Zeng J., Huang X., 2010. Design, fabrication and performance evaluation of a miniature air breathing direct formic acid fuel cell based on printed circuit board technology. *Journal of Power Sources* **195**, Pp. 7332–7337.

Hong P., Liao S.J., Zeng J.H., Zhong Y.L., Liang Z.X., 2011. A miniature passive direct formic acid fuel cell based twin-cell stack with highly stable and reproducible long-term discharge performance. *Journal of Power Sources* **196**, Pp. 1107–1111.

Hou H., Wang S., Jin W., Jiang Q., Sun L., Jiang L., 2011. KOH modified Nafion 112 membrane for high performance alkaline direct ethanol fuel cell. *International Journal of Hydrogen Energy* **36**, Pp. 5104–5109.

Hou H.Y., Wang S., Jiang Q., Jin W., Jiang L., Sun G., 2011. Durability study of KOH doped polybenzimidazole membrane for air breathing alkaline direct ethanol fuel cell. *Journal of Power Sources* **196**, Pp. 3244–3248.

Huang Q., Jiang J., Chai J., Yuan T., Zhang H., Zou Z., Zhang X.G., Yang H., 2014. Construction of porous anode by sacrificial template for a passive direct methanol fuel cell. *Journal of Power Sources* **262**, Pp. 213–218.

Huang Y.F., Chuang L.C., Kannan A.M., Lin C.W., 2009. Proton conducting membranes with high selectivity from crosslinked poly (vinyl alcohol) and poly (vinyl pyrrolidone) for direct methanol fuel cell applications. *Journal of Power Sources* **186**, Pp. 22–28.

Ismail A.F., Othman N.H., Mustafa A., 2009. Sulfonated polyether ether ketone composite membrane using tungstosilicic acid supported on silica–aluminium oxide for direct methanol fuel cell (DMFC). *Journal of Membrane Science* **329**, Pp. 18–29.

James D.D., Pickup P.G., 2010. Effects of crossover on product yields measured for direct ethanol fuel cells. *Electrochimica Acta* **55**, Pp. 3824–3829.

Jang J.H., Chiu H.C., Yan W.M., Sun W.L., 2008. Effects of operating conditions on the performances of individual cell and stack of PEM fuel cell. *Journal of Power Sources* **180**, Pp. 476–483.

Jeong K.J., Miesse C.A., Choi J.H., Lee J., Han J., Yoon S.P., Nam S.W., Lim T.H., Lee T.G., 2007. Fuel crossover in direct formic acid fuel cells. *Journal of Power Sources* **168**, Pp. 119–125.

Jewett G., Guo Z., Faghri A., 2007. Water and air management systems for a passive direct methanol fuel cell. *Journal of Power Sources* **168**, Pp. 434–446.

Ma Jia, Nurul A. Choudhury., Yogeshwar Sahai., 2010. A comprehensive review of direct borohydride fuel cells. *Renewable and Sustainable Energy Reviews* **14**, Pp. 183–199.

Ma Jia, Yogeshwar Sahai., Rudolph G. Buchheit., 2012. Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells. *Journal of Power Sources* **202**, Pp. 18–27.

Jiang L., Sun G., Wang S., Wang G., Xin Q., Zhou Z., 2005. Electrode catalysts behaviour during direct ethanol fuel cell life-time test. *Electrochemistry Communication* **7**, 663-668.

Jochen A. Kerres., 2001. Development of ionomer membranes for fuel cells. *Journal of Membrane Science* **185**, Pp. 3–27.

Juan Matosa., Andrzej Borodzinski., Anna Mikolajczuk Zychora., Piotr Kedzierzawski., Bogusław Mierzwa., Karol Juchniewicz., Marta Mazurkiewicz., Juan C. Hernández-Garrido., 2015. Direct formic acid fuel cells on Pd catalysts supported on hybridTiO_2-C materials. *Applied Catalysis B: Environmental* **163**, Pp. 167–178.

Kamarudin M.Z.F., Kamarudin S.K., Masdar M.S., Daud W.R.W., 2013. Review: Direct ethanol fuel cells, *International Journal of Hydrogen Energy* **38**, Pp. 9438–9453.

Kamarudin S.K., Achmad F., Daud W.R.W., 2009. Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices, *International Journal of Hydrogen Energy* **34**, Pp. 6902–6916.

Kim C., Kim K.J., Ha M.Y., 2008. Investigation of the characteristics of a stacked direct borohydride fuel cell for portable applications. *Journal of Power Sources* **180(1)**, Pp. 114–121.

Kim C., Kim K.J., Ha M.Y., 2008. Performance enhancement of a direct borohydride fuel cell in practical running conditions. *Journal of Power Sources* **180(1)**, Pp. 154–161.

Klaus Tüber., Marco Zobel., Heribert Schmidt., Christopher Hebling., 2003. A polymer electrolyte membrane fuel cell system for powering portable computers. *Journal of Power Sources* **122**, Pp. 1–8.

Knights S.D., Colbow K.M., St-Pierre J., Wilkinson D.P., 2004. Aging mechanisms and lifetime of PEFC and DMFC. *Journal of Power Sources* **127**, Pp. 127–134.

Kontou S., Stergiopoulos V., Song S., Tsiakaras P., 2007. Ethanol/water mixture permeation through a Nafion® based membrane electrode assembly. *Journal of Power Sources* **171 (1)**, Pp. 1–7.

Li Y.S., Zhao T.S., Liang Z.X., 2009. Performance of alkaline electrolyte-membrane-based direct ethanol fuel cells. *Journal of Power Sources* **187**, Pp. 387–392.

Li Y.S., Zhao T.S., Yang W.W., 2010. Measurements of water uptake and transport properties anio-exchange membranes. *International Journal of Hydrogen Energy* **35**, Pp. 5656–5665.

Li Z.P., Liu B.H., Arai K., Suda S., 2003. A fuel cell development for using borohydrides as the fuel. *J. Electrochem. Soc*. **150**, Pp. A868–72.

Li Z.P., Liu B.H., Zhu J.K., Suda S., 2006. Depression of hydrogen evolution during operation of a direct borohydride fuel cell. *Journal of Power Sources* **163**, Pp. 555–559.

Li Z.P., Liu Z.X., Qin H.Y., Zhu K.N., Liu B.H., 2013. Performance degradation of a direct borohydride fuel cell. *Journal of Power Sources* **236**, Pp. 17-24.

Liliane C. Battirola., Jose F. Schneider., Iris C.L. Torriani., Germano Tremiliosi-Filho., Ubirajara P. Rodrigues-Filho., 2013. Improvement on direct ethanol fuel cell performance by using doped-Nafion® 117 membranes with Pt and Pt-Ru nanoparticles. *International Journal of Hydrogen Energy* **38**, Pp. 12060–12068.

Lin C.K., Kuo J.F., Chen C.Y., 2009. Preparation of nitrated sulfonated poly (ether ether ketone) membranes for reducing methanol permeability in direct methanol fuel cell applications. *Journal of Power Sources* **187**, Pp. 341–347.

Liu B.H., Li Z.P., Zhu J.K., Suda S., 2008. Influences of hydrogen evolution on the cell and stack performances of the direct borohydride fuel cell. *Journal of Power Sources* **183**, Pp. 151–156.

Liu B.H., Suda S., 2008. Hydrogen storage alloys as the anode materials of the direct borohydride fuel cell. *Journal of Alloys and Compounds* **454**, Pp. 280–285.

Liu F., Wang C.Y., 2008. Water and methanol crossover in direct methanol fuel cells-Effect of anode diffusion media. *Electrochimica Acta* **53**, Pp. 5517–5522.

Liu J.G., Zhao T.S., Liang Z.X., Chen R., 2006. Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells. *Journal of Power Sources* **153**, Pp. 61–67.

Ma J., Sahai Y., 2012. Cost-effective Materials for Direct Borohydride Fuel Cells. *ECS Transactions*, **42 (1)**, Pp. 101-106.

Maab H., Nunes SP., 2010. Modified SPEEK membranes for direct ethanol fuel cell. *Journal of Power Sources* **195**, Pp. 4036–4042.

Maab H., Shishatskiy S., Nunes SP., 2009. Preparation and characterization of bilayer carbon/polymer membranes. *Journal of Membrane Science* **326**, Pp. 27–35.

Marcinkoski J., James BD., Kalinoski JA., Podolski W., Benjamin T., Kopasz J., 2011. Manufacturing process assumptions used in fuel cell system cost analyses. *Journal of Power Sources* **196**, Pp. 5282–92.

Martins J.I., Nunes M.C., Koch R., Martins L., Bazzaoui M., 2007. Electrochemical oxidation of borohydride on platinum electrodes: The influence of thiourea in direct fuel cells. *Electrochim. Acta* **52**, Pp. **6443–6449**.

Neburchilov V., Martin J., Wang H., Zhang J., 2007. A review of polymer electrolyte membranes for direct methanol fuel cells. *Journal of Power Sources* **169**, Pp. 221–238.

Choudhury A. Nurul, Jia Ma., Yogeshwar Sahai., 2012. High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells. *Journal of Power Sources* **210**, Pp. 358–365.

Odeh AO., Osifo P., Noemagus H., 2013. Chitosan: A low cost material for the production of membrane for use in PEMFC a review. *Energy Sources, Part A* **35**, Pp. 152–163.

Omar Z. Sharaf., Mehmet F. Orhan., 2014. An overview of fuel cell technology: Fundamentals and applications. *Renewable and Sustainable Energy Reviews* **32**, Pp. 810–853.

Park K.T., Jung U.Ho., Jeong S.U., Kim S.H., 2006. Influence of anode diffusion layer properties on performance of direct borohydride fuel cell. *Journal of Power Sources* **162**, Pp. 192–197.

Peled E., Blum A., Aharon A., Philosoph M., Lavi Y., 2003. Novel Approach to Recycling Water and Reducing Water Loss in DMFCs, Electrochem. *Solid-State Lett*. **6**, Pp. A268–A271.

Peng H.C., Chen P.H., Chen H.W., Chieng C.C., Yeh T.K., Pan C., Tseng F.G., 2010. Passive cathodic water/air management device for micro-direct methanol fuel cells. *Journal of Power Sources* **195**, Pp. 7349–7358.

Raman R.K., Shukla A.K., 2007. A Direct Borohydride/Hydrogen Peroxide Fuel Cell with Reduced Alkali Crossover. Fuel Cells **7(3)**, Pp. 225–231.

Rhee Y.W., Ha S.Y., Masel R.I., 2003, Crossover of formic acid through Nafion® membranes. *Journal of Power Sources* **117**, Pp. 35–38.

Schmittinger W., Vahidi A., 2008. A review of the main parameters influencing long term performance and durability of PEM fuel cells. *Journal of Power Sources* **180(1)**, Pp. 1–14.

Shaffer C.E., Wang C.Y., 2009. Role of hydrophobic anode MPL in controlling water crossover in DMFC. *Electrochimica Acta* **54**, Pp. 5761–5769.

Song S., Yi W., Peikang S., 2007. Thermodynamic and kinetic considerations for ethanol electrooxidation in direct ethanol fuel cells. *Chinese Journal of Catalysis* **28(9)**, Pp. 752–754.

Song S., Zhou W., Liang Z., Cai R., Sun G., Xin Q., Stergiopoulos V., Tsiakaras P., 2005. The effect of methanol and ethanol cross-over on the performance of PtRu/C-based anode DAFCs. *Appl. Catal. B Environ.* **55**, Pp. 65–72

Song S., Zhou W., Tian J., Cai R., Sun G., Xin Q., Kontou S., Tsiakaras P., 2005. Ethanol crossover phenomena and its influence on the performance of DEFC. *Journal of Power Sources* **145**, Pp. 266–271.

Suda S., 2002. Method for Generation of Hydrogen Gas, U.S. Pat. 6,358,488.

Sun Y., Delucchi M., Ogden J., 2011. The impact of widespread deployment of fuel cell vehicles on platinum demand and price. *International Journal of Hydrogen Energy* **36(17)**, Pp. 11116–11127.

Suresh N.S., Jayanti S., 2011. Cross-over and performance modeling of liquid-feed Polymer Electrolyte Membrane Direct Ethanol Fuel Cells. *International Journal of Hydrogen Energy* **36**, Pp. 14648–14658.

Takuya Tsujiguchi., Soshi Hirano., Takanori Iwakami., Nobuyoshi Nakagawa., 2013. The performance degradation of a passive direct formic acid fuel cell and its improvement by a hydrophobic filter. *Journal of Power Sources* **223**, Pp. 42-49.

Thiam H.S, Daud W.R.W., Kamarudin S.K, Mohammad A.B., Khadum A.A.H., Loh K.S, Majlan E.H., 2011. Overview on nanostructured membrane in fuel cell applications. *International Journal of Hydrogen Energy* **36**, 3187-205.

Thiam H.S., Daud W.R.W., Kamarudin S.K., Mohamad A.B., Kadhum A.A.H., Loh K.S., Majlan E.H., 2013. Performance of direct methanol fuel cell with a palladium–silica nanofibre/Nafion composite membrane. *Energy Conversion and Management* **75**, 718-726.

Tripathi B.P., Shahi V.K., 2009. Surface redox polymerized SPEEK–MO2–PANI (M =Si, Zr and Ti) composite polyelectrolyte membranes impervious to methanol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **340**, 10-19.

Wan C.H., Chen C.L. 2009. Mitigating ethanol crossover in DEFC: a composite anode with a thin layer of Pt 50–Sn 50 nanoparticles directly deposited into Nafion® membrane surface. *International Journal of Hydrogen Energy* **34(23)**, Pp. 9515–9522.

Wan C.H., Lin M.T. 2013. Mitigating methanol crossover with self-assembled Pt 35–Ru 65 catalyst on Nafion surface. *Journal of Power Sources* **222**, Pp. 470–476.

Wang X., Hu J.M., Hsing I.M., 2004. Electrochemical investigation of formic acid electro-oxidation and its crossover through a Nafion® membrane. *Journal of Electroanalytical Chemistry* **562(1)**, Pp. 73–80.

Wu Q.X., Zhao T.S., Chen R., An L., 2013. A sandwich structured membrane for direct methanol fuel cells operating with neat methanol. *Applied Energy* **106**, Pp. 301–306.

Wu Z.L., Wang X.H., Teng F., Li X.Z., Wu X.M., Liu L.T., 2013. A long-term stable power supply μDMFC stack for wireless sensor node applications, *Journal of Physics: Conference Series* **476**.

Xu C., Faghri A., Li X., Ward T. 2010. Methanol and water crossover in a passive liquid-feed direct methanol fuel cell. *International Journal of Hydrogen Energy*, **35(4)**, Pp. 1769–1777.

Xu Q., Zhao T.S., Yang W.W., Chen R., 2011. A flow field enabling operating direct methanol fuel cells with highly concentrated methanol. *International Journal of Hydrogen Energy* **36**, Pp. 830–838.

Yang C.C., Lee Y.J., Yang J.M., 2009. Direct methanol fuel cell (DMFC) based on PVA/MMT composite polymer membranes. *Journal of Power Sources* **188**, Pp. 30–37.

Yang C.C., Lin C.T., Chiu S.J., 2008. Preparation of the PVA/HAP composite polymer membrane for alkaline DMFC application. *Desalination* **233**, Pp. 137–146.

Yang W.W., Zhao T.S., 2009. Numerical investigations of effect of membrane electrode assembly structure on water crossover in a liquid-feed direct methanol fuel cell. *Journal of Power Sources* **188**, Pp. 433–446.

Yu X.W., Peter G. Pickup., 2008. Recent advances in direct formic acid fuel cells (DFAFC). *Journal of Power Sources* **182**, Pp. 124–132.

Yuan T., Pu L., Huang Q., Zhang H., Li X., Yang, H., 2014. An effective methanol-blocking membrane modified with grapheneoxide nanosheets for passive direct methanol fuel cells. *Electrochimica Acta* **117**, Pp. 393–397.

Yuan W., Tang Y., Yang X.J., 2013. High-concentration operation of a passive air-breathing direct methanol fuel cell integrated with a porous methanol barrier. *Renewable Energy* **50**, Pp. 741–746.

Zhang H., Hsing I., 2007. Flexible graphite-based integrated anode plate for direct methanol fuel cells at high methanol feed concentration. Journal of Power Sources 167, Pp. 450–454.

Zhong S., Cui X., Fu T., Na H., 2008. Modification of sulfonated poly (ether ether ketone) proton exchange membrane for reducing methanol crossover. *Journal of Power Sources* **180**, Pp. 23–28.