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A Novel Structure of a Direct Methanol Fuel Cell: Design, Research and Assembly

by

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Abstract

As portable electronics are consuming an increased amount of energy, the current metal-based secondary batteries will be beyond their abilities due to their physical constraints. Driven by the high power requirements of portable electronic devices, which can hardly meet the conventional secondary battery systems, a portable Fuel Cell (FC) is thought to be a possible alternative with several advantages. It seems that FCs could be competitive in powering portable devices and billions of money has been put into the research of Portable FC (PFC). However, practical PFC applications are rare; several challenges in commercialization of FCs still exist. Solutions that can overcome the barriers of PFC development will be a great help for both FC research and portable electronics development. Thus, the aim of this dissertation is to study practical FC for portable electronics. The dissertation is approaching the aim by designing a novel structure Direct Methanol FC (DMFC).

In this dissertation the original motivation and the research approaching a Novel structure of DMFC (N-DMFC) is described. By focusing on the passive systems, design, testing and assembly of the N-DMFC is introduced in detail. In the N-DMFC, the current collector, gas diffusion layer, and catalyst layer are embedded together. No clear layer boundaries exist between different functional layers. A metal mesh was directly welded onto the Proton Exchange Membrane (PEM), and then the catalyst ink was sprayed on to it. The N-DMFC simplifies the conventional structure mange to save the cost, space and weight. Compared with the conventional structure, the new structure can withstand curling to some extent. This means that the structure can be used in places where flow fields cannot be utilized, such as vaulted or camber structures. Moreover, this N-DMFC is a ready-made product after welding. No mechanical pressure is needed to push the layers together.

In the first section of the dissertation, the background knowledge of FC, its challenges and research status are explained. Based on background information, the section is focusing on explaining the origins and motives of the research, research question, research approach, and the structure of the dis-

sertation. Section two gives a brief introduction of DMFCs. Then a description of the N-DMFC has been made. Based on the design, experimentation was carried out to test the rationality of the N-DMFC. In section three, the scale-up of manufacturing process is discussed. Two critical aspects, the catalyst loading and different assembly, are discussed separately. A sub-section on the entire assembly process concludes the section. The final section, four, draws the conclusion for the dissertation. The implications of future research possibilities are also introduced.

Keywords: Portable fuel cell, Direct methanol fuel cell, Novel structure, Assembly

Foreword

I can still remember when I was young; I sat around my father's drawing board, watching him draw pipes and lines. Maybe from that moment on, a little seed to become a "geek" has grown in my heart. It is hard to see what my life would be if I had not grown in this way. In case there are multiple universes, I would enjoy the possibility of there being another me who am a singer or a writer. But in this universe, I would like to be a scientist who can finally make a change in this world. This dissertation is my starting point. I hope that after 10 years, when I am looking at my dissertation, I can still feel the effort I have put into it and laugh at the naive point I have insisted on.

I would like to thank my supervisors Professor Aulis Tuominen and Dr. Arho Suominen. Without their help I maybe never could have accomplished this task. In addition, I would like to thank the coworkers I had the pleasure of working with in my research group. I would also like to thank M.Sc. Jarno Kankaanranta and M.Sc. Henrik Lagercrantz, for co-authoring papers, which were added to this dissertation, during the final stages of my work. In addition I would like to thank Ms. Miranda S. Miller and Joanna Airiskallio, who has been helping so much with my English editing.

I also thank Professor Riitta Keiski and Dr. Anja Ranta on their significant effort during the review process. It is through discussion that science is created.

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Not to forget the most important people in my life, a thank you is in order to my father Keming Zheng and mother Lina Sun for all the support during different times in my life. Thank you to my grandparents who have had a significant effort on me growing up. Thank you also to my wife Yiding who is always beside me, no matter what choices I have made, thank you for all the

times you have held my hand. I also thank my extended family for their support during my endeavors.

Finally, I want to thank all my friends, thank you for spending your time just listening to me talking about my research.

Salo 25.10.2011

Wukui Zheng
PhD student

List of original publications included in the thesis

This thesis is based on the following original publications, which are referred to in the text by the Roman numerals I-VI:

I. Arho Suominen, Wukui Zheng, Aulis Tuominen, Morphological analysis of technology: portable fuel cell development, Manuscript

II. Wukui Zheng, Arho Suominen, Jarno Kankaanranta, Aulis Tuominen, Design of Experiment method applied into DMFC characterization testing and research, Fuel cells, Under Review

III. Wukui Zheng, Arho Suominen, Henrik Lagercrantz, Aulis Tuominen, A 2D model for CO2/fuel multiphase flow on the anode side of a DMFC, Journal of Fuel Cell Science and Technology, Volume 9, Issue 1, Feb. 2012

IV. Wukui Zheng, Arho Suominen, Aulis Tuominen, A new Structure of a Passive Direct Methanol Fuel Cell, Chemical Engineering Science, Volume 76, Issue 9, July 2012, pp. 188-191

V. Wukui Zheng, Arho Suominen, Jarno Kankaanranta, Aulis Tuominen, Ultrasonic welding application in DMFC MEA manufacture, Under Review

VI. Wukui Zheng, Arho Suominen, Aulis Tuominen, Discussion on the challenges of DMFC catalyst loading process for mass production, Energy Procedia, Proceedings of the Fuel Cells 2012 conference, Forthcoming

Publication I, author has been doing the analysis with Arho Suominen and written the paper, author is focusing on the fuel cell case study.
Publication II, author has been doing the analysis with Arho Suominen and Jarno Kankaanranta, then written the paper, author is focusing on the experiment and testing.
Publication III-VI, author has carried out the tests and written the papers.

Contents

Abbreviations

AFC	Alkaline fuel cell
DBFC	Direct borohydride fuel cell
DMFC	Direct methanol fuel cell
DSC	Differential scanning calorimetry
DFAFC	Direct formic acid fuel cell
DOE	Design of Experimental
FC	Fuel cell
FTIR	Fourier transform infrared spectroscopy
GDL	Gas diffusion layer
H_2	Hydrogen
I-MR	Individual Moving Range
MCFC	Molten carbonate fuel cell
MEA	Membrane electrode assembly
MFC	Microbial fuel cell
n	Number of cell
N-DMFC	Novel structure DMFC
O_2	Oxygen
PAFC	Phosphoric acid fuel cell
PCB	Printed circuit board
PEM	Polymer electrolyte membrane
PEMFC	Polymer electrolyte membrane fuel cell
PFC	Portable FC
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidenefluoride
SOFC	Solid oxide fuel cell
SPC	Statistical Process Control
T	Production time
XRD	X-ray diffraction

Figures

Tables

1. Introduction

The aim of this section is to give a brief introduction of "what has been done and why" in the thesis work. In this section, the background knowledge of fuel cell technology, its history and its sub-categories are explained. This leads to the challenges and the current research status of fuel cells being explained. Based on the background information, the section focuses on explaining the origins and motives of the research, research question, research approach, and the structure of the dissertation. All of the above are introduced in individual sub-sections.

1.1. Fuel cell

A Fuel Cell (FC) is a device that converts chemical energy into electricity. It has several advantages: high power density, perceived environmental friendliness, convenient size and weight, and no moving parts. The principle of FC was discovered in 1838 and was published in one of the scientific journals of that time (Wolf, Arnold and Hubert 2003). It was explained that electricity was used to split water molecules into hydrogen and oxygen molecules, thus leading to the understanding that the reaction should be possible in the other direction as well. Soon after, an

experiment on reverse electrolysis, or the FC as we now know it, was successful (Frano 2005).

A FC structure can be divided into layers. The heart of the structure is the ion conducting medium. Ions can be cations or anions depending on the FC type. Taking a Hydrogen (H_2) Polymer Electrolyte Membrane FC (PEMFC) as an example, the ion conducting medium is a polymer membrane. This membrane separates the anode and the cathode electrodes of the FC. In the anode, the fuel (H_2) is oxidized into protons and electrons. The electrons are conducted via an external load to the cathode side. Protons move through the membrane to the cathode. In the cathode, the oxygen (O_2) gas in the air reacts with protons and electrons to form water molecules (**Figure 1-1**). Water formation and decomposition of hydrogen are catalyzed by a noble metal, usually platinum. These reactions can be presented as reaction formulas:

Anode:	$2H_2 \rightarrow 4H^+ + 4e^-$	Eq. 1-1
Cathode:	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	Eq. 1-2
Overall reaction:	$2H_2 + O_2 \rightarrow 2H_2O$	Eq. 1-3

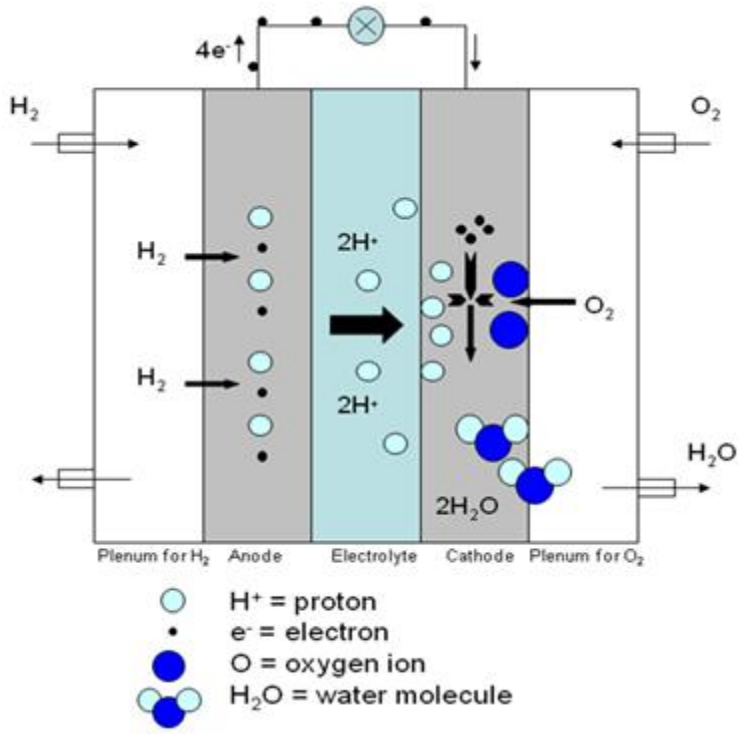

Figure 1-1: The working principle of FC.

In their 170 years history, FCs have developed into a variety of sub-groups. If classified by electrolyte, this includes for example Polymer Electrolyte Membrane (PEM) FC, Alkaline FC (AFC), Phosphoric Acid FC (PAFC), Molten Carbon FC (MCFC), and Solid Oxide FC (SOFC). If classified by fuel, it includes for example H2 FC, ethanol FC, formic acid FC and methanol FC. If classified by working temperature, FCs would be classified as low temperature FC (<200°C) and high temperature FC (>500°C). Regardless of the type, FCs have the same overall working principles. The differences are their electrolyte, working environment or fuel supply. However, due to the differences, application of different FCs is also varied. The sub-groups and their applications are reviewed in **Figure 1-2**.

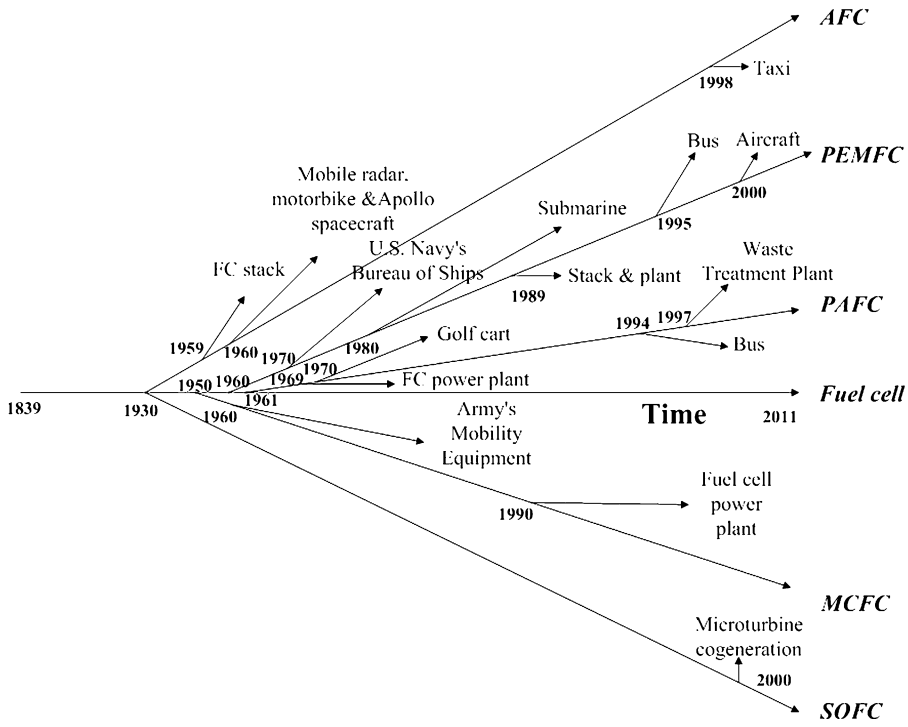

Figure 1-2: The development of FC applications[1].

Figure 1-2 shows that in the first 100 years after FCs have been discovered, there has not been significant development, but during the last 50 years, this technology has been applied in several practical uses. The low temperature FCs, such as AFC, PEMFC, and PAFC have had more applications (such as military applications and vehicles) than the high temperature FCs.

According to FCs' perceived advantages such as high power density and quick refilling, it would seem that FCs could compete as a power source in the portable electronics market. However, to the author's knowledge and **Figure 1-2**, the public is seldom aware of portable FCs. It is because Portable FCs (PFCs) have to overcome several challenges before they become practical. As reviewed by Suominen and Tuominen (2010), the challenges of PFC technology can be divided into several barriers, most significantly to lifetime, cost and commercialization. Technological barriers are analyzed in detail by Kamarudin et al. (2009). Cost as a factor is

[1] Figure is based on the review of references given in Appendix I.

also analyzed by several authors. As in the work of Wee (2006), DMFC based fuel cells were seen as more expensive than conventional lithium-ion batteries in both manufacturing cost and operational cost[2]. Dyer (2002), however, found contradictory results. The rare applications of FCs would argue against Dyer's results. For detailed analysis on the lifetime and cost barriers refer to e.g. Kamarudin et al. (2009) and Wee (2006).

Since there are several challenges in PFC commercialization, in both application and research, several attempts have been made to search the most suitable PFC for applications. This is discussed in Publication I: Technology foresight and planning through Morphological analysis. Besides the other researchers' discussion, we have chosen the Morphological analysis as our research model. In the Morphological analysis, we classified the PFC to seven characteristics seen in **Table 1-1**. They were overall type of the fuel cell, system type, control electronics system used, stack structure, fuel phase, operation modes, and operational purpose.

Table 1-1: Parametric possibilities of portable FCs.

	Parameter	States
$\mathbf{p}_1^{1,2,3,4,5,6}$	Fuel cell type	PEMFC, AFC, PAFC, MCFC, SOFC, MFC
$\mathbf{p}_2^{1,2}$	FC system	passive, active
$\mathbf{p}_3^{1,2,3}$	FC electronic system	hybrid, independent, half-independent
$\mathbf{p}_4^{1,2}$	stack structure	bipolar, monopolar
$\mathbf{p}_5^{1,2,3}$	fuel phase	gas, liquid, solid
$\mathbf{p}_6^{1,2}$	operation	continuous, intermittent
$\mathbf{p}_7^{1,2}$	purpose	one time use, cyclical

Review of the currently available products categorized by the above characteristics can be organized in **Table 1-2**.

[2] The low number of applications is also related to difficulty to compete with a mature well-known and globally spread technology since lacking infra for fuel distribution.

Table 1-2: Morphological analysis summary of FC products.

	FC type	System	Electronic system	Stack structure	Fuel phase	Operation	Purpose	Product
1	DMFC	P	Hybrid	Mono-polar	L	intermittent	C	Dynairo
2	PEMFC	P	Independent				C	MTI Micro
3	PEMFC	A	Hybrid				C	Samsung
4	AFC	P	Independent	Mono-polar	L	continuous	S	Medis 24/7
5	SOFC	A	Hybrid				C	Lilliputian Systems
6	PEMFC	P			G	intermittent	C	MiniPAK
7	PEMFC	P	Hybrid		G	intermittent	C	PowerTrekk
8	DMFC	A	Half-independent		L	intermittent	C	EFOY 1200
9	PEMFC	A	Hybrid		G	intermittent	C	XX25
10	PEMFC	P	Independent		G	intermittent	C	G2 source
11	PEMFC				G	intermittent	C	Ang-strom Micro
12	PEMFC	A			G	intermittent	C	Horizon's racing car

C = Cyclic, S= Single-use, L= liquid, G= gas, P=Passive, A=Active

Referring to **Table 1-1** and **Table 1-2**, the H_2 PEMFCs and DMFCs are the first leaders in the PFC application. SOFC and AFC are rare, but they do exist. In addition to type, two system approaches to FCs have been adopted, the passive system and active system. The active and passive characteristics are of equal importance in the PFC development. In the active system, the accessorial system (heater, pump or fan) is used to help the mass/heat transport. It can offer a better reaction environment to produce electricity (Qian, et al. 2006). In the passive system, without additional power-consuming active sensors and actuators for operation, the mass/heat transport is completed by the natural capillary forces of diffusion; convection and evaporation are the driving forces behind the processes (J. Liu, et al. 2006). The compactness, reliability, and relatively low cost make the passive system an intriguing solution for portable applications. But on the contrary, an active system pro-

duces more electricity and offers more power than the passive system. No conclusion about either of the two systems has been reached so far; the purpose of use ultimately decides which system will be applied.

Looking at current portable-type solutions, we see a hybrid power management system emerging as a design of choice for PFC applications. A hybrid system integrates a FC to a secondary battery system. In this, the FC works as a battery-life extension, loading the battery while the device in unplugged from the mains. The benefits of adopting a hybrid system come from keeping the power management design of the device fairly similar although adopting a new technology. The hybrid system requires a significant amount of balance of plant to operate. This ultimately increases size, weight and cost. Size, weight, and cost are also of importance when focusing on the stack structure.

In stack structures, we see the basic unit cell configured as a unit single cell or a unit bi-cell. In a bipolar structure, two cells are placed with their anodes spaced apart and facing each other the cells use the same fuel tank/channel. With this layout, fuel is distributed to the sealed anode space by either active or passive means. On the other hand, atmospheric oxygen air is easily accessed from the outside-facing cathodes. (Qian, et al. 2006). (**Figure 1-3**)

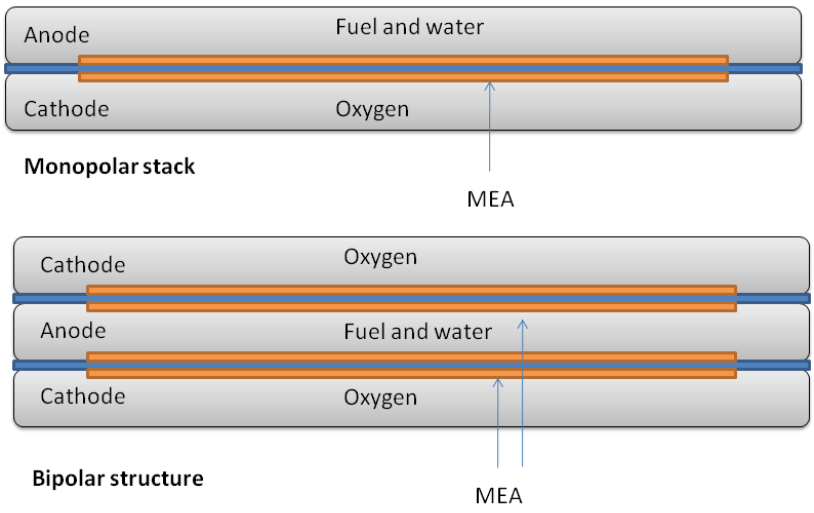

Figure 1-3: Monopolar stack and bipolar structure of PEMFC.

As seen in **Table 1-2**, passive systems are often based on the simpler monopolar structure consisting of a unit single cell. The fuel supply and balance of a bipolarity structure would be challenging for a passive system. Stack structure also affects the dynamics of the fuel. Fuel-phase, solid, liquid or gas, limits the design of a PFC. The fuel-phase, in **Table 1-2**, describes the fuel supplied. Liquid and gas forms of fuel are usually used in PFC. No solid fuels have been introduced to PFCs. The gas form is monopolar stack usually stored in a hydride metal, while liquid fuel is often in cartridges.

By considering the high cost of a FC, the FC usually is not intended for single-use. But for some special purposes or special applications, such as emergency/military, the cost can be neglected. There is a single-use continuous FC product available in the market as shown in **Table 1-2**, and they claim to manage saving the cost by using AFC rather than PEMFC. The other types are designed for cyclic use.

Although no successful solution is available, the results in Publication I also show that, the applications of PFC are currently focused on PEMFC. When searching the "PFC" and the different types of FCs in the Science Direct database, seen in Figure 1-4, the same conclusion can be reached. As seen in the figure, the PEMFCs have been researched the most in the field of PFCs (Urbani, et al. 2007, Taber, et al. 2003, Shimpalee, et al. 2009, Oszcipok, Zedda and Hesselmann, et al. 2006, Oszcipok, Zedda and Riemann, et al. 2006, Kim, Kim and Ha 2008, Miesse, et al. 2006, Liu, Li and Suda 2008, Farhad and Hamdullahpur 2010, Raman, Prashant and Shukla 2006). This is followed by DMFC (Achmad, et al. 2011, Baglio, et al. 2009, Pan 2006, Eccarius, et al. 2008, Blum, et al. 2003, Chen, Shiu and Lee 2006) and SOFC (Achmad, et al. 2011, Cheekatamarla, et al. 2009, Ding, Liu and Yin 2011, Kuhn, et al. 2008, Kundu, et al. 2007). AFC, Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and microbial FC are rarely studied in this context. (Ascoli, Pandya and Redaelli 1989, Zervas, et al. 2008, Lan, et al. 2010, Ward, et al. 1993, Sung and Choi 2007, Modestov, et al. 2009, Sollogoub, et al. 2009, Li, Zhao and Liang 2009, Hou, et al. 2011, Jain, et al. 2008)

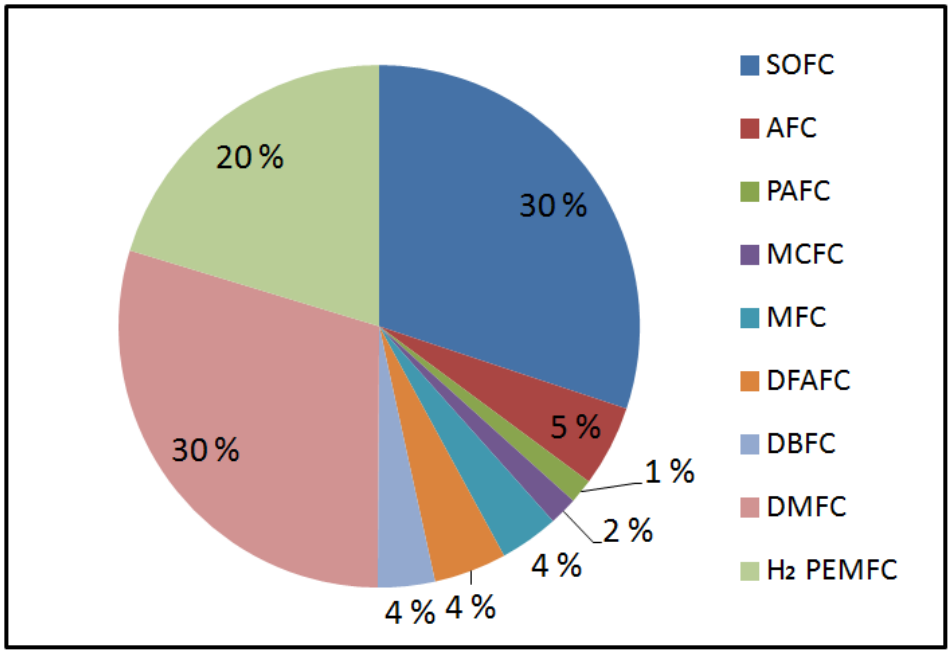

Figure 1-4: Research paper numbers in Science Direct Database[3].

A conclusion from **Figure 1-4** is that even if there are several different types of FCs, not all of them are practical in portable applications. It is surprising that the high temperature FC, SOFC, has been studied in regard to portable applications. However, currently the PFC research and applications are focused on the PEMFC, especially to its sub-category, DMFC[4].

[3] There are some overlaps in the results. The PEMFC also contains parts of the DMFC, DFAFC, Direct borohydride fuel cell (DBFC) articles.

[4] It has to be clear that the DMFC and PEMFC are two different categories. DMFC is categorized by its fuel, and PEMFC is categorized by its electrolyte. DMFCs do not need to be a PEMFC, and PEMFC does not only include DMFCs. Recently, most of the DMFCs are using PEM as its electrolyte, so most of the DMFCs are currently PEMFC. In this dissertation, we categorize DMFC as a sub-group of PEMFC.

1.2. Origins and motives

In the previous section, it is stated that the FCs are not mature for portable application. But as portable electronic devices have been designed with an increasing amount of functions, more energy is needed. Mobile phones for example, can be used as a GPS device, mini-computer, or as a camera. Even if consumers would accept a day to day load cycle, secondary battery technology will face challenges if even a little more power is needed. Driven by the high power and lifetime requirements of portable devices, that are hardly met by the conventional secondary battery systems, PFCs will be the alternative in the future (Michel and Graham 2004, Eckfeld, Manders and Stevenson 2003, Dillon, et al. 2004).

To be a viable alternative, FCs should overcome several barriers, most significantly the cost. This leads us to the research idea "could we find out a way to reduce the cost of PFC significantly in order to produce a commercially available end product?". If this idea could be realized, it would change the current approaches toward portable power sources. This is the motivation for this work.

In the beginning of this work, we were supported by Tekes to study the new opportunities of PFCs and their commercialization. This resulted in the funding of a project called *Portable fuel cell Research and Productization.* The project focused on applied research and evaluating the commercial possibilities of PFCs. During this project, the idea of creating a novel PFC structure that would be cost effective and simple was thought of.

1.3. Research questions

Going back to the background of FCs, the research questions are based on the notion, "what can we do with the PFCs in order to reduce cost?" Based on the previous discussion and Publication I, we selected the DMFC as our research target. Usually the DMFC structure is sandwich-like, with the polymer electrolyte membrane (PEM) in the middle, with a catalyst layer, gas diffusion layer, and flow field on each side, and sometimes with an additional metal plate for electricity conductivity. (Coutanceau, et al. 2006, Rayment and Sherwin 2003, Alexandre 2005, J. Liu, et al. 2006, McLean 2005, Chen and Zhao 2007, Yalcinoz and Alam 2008,

Zhao, et al. 2009, Yang, Chou and Shu 2007, Guo and Cao 2004). The structure has its advantages when considering liquid/gas transport and methanol crossover (Frano 2005). However, this structure also leads to additional impedance, weight, and volume. For example, current collectors can account for 10-15% of the total fuel cell stack cost, more than 80% of the stack weight, and nearly all the stack volume (Qian, et al. 2006).

By reviewing several works (Neburchilov, et al. 2007, Cindrella, et al. 2009, Liu, et al. 2006, Mehta and Cooper 2003, J. Wee 2007), it has been thought whether "a passive PFC needs to be as complex as an active PFC?". Since without additional power consumption, a passive system usually operates at a low current density. It means that the passive system needs a reduced cooling load, fewer water management issues, less produced heat, and a lower fuel delivery rate.

From the background and origins of the study the following research targets were made:

> *Could a novel structure FC be designed, for passive operation, to save cost?*

If so,

> *How well does this PFC design work when compared with others?*

If so,

> *Is there a practical assembly process for this novel PFC?*

The questions propose an entire process from the design of the novel structure FC to the analysis of the mass production possibility of it. The whole dissertation is structured to answer the above questions.

1.4. Structure of the dissertation

As described in the background, the research has been first carried out by a morphological analysis of PFC in Publication I. The morphological analyses classify the available PFC products and summarize current research directions. This publication also points out the possibilities of PFC applications. Based on this paper, we have chosen the DMFC as our FC sub-category.

In order to create a baseline of knowledge, an analysis of the DMFC structure was carried out. A statistic approach to the DMFC functional structure was done by using a design-of-experiment method in Publication II. The result shows that the balance of a DMFC structure itself and its environment are more important than catalyst's loading amount or membrane quality which has often been studied. It offered an idea of changing the structure of DMFC to meet the balance instead of improving the performance by studying one part of DMFC.

After creating a knowledge base, the study focused on the mass transfer phenomenon of DMFC, trying to build a computer model to explain what has happened during the mass transfer in Publication III. During the study, an idea was created that the structure could be formed without any actual boundary. Function of the structure is a more important criterion than the structure itself.

With the knowledge created, a Novel DMFC design (N-DMFC) was suggested in Publication IV. This creates the core of the research done. In the publication, several experiments were conducted with the N-DMFC. The result suggested that when the N-DMFC was compared with the current passive DMFC research, using (maximum power output)/(catalyst amount), the new structure demonstrates an average performance with a simpler structure. It saves cost, simplifies production process, and is thinner than conventional DMFC designs. It may have better applicability and can lead to a new passive DMFC design.

In conclusion, two publications, Publication V & VI, discuss the assembly process of a N-DMFC. The Publication V analyzes the ultrasonic welding and its application in the N-DMFC assembly. The analysis includes two parts, the qualitative analysis and quantitative analysis. It concludes that ultrasonic welding is suitable for N-DMFC and it is a practical choice for the DMFC assembly. The Publication VI discusses the catalyst loading process of DMFC. It first reviews the different loading methods and gives a comparison study concerning the mass production. The final result shows that the screen printing is the most practical method for DMFC scale-up.

The dissertation is, in addition to the sections included and original publications listed, mainly focused on the N-DMFC. The other part, other than the contents mentioned, also includes discussion on the raw material selection, the screen printing used for N-DMFC and the assembly process analysis.

The dissertation is structured as follows. The following section, section two, gives a brief introduction to DMFCs. Then a description of the N-DMFC has been made. Based on the design, experimentation was carried out to test the rationality of the N-DMFC. In section three, the scale-up of the manufacturing process is discussed. Two critical aspects, the catalyst loading and different assembly, are discussed separately. A sub-section on the entire assembly process concludes the section. The final section, four, draws a conclusion for the dissertation. The implications of future research possibilities are also introduced.

2. A novel structure of passive DMFC

In this Section, a N-DMFC is introduced to answer research questions one and two.

> *"Could a novel structure FC be designed, for passive operation, to save cost?*

If so,

> *How well does this PFC design work when compared with others?"*

A N-DMFC has been designed, tested and discussed. This section is divided into three parts. In the first part, the DMFC is introduced. This is followed by a description of the structure of N-DMFC. The selection of raw materials is discussed in part three. The section is concluded by the tests and discussion on the N-DMFC.

2.1. Introduction to DMFCs

DMFCs are one type of FCs. By definition, DMFCs use methanol directly as fuel. A DMFC is a viable FC solution as it operates at ambient temperatures and has

good energy density due to its high specific energy of the methanol. Since using a liquid fuel, the DMFC is easy to refuel, store and transport (Shimizu, et al. 2004). DMFCs will significantly reduce the thermal management challenges for a small system and may extend the stand-by time of laptops or mobile phones. Thus, DMFCs are one of the possible alternative power sources for future portable electronic devices. However, there are several questions that should be solved before this technology is applied into products. Besides the slow reaction rate on the anode side and crossover of methanol, the first and most important challenge is cost (Agnolucci 2007, Kim, Kim and Ha 2008, J. Wee 2007). The price of a DMFC can be accounted to membrane, catalyst materials, and to the overall structure of the stack. Cost is a huge barrier keeping this technology from commercialization.

In a DMFC, the working principle is the same as in the H_2 PEMFC. Differences exist in the fuel, catalysts and reaction products. In a DMFC, the fuel is a methanol/water mixture. When methanol is oxidized into electrons and protons, carbon dioxide is formed. Carbon dioxide is waste, formed at the anode, in addition to water that is formed at the cathode.[5] The catalytic decomposition of methanol occurs on a platinum-ruthenium catalyst (Abdelkareem, Tsujiguchi and Nakagawa 2010). The DMFC reaction formula can be written as follows:

Anode:	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	Eq. 2-1
Cathode:	$4H^+ + O_2 + 4\,e^- \rightarrow 2H_2O$	Eq. 2-2
Overall reaction:	$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$	Eq. 2-3

The basic structure of DMFC is (also) a layer sandwich model as previously discussed and illustrated in **Figure 2-1**.

[5] It has to be mentioned that, during the reaction, there is also a significant amount of heat produced. This is, however, not related to our topic.

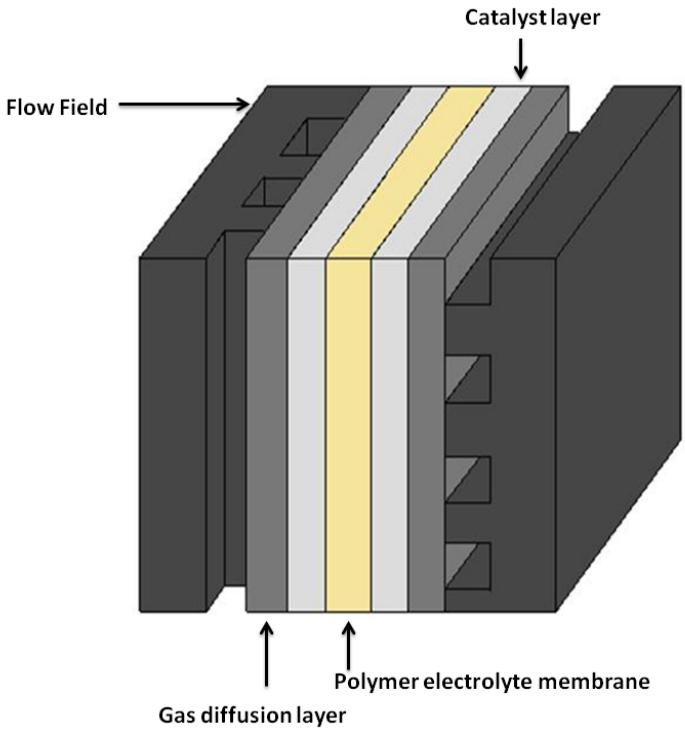

Figure 2-1: Basic structure of DMFC.

As shown in **Figure 2-1**, the structure has the PEM surrounded by a catalyst layer, a gas diffusion layer, and a flow field on each side. In this structure, each layer is clearly separated from each other. Additional forces are needed to press the layers together in order to make it work properly and to avoid fuel leaking in operation. The working principle of a DMFC is shown in **Figure 2-2** in a diagram.

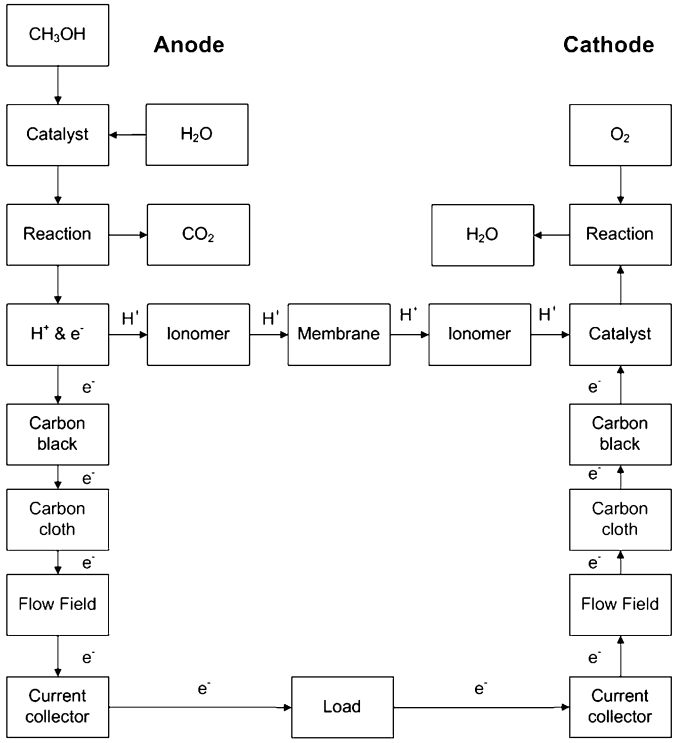

Figure 2-2: The basic working process of DMFC.

In **Figure 2-2**, it can be seen that the start of the whole reaction is when H_2O, CH_3OH and O_2 are fed into the DMFC. The protons are going through the membrane while the electrons are going through the load which produces the electricity. The final products of the reaction are H_2O, CO_2 and heat.

2.2. Description of the novel structure

By analyzing the DMFC structure, applying DOE methods and computer simulation in Publication II and III, several notices were made. The results showed that the balance of a DMFC structure is more important than improving one functional structure performance. As the research question called for a simpler structure of a DMFC, which is discussed in Publication IV, the N-DMFC, where the current collector, gas diffusion layers, and catalyst layers are embedded together, was designed. In the design, no clear layer boundaries exist between the different layers.

A metal mesh was welded directly onto the PEM, and then sprayed with catalyst ink forming the FC. The structure is shown in **Figure 2-3**.

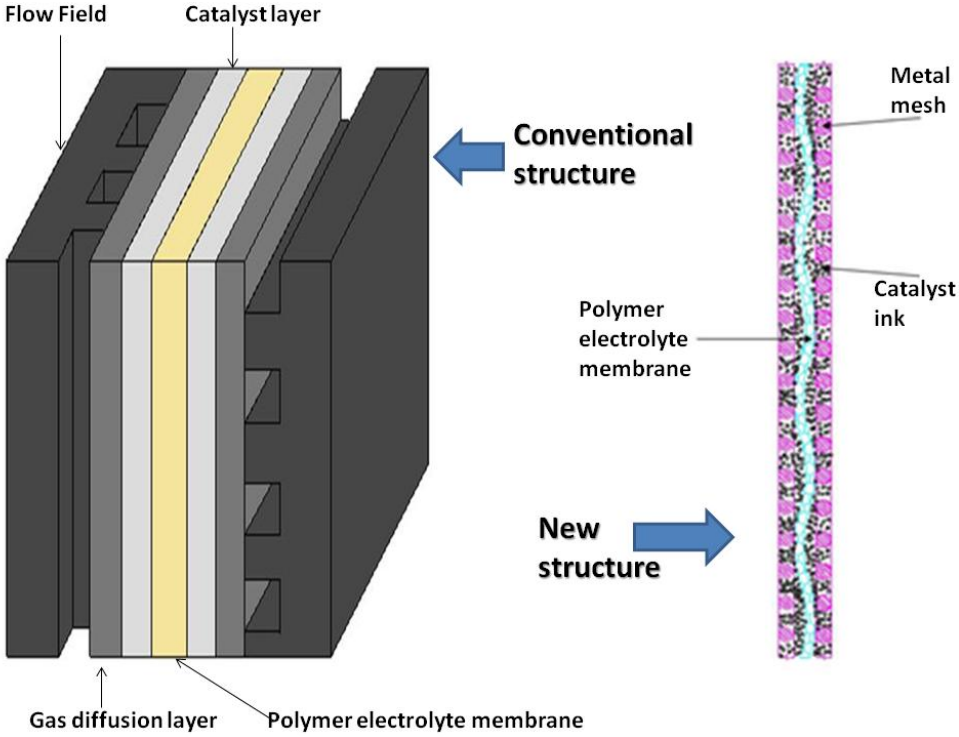

Figure 2-3: N-DMFC structure.

The metal mesh in the N-DMFC is the critical part. It is the electrode that holds the catalyst, and it acts as part of the gas/water diffusion layer and a mechanical support. Compared with a conventional structure, the novel structure can withstand curling to some extent. This means that this structure can be used in places where flow fields cannot be utilized, such as vaulted or camber structures. Moreover, this N-DMFC is a ready-made product after welding. No mechanical pressure is needed to press the layers together.

2.3. Material selection

The characteristics of materials are vital to the application of the N-DMFC, since the materials are directly related to the DMFC performance and the total cost. Choices have to be made to balance between price and performance.

2.3.1 Membranes

Plenty of research has been done to discover new kinds of membrane materials, such as DOW Chemical's XUS membrane, 3P energy membrane, and organic-inorganic composite membranes (Neburchilov, et al. 2007). In this specific case, simple and high proton conductive membranes were used. Three different membranes, PVDF-g-PSSA, Nafion, and Fumatech are discussed as possible alternatives.

PVDF-g-PSSA

Poly vinylidene fluoride (PVDF) itself is not a proton conductor. It can be made to conduct protons by adding other polymers, in this case styrene and sulphonation-other. As a result, a co-polymer chemical structure is formed in **Figure 2-4**.

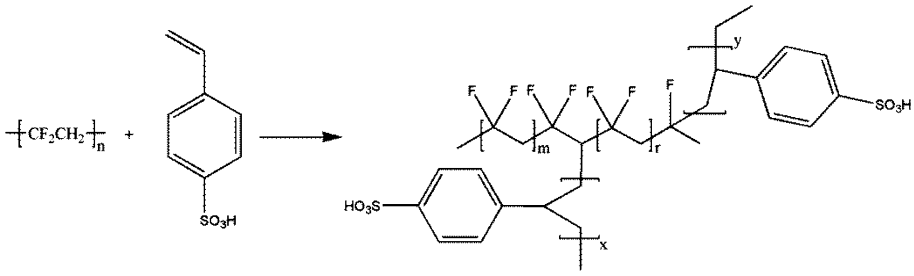

Figure 2-4: Chemical structure of PVDF-g-PSSA.

PVDF-g-PSSA membranes are well-suited for use in FCs. The open circuit voltage can reach the level 0.7 voltage even if the current collector connection is inadequate. The downside of using PVDF-g-PSSA membranes is their swelling property. In addition, they are difficult to attach to the electrode. Generally, PVDF-g-PSSA is not intolerant to water, but it swells a lot if ion exchange capacity is high and the membrane is not crosslinked. In this case, the membrane's water uptake is relatively high compared to Nafion or Fumapem F-14100.

Nafion

The most commonly used membrane in DMFCs is DuPont's Nafion membrane. Nafion is relatively durable and has a high ionic conductivity and good chemical stability. Nafion's hydrophobic polytetrafluoroethylene (PTFE) backbone provides thermal and chemical stability. Its structure holds a PTFE backbone and perfluorinated side chains containing sulfonic acid groups. This basic structure of Nafion is illustrated in **Figure 2-5**.

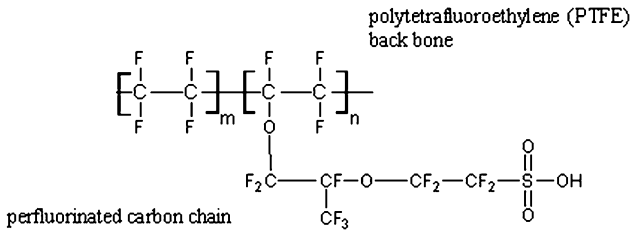

Figure 2-5: Chemical structure of Nafion.

Nafion membranes do have several disadvantages (Cowey, et al. 2004), which are:

1. *High cost, 600-1200 $/m^2.*
2. *High methanol crossover rate.*
3. *High ruthenium crossover (in the case that the anode catalyst contains Ru) from the anode and its re-deposition on the cathode.*

Despite of the mentioned disadvantages the properties of Nafion are superior to the other membranes at the moment (Neburchilov, et al. 2007). However, since cost is considered more in N-DMFC, Nafion membrane is not considered the most suitable membrane in this dissertation.

Fumapem F-14100

The German company Fumatech GmbH has developed cost effective sulfonated polyaryletherketone membranes (FKE Series, 50 μm thick) that have a high mechanical stability while demonstrating increased efficiency and significantly higher power density. This is due to considerably lower methanol permeability, compared to that demonstrated in Nafion membranes.

The Fumapem F-14100 is a perfluorinated sulfonic acid membrane. It is cheaper than the Nafion membrane. It is more suitable for the ultra-sonic welding process than the other two membranes mentioned, since it has the lowest water uptake rate.

Comparisons of these three membranes are described in **Table 2-1**.

Table 2-1: Membrane comparison.

Membrane	Thickness (dry) / µm	Water uptake / wt%
PVDF-g-PSSA 50µm (DOG = 20.3%)	58.2±2.2	16.1
PVDF-g-PSSA 100µm (DOG = 49.5%)	135±12	36.1
Nafion 115	103±6	15.4
Fumapem F-14100	77.7±2.2	10.8

The general methods of measuring and evaluating the PEM properties have been investigated: proton conductivity, ion exchange capacity, water uptake, gas permeability, methanol permeability, durability, thermal stability and performance test (Peighambardousta, Rowshanzamir and Amjadi 2010). In a N-DMFC, the first important factor for membrane is if it can attach with the meshes. Second and third, there are two important technical characteristics for the membrane used for N-DMFC, thickness and water uptake. Water uptake describes the membrane volume changes. It is especially important in N-DMFC. In the N-DMFC, the metal meshes are connected to the membrane directly. If the membrane volume changes too much after feeding the fuel, disconnection between the mesh and membrane will be caused. In the N-DMFC, the low water uptake is mandatory. The thickness of the membrane also needs to be considered. It has to be thick enough to connect to the metal meshes without detaching, but not too thick to influence the membrane performance. When comparing the three different membranes, Fumapem has the highest ion exchange capacity, and the lowest water uptake. It means that Fumapem is the best choice for the N-DMFC. As it is also reasonably priced, Fumapem was selected as the membrane in our research.

2.3.2 Other structural elements

Catalyst

When developing the N-DMFC, the catalyst (Pt) content was kept at a low level, around 0.5 mg×cm^{-2}. This was done to keep the total cost of one unit cell competitive. As the catalyst load used was low, carbon should be used to support the plati-

num. This will give a suitable layer, with an acceptable high surface area. The most commonly used catalyst Pt(Pt/Ru) on carbon (BASF) was chosen as the catalyst. Also, it is argued that 28% ionomer content is the best ratio with the FC catalysts (Barbir 2005). In our project, a 30% Fumion ionomer solution was used in the catalyst ink.

Metal mesh

In comparison to the conventional structure, a metal mesh is used in the N-DMFC. As mentioned, the metal mesh in the N-DMFC is a critical part in the structure. Three characteristics are used to define the metal mesh: material, thickness, and eye size. Experiments have been applied to exam the best suitable mesh in Publication IV.

In the experiment, three metal meshes were tested. The first two were stainless steel meshes with different thicknesses, and the third was a stainless steel mesh but gold-plated. Parameters are shown in **Table 2-2**.

Table 2-2: List of the metal meshes and their physical characteristics (Gandy 2007).

	Thick-ness/µm	**Eye size/µm**	**Electrical resistivity (20°C)/22.14 nΩ·m**
Thicker acid-proof steel meshes	125	100	96.1
Thinner acid-proof steel meshes	70	50	96.1
Gold-plated meshes	70	50	22.14

The test result showed that the use of gold-plated meshes on both the anode side and the cathode side increased the performance of a passive DMFC (**Figure 2-6**). The maximum usable current density and the open cell voltage increased. However, voltage reduced when the load was connected, and then the voltage stayed at a level similar to the other tested cells. This indicates that the current collector has a great influence on the fuel cell performance before the load is connected. Once the load was connected, the current density was limited by electrochemical reactions, and the current collector did not have such a significant influence.

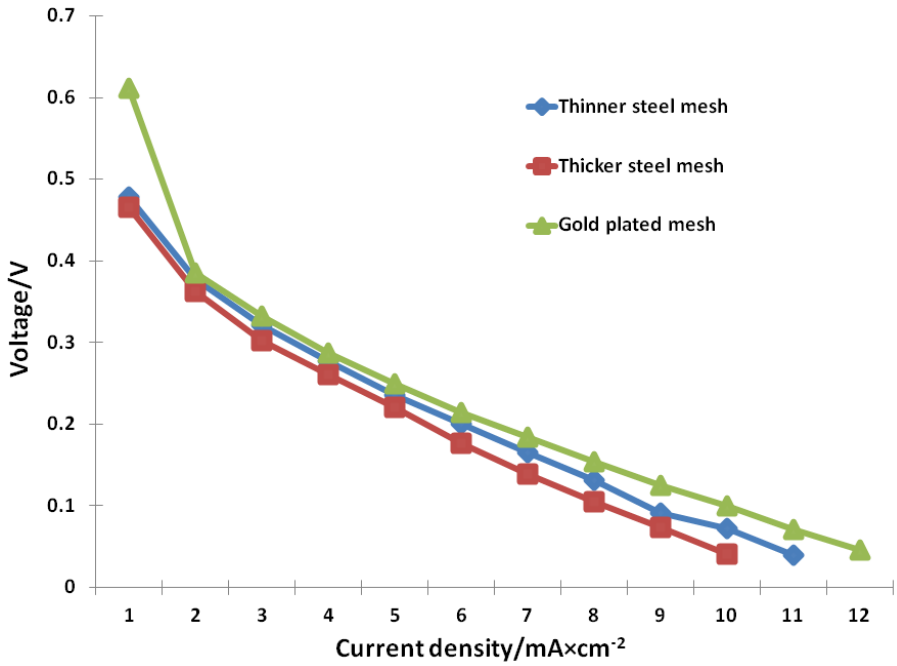

Figure 2-6: N-DMFC performance with different metal meshes.

Considering cost and performance, a thinner acid-proof steel mesh is the best choice, as there is no significant difference between the gold-plated mesh and acid proof mesh in loadings.

2.4. Experiment and discussion

Practical experiments were done after the material was selected. As described in Publication IV, the experiments were carried out by the following procedures: the membrane used is Fumapem F-14100 (Fumatech GmbH). It was pretreated as follows. The membrane samples were placed in an aqueous 10 wt-% HNO_3 solution for 12 hours at t=80 °C, treated for 1 hour in dimineralised water at t=80 °C, and then rinsed with dimineralised water. Finally, the membrane is dried in ambient air.

The mesh used in experiment is stainless steel 304 (thickness: 70 µm, eye size: 50µm) cut to 1.5×1.5 cm with an extra current collector tail (as shown in **Figure 2-**

7), which was cleaned with an ultrasonic cleaner. Then the mesh was left to dry in ambient air. The meshes were then assembled to the membrane with ultrasonic welding equipment (MP702, Ritmacon Oy) opposed to the commonly used hot-pressing method. The probe area of welding equipment was ø2.5 mm. Parameters in the welding device are shown in **Table 2-3**. In the experiment, meshes are placed both above and beneath the membrane. The ultrasonic probe will contact the surface of the upper mesh and then weld the whole parts. This process joins the three parts, membrane, anode-side mesh, and cathode-side mesh, together.

Table 2-3. Ultrasonic welding parameters.

Parameters	Value
Welding energy	4.0Ws
Pressure	0.5MPa
Trigger[6]	5
Hold time	1s
Amplitude[7]	7

After the welding process, the catalyst ink was prepared by dispersing 60% carbon-supported Pt/PtRu (BASF) into iso-propanol water (5:1) solution with 30 wt-% ionomer (FLNA-905, Fumatech GmbH). The catalyst ink 0.5 $mg \times cm^{-2}$ produced was loaded with an air brush onto the membrane-mesh-assembly.

The pictures of N-DMFC ready-made samples are shown in **Figure 2-7**.

[6] This parameter adjusts the triggering of the ultrasonic generator. The higher the value, the higher the pressure on the object to be welded. The value range is 0-9.9 without unit.

[7] The output amplitude can be set to one of five levels from 100% down to 60%.

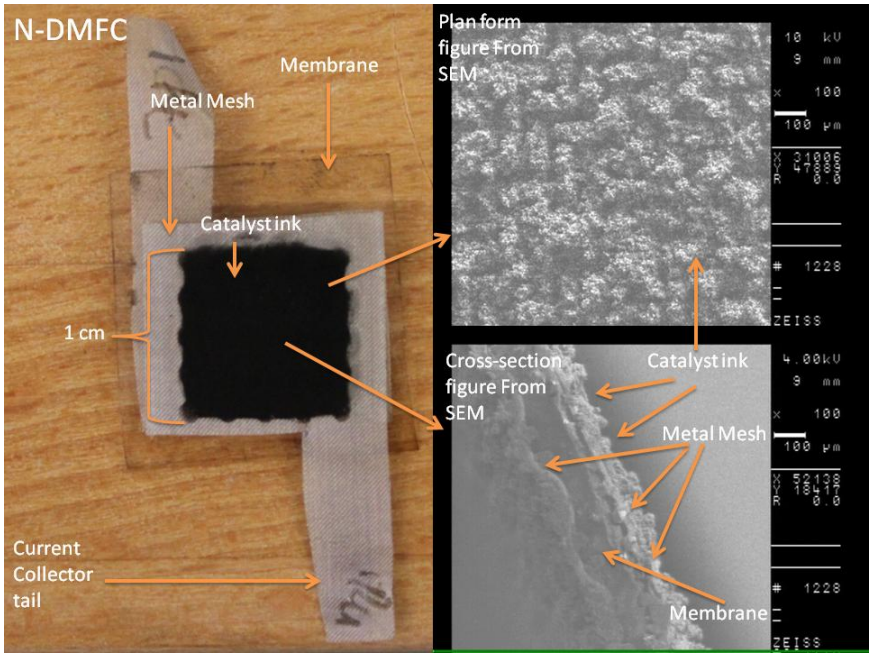

Figure 2-7: Ready-made samples.

As seen in **Figure 2-8**, an open fuel tank was used for testing. Fuel is supplied to the anode side, and the cathode side is open to air, and therefore the whole DMFC is a pump-free system and self-activated by electrochemical reactions. The methanol concentration is 2 mol×L^{-1} (6 wt%). The whole experiment was conducted at room temperature (20 °C). Polarization curves were obtained by using an electronic load system (3711A, DC, Array Electronic). An active area of MEA was 1 cm^2 in the testing.

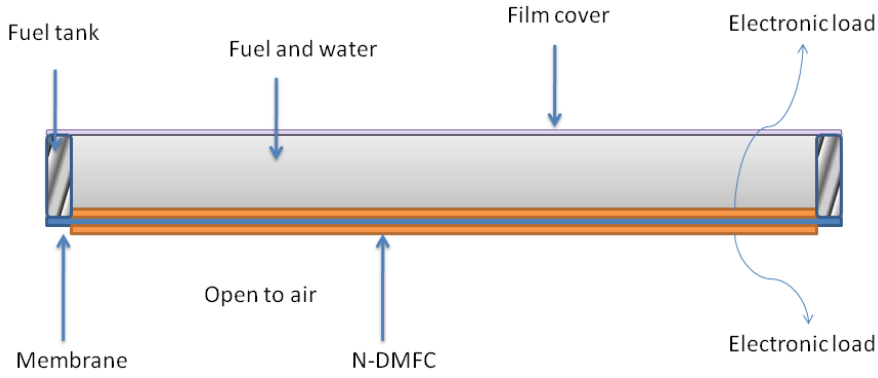

Figure 2-8: N-DMFC testing setup.

In the experiment, voltage-current measurements were taken after the methanol solution had been in contact with the cell for 20 minutes. Each data point represents a typical steady state voltage that was measured after continuous operation of 5 minutes at the indicated current density.

Results show that the N-DMFC runs successfully with the 2 mol×L^{-1} methanol concentration. It produces a power density of 1.61 mW×cm^{-2}, which was reached at a current density of 8mA×cm^{-2} at a voltage of 0.202 V. Results are shown in **Figure 2-9**.

The results were compared with conventional designs (Shimizu, et al. 2004, Ali Abdelkareem and Nakagawa 2006, Bae, et al. 2006, Baglio, et al. 2009, Lai, et al. 2008, J. G. Liu, et al. 2005, Martin, et al. 2007) in **Figure 2-10**[8]. It seems that the N-DMFC performance ranks in the middle of the samples. Considering its simple structure, it may have better applicability at 2 mol×L^{-1} and it can lead to better cost efficiency than the conventional DMFC. These results all stem from methanol operating in a totally passive situation with no fans or pumps installed.

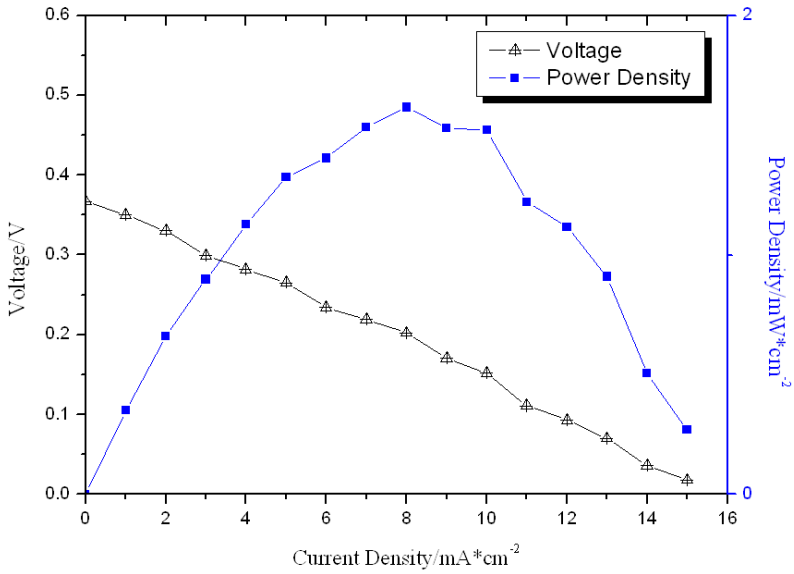

Figure 2-9: N-DMFC performance chart.

[8] It has to be mentioned that other scholars are using Nafion membrane and we are using Fumapem membrane in the experiment. This may influence the results.

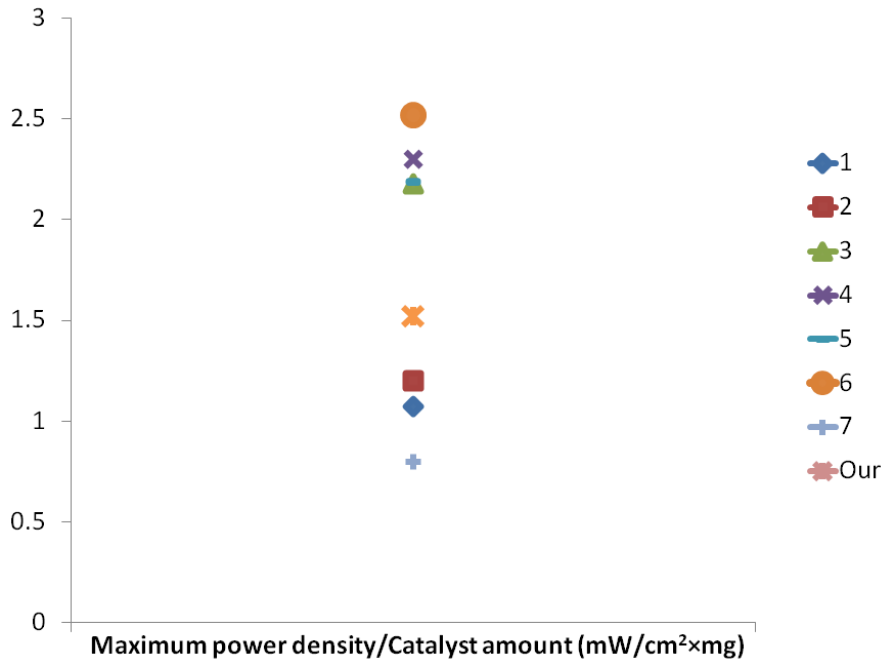

Figure 2-10: Performance/catalyst figure with different samples (Shimizu, et al. 2004, Ali Abdelkareem and Nakagawa 2006, Bae, et al. 2006, Baglio, et al. 2009, Lai, et al. 2008, J. G. Liu, et al. 2005, Martin, et al. 2007).

The properties of the N-DMFC can be summarized as follows: in the N-DMFC, the current collector, gas diffusion layer, and catalyst layer are embedded together. No clear layer boundaries exist between different functional layers. A metal mesh was directly welded onto the PEM, and then the catalyst ink was sprayed on to it. The N-DMFC overcomes the cost-barrier and simplifies the structure in order to save the cost, space and weight. Compared with the conventional structures, the new structure can withstand curling to some extent. This means that the structure can be used in places where flow fields cannot be utilized, such as vaulted or camber structures. Moreover, this N-DMFC is a ready-made product after welding. It can be used directly. No mechanical pressure is needed to push the layers together. It may have better applicability and lead to new application areas for passive DMFC.

3. Assembly process

After establishing that the N-DMFC could work properly, our research focused on how to assemble this structure in a simple way that can easily be scaled-up. In general, the assembly of a DMFC MEA is not complicated. It includes two steps: the loading of the catalyst and the assembly of all the different layers. In this section, the contents are divided as these two steps. First the assembly of all the different layers is discussed, and then the loading process is reviewed. At last, a discussion about the automated process and cost analysis is carried out.

3.1. Welding

Assembling different layers together will influence the performance of the DMFC heavily (Tang, et al. 2007, Hu, et al. 2006). A good connection will help the mass and heat transfer and at the same time will not change the catalyst and membrane properties. Currently, a hot-pressing method is used. There are several advantages in hot-pressing for the MEA assembly. It is a simple process with simple joint preparation, the equipment is relatively inexpensive, it is fast, joints are of high quality, no additives are needed, few skilled operators are required, and it is easy to apply into mass production. Much research has been done in this field (Park, et al.

2011, Yang, Lin and Chiu 2008, Wang, Liu and Linkov 2006). However, hot-pressing is not the only method to connect different layers. Some other methods are also applied for the DMFC assembly (Steven and Pratt 2000). In this dissertation, N-DMFC is assembled by using ultrasonic welding, since in our structure the mesh and the membrane cannot easily connect with hot-pressing.

The discussion on ultra-sonic welding used for N-DMFC is divided into two parts in Publication V. It has been separated to a qualitative analysis and a quantitative analysis.

Qualitative analysis is used to test if the ultrasonic welding changed the organic PEM structure, which will indicate whether ultrasonic welding can be applied. Quantitative analysis via microscope is used to test the ultrasonic welding quality, i.e., how well these two materials join together.

Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used in the quantitative test. FTIR is used to examine different organic functional groups, and XRD is used as a reference to examine the space structure of the membrane.

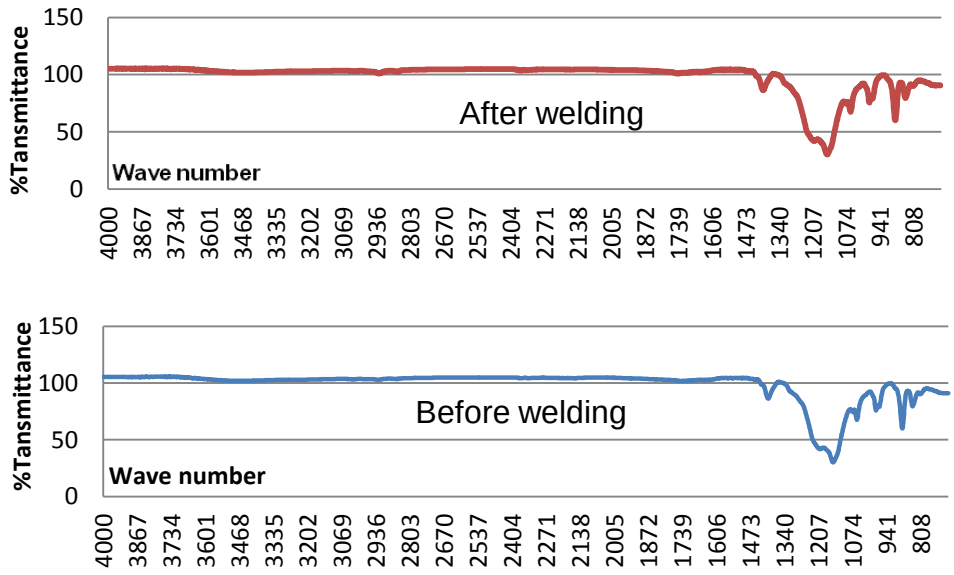

Figure 3-1: IR spectrum for membrane before welding and after welding.

The qualitative analysis confirms (**Figure 3-1**) that no significant changes to the membrane have happened in the welding process. Ultrasonic welding can be used on the membrane without changing its properties.

A quantitative approach is used to study the embedded distance between the membrane and the mesh. This distance should be deep enough to avoid detaching after the welding. The distance should also be as low as possible to avoid too much crossover while the DMFC operates. The measurements were carried out for 10 samples with the same welding parameter. Measuring was made via microscope from cross-section samples that were embedded in epoxy. The cross-section analysis was conducted from the center of the weld.

These tests indicate that there were no visible damages on the membrane surface. There was no detachment of the membrane and the meshes or structural change after absorbing the fuel. The membrane can be bent and can withstand tensile force which, if exceeded, will break the membrane without detachment. Measurements of each sample are shown in **Figure 3-2**.

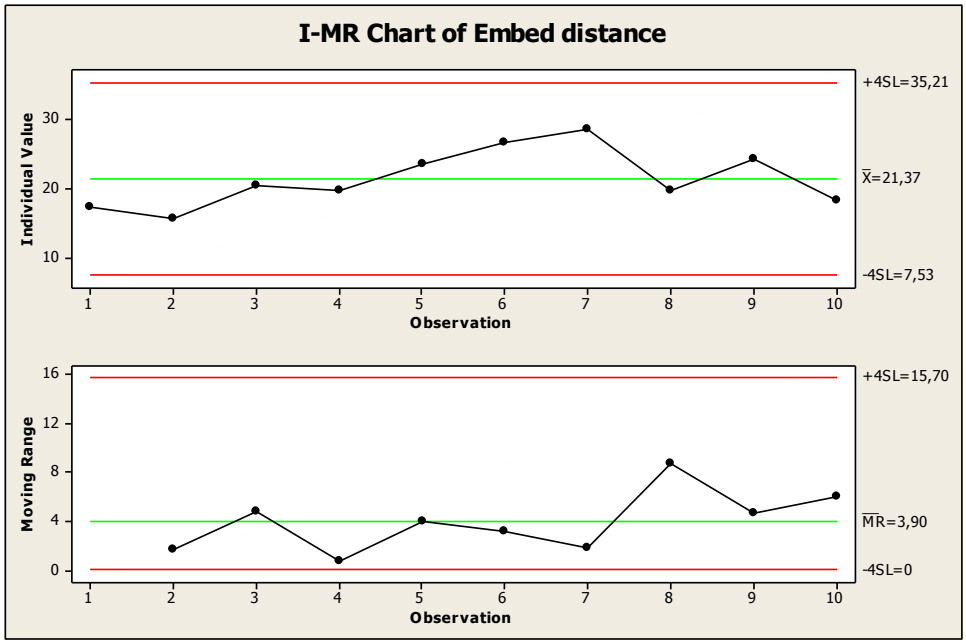

Figure 3-2 : I-MR SPC Chart of Embedded distance.

Individual Moving Range (I-MR) Statistical Process Control (SPC) chart is used to test if the process is stable or not (Shewhart 1930, Wheeler 1995). In **Figure 3-2**, the measurements of each sample's embedded distance are shown in an I-MR SPC chart. It indicates that the welding results are stable[9].

3.2. Catalyst ink loading process

Several methods have been developed for the DMFC catalyst loading, such as spreading, spraying, sputtering, painting, screen printing, decaling, electro-deposition, evaporative deposition, and impregnation reduction (Frano 2005). Discussion on why a specific catalyst loading process is used is, however, scarce.

We have analyzed the most efficient methods to scale-up the catalyst loading process in Publication VI. It shows that the screen printing method is one of the most suitable processes as shown in **Figure 3-3**.

[9] It has to be mentioned that traditionally in SPC charts there are 3-sigma limits used as control limits. In individual charts this is not the right way to do it. The assumption for most continuous data SPC charts is normal distribution. Normal distribution could be characterized as follows: $x \sim N(\mu,\sigma^2)$. This means that x follows normal distribution with two parameters μ (=population mean) and σ^2 (=variance). In different Xbar charts, the mean of subgroups is calculated. Based on central limit theorem (CLT), the distribution of these means could be characterized as $xbar \sim N(\mu,(\sigma^2/n)$. This means that the mean of the subgroups follows normal distribution with two parameters μ (=population mean) and $(\sigma^2)/n$ (=variance/subgroup size). Because these variances are different, different limits need to be used. If the same limits are used, the charts give fault signals. This is why 4-sigma limits are used for individual charts.

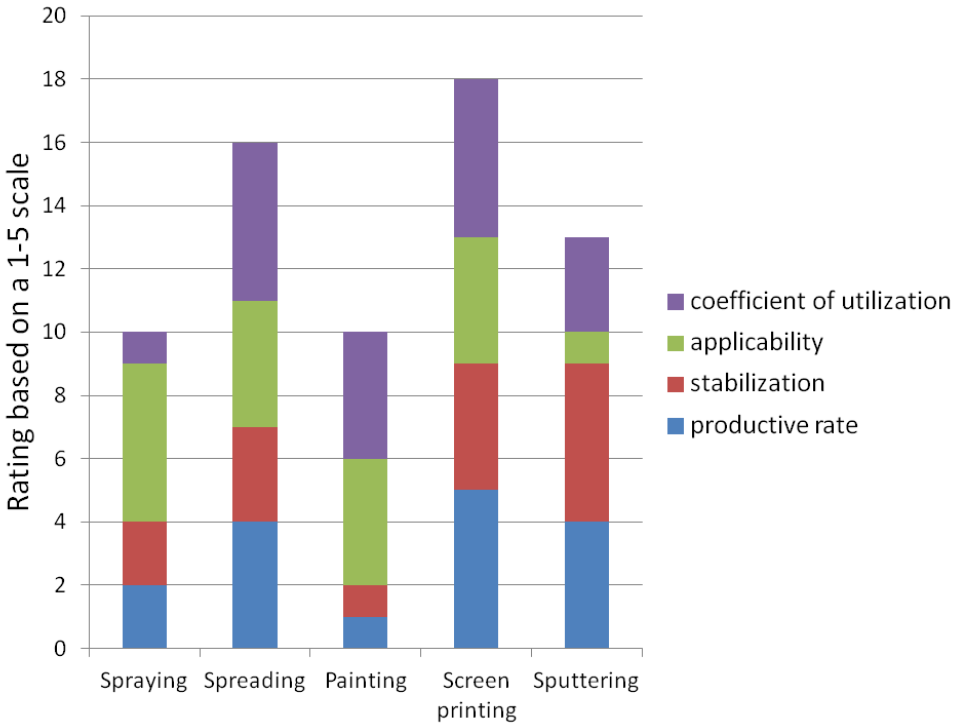

Figure 3-3: Comparisons of the common methods.

The assumptions made suggest that applying screen printing would be practical. In screen printing, the ink is a paste form ink. The thickness of the catalyst layer has to be controlled since a too thin layer will cause an open circuit; on the other hand, a too thick layer will influence the mass transfer and may cause deformation and cracks on the catalyst layer.

Based on the experiment, a reasonable catalyst content rate for screen printing is shown in **Table 3-1**. It is imperative to mention here that liquid should be added drop by drop in order to keep it in paste form. Adding superfluous liquid in a short period of time may transfer the paste into liquid form.

Table 3-1: Catalyst paste content.

	Amount
Pt 60% on Carbon black (Cathode)	16.7 mg
Pt 30% Ru 30% on Carbon black (Anode)	16.7 mg
Fumion	5 mg
Carbon black	173.3 mg
Distilled water	5 ml
Iso-propanol	10 ml

After the paste was ready, a screen printing machine was used (AP25, MPM Corporation) to print the catalyst ink on the membrane. The membrane is placed on the surface of a Printed Circuit Board (PCB) for an added structural support. The catalyst ink was used as a paste, and stainless steel plate, with an opening of 1cm by 1 cm was used as a stencil. The membrane used in this experiment was Fumapem F-14100 (dry thickness: 100-120 um, Fumatech GmbH). This membrane was pretreated as described in Section two. The catalyst ink was prepared as described above.

The experimental results showed that the screen printing method could be applied to the N-DMFC. From the cross-section and microscopic figures, seen in **Figure 3-4**, the catalyst layer is as thick as the membrane and it is uniform. The N-DMFC has no problems of membrane swelling or wrinkling.

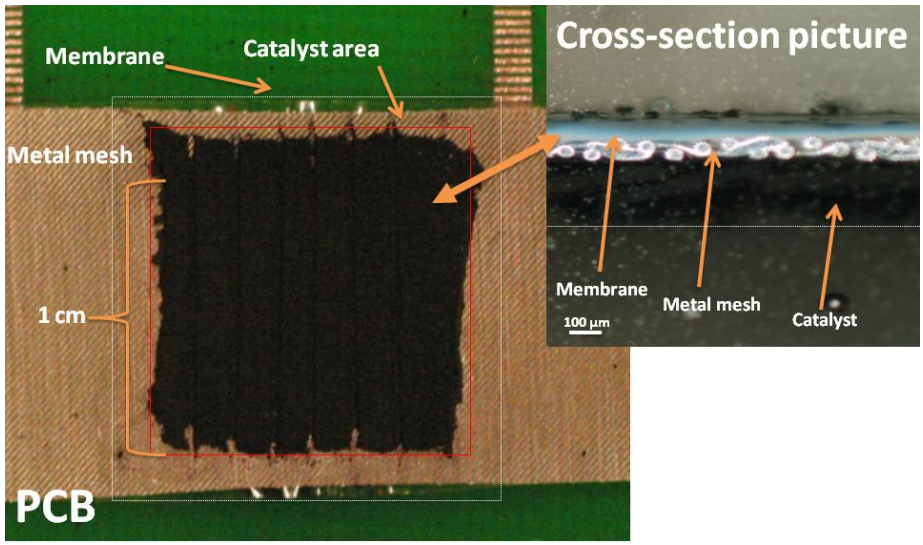

Figure 3-4: Screen printing results.

The advantages of this method are:

1. *quick process,*
2. *easy paste preparation,*
3. *low waste.*
4. *ability to print,*
5. *impurity tolerance,*
6. *easy scale-up.*

However, the process also presents challenges. First, screen printing a large area such as 1 cm by 1 cm will require the catalyst paste to have precise geometries allowing complex interconnection patterns to be generated. A too dry paste will fracture the catalyst layer; a too wet paste will cause a boundary effect, which causes the edge of the catalyst layer to be thicker than the middle. In this case study, silk threads were applied as a mesh on top of the membrane, which divide the membrane into six small areas. It helps to reduce the boundary effect influence. Therefore, the screen printing properties should be considered case by case, in order to get the optimized results.

3.3. Overall N-DMFC assembly process

As in **Figure 2-2**, the N-DMFC assembly can be divided into three steps: pretreatment, assembling and loading. A batch process was discussed previously in section two. In this section, the automatic production period is discussed.

Step 1: Pretreatment

Step 1 includes the pretreatment of the membrane, the mesh and the catalyst ink. In this step, the meshes were cut into two mesh tapes, with size 3.5×40cm, then cleaned with ultrasonic cleaner. It took around six minutes. The catalyst was prepared as described in screen printing experiment. It took another six minutes. The membrane was cut into a 4×40cm piece, then resin and cleaned. It took eight hours: five hours for resin, three hours for cleaning.

Step 2: Assembly

Ultrasonic welding is used for the membrane and mesh assembly; the quality of which has been discussed in Section 3.1. It is suitable for DMFC assembling. However, ultra-sonic welding utilizes high-frequency ultrasonic acoustic vibrations

to weld different parts together. In this case, the metal mesh and membrane should be held together. Otherwise, shaking and movement of the materials can occur, resulting in bad quality and poor uniformity.

In the assembly, a roll-to-roll system has been seen practical in creating a feasible solution. This system does not need neither pretreatment nor after-treatment for the materials and can be easily applied into an automatic assembly line.

Step 3: Catalyst loading

The screen printing method was used for catalyst loading, it took around six minutes.

The time consumption of the assembly process is portrayed in Table 3-2.

Table 3-2: DMFC process.

Process	Start time	Processing time (hour)	End time
Membrane preparation	0.00	8	8
Mesh preparation	0.00	0.10	0.10
Ink preparation	0.00	0.10	0.10
Welding	8	0.05	8.05
Printing	8	0.1	8.1

The production rate is a critical parameter for an automatic production line. In this N-DMFC production, the process is semi-continuous or semi-batch. The preparation of the membrane is a batch process, and the membrane preparation of one membrane takes the same amount of time as it takes to prepare 100 membranes (8 hours). When assuming that we are going to prepare 8/n DMFCs at a time, the production rate is 8/n per DMFC. In the manufacturing process, welding can commence after the preparation of the membrane and mesh, and printing can commence after welding and ink preparation. The welding and printing for each MEA takes a certain amount of time, and it is a continuous process. The mesh preparation could be performed simultaneously with the membrane preparation. The mesh preparation process is much easier than the membrane preparation process and thus does not consume as much time. The bottle neck process is the membrane preparation, which always takes 8 hours, making the production rate per cell 8/n. While the printing is being performed, the welding could already be executed, thus eliminating the influence of welding on production time. Comparing the printing process

which takes 0.1 hours to the welding process which takes 0.05 hours, the printing process is the bottle neck.

Production time for each cell is:

$$\begin{cases} T = \frac{8}{n} + 0.05 + 0.1 \ (n = 1) & \text{Eq. 3-1} \\ T = \frac{8}{n} + 0.1 \ (n \in (1,100]) & \text{Eq. 3-2} \end{cases}$$

T= production time for one cell

n = number of cells

These equations show that the more we produce, the less time each manufactured unit will require. The limit T is 0.18 hours, while n=100. Thus, the timing of the entire process is mainly controlled by the printing process. If we wish to shorten the processing time, the number of printing equipment should be increased. The optimized result for the manufacturing of one cell is 0.2 hours, which is 12 min.

3.4. Cost analysis

In the N-DMFC, several materials have been used for manufacturing. The costs of important materials used in a 3×3 cm N-DMFC is listed in **Table 3-3**. Other materials used, such as carbon black, iso-propanol and distilled water, are neglected due to their inexpensive price.

Table 3-3: Price list of each material.

	Item	Amount/size	Price (Euro)
1	Metal Meshes	3.5×3.5 cm^2 ×2	24.5×350/50000=0.1715
2	Fumatech membrane	4×4 cm^2	370×16/10000=0.592
3	Catalyst (anode)	0.5 mg ×9	4.5×816/1000=3.672
4	Catalyst (cathode)	0.5 mg ×9	4.5×816/1000=3.672
5	Ionomer	1.35 ml	1.35×75/100=1.0125
		Total	**9.12**

From the table, it can be seen that a single N-DMFC's cost is around 9 € without the shell. If it is divided by its size, the price is around 1 euro×cm^{-2}. It also means 1.61 mW per € and 621 € per watt.[10]

As it is discussed by Agnolucci (2007), the prospect PFC price is 3 $ per watt. Even through the mass production price could be cheaper than the price in the laboratory, the cost estimation of the N-DMFC is still far away from being commercially available. The cost of N-DMFC is mainly due to the catalyst used. It takes more than 90% of the total price. By using this N-DMFC, the price of the other parts of the DMFC has been limited to a very small amount, less than 10%. It can be claimed that the N-DMFC has a simple structure and it saves the costs also. However, at this stage, the efficiency of the catalyst in N-DMFC has been the more prominent problem. More studies focusing on this are required. In the future research, it could be the key point to farther enhance the N-DMFC performance, and make it commercially available.

[10] The cost analysis is made for materials only and based on laboratory experiments.

4. Conclusions

The final section 4 draws the conclusions to the dissertation. The implications of future research possibilities are also introduced. The section is sub-sectioned as follows. Section 4.1 Summary of the publications elaborates on the original publications included in the thesis. The publications are discussed individually and insights to the origins of the publications are given. Section 4.2 Contribution elaborates the overall findings of the publications. Section 4.3 analyzes the limitations of the work and simultaneously suggests future research efforts.

4.1. Summary of the publications

As discussed in the first section, each publication has its own contributions to the whole dissertation. The structure of how the publications are organized is shown in **Figure 4-1**.

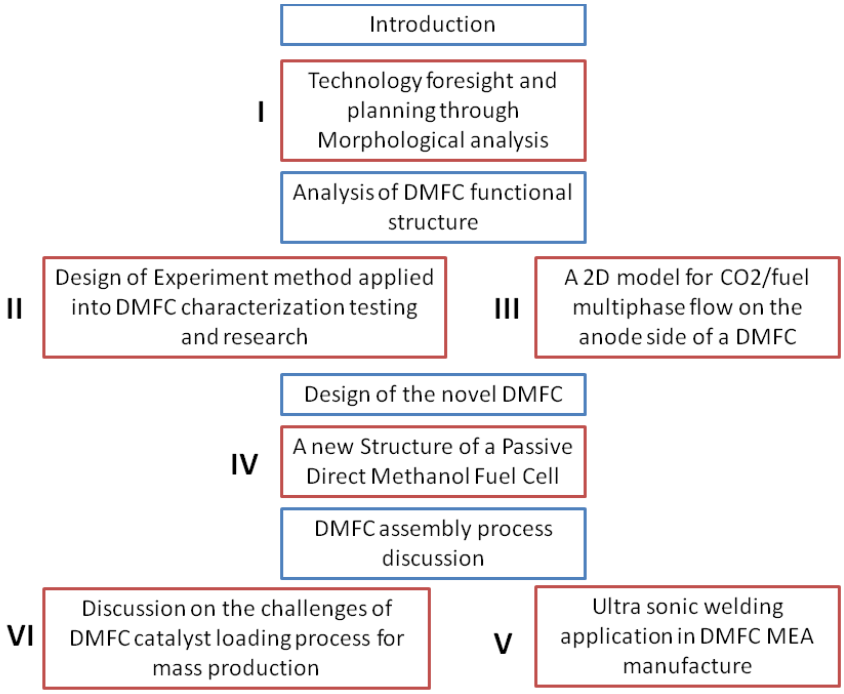

Figure 4-1: Structure of publications.

In **Figure 4-1**, the publications are shown in a logical flow. Publication I is an overall suggestion of a portable FC research direction, which is the original idea of why and where we should start our research. Publication II and III are the technical papers which analyze the DMFC function structure. Publication IV is the core paper of this research, and Publications V and VI are focused on the DMFC assembly process.

4.2. Contribution and conclusion

In this dissertation, a N-DMFC was researched to meet our goal. The N-DMFC overcomes the cost barrier, as well as saves space and weight. Compared with the conventional structure, the new structure can withstand curling to some extent. This means that the structure can be used in places where flow fields cannot be utilized, such as vaulted or camber structures. Moreover, this N-DMFC is a ready-

made product after welding. It can be used directly. No mechanical pressure is needed to push the layers together. The original analysis, new structure description, and assembly process research have been discussed herein.

Results show that, the N-DMFC works with a maximum peak power density as high as 1.52 $mW \times cm^{-2}$ reached at current densities of 9 $mA \times cm^{-2}$ at a voltage of 0.169 V. Compared with the other current passive DMFCs, the new structure demonstrates an average performance with the simplest structure. It saves cost, simplifies production, and is thinner than conventional DMFC designs.

It has been calculated that a single N-DMFC's cost is around 9 €. If it is divided by its size, the price is around 1 €/cm^2. It also means 1.61 mW/€ and 621 €/W. Even though the mass production price could be cheaper than the price in the laboratory, the cost estimation for the N-DMFC is still far away from being commercially available. The cost of the N-DMFC is mainly due to the catalyst used. It takes more than 90% of the total price. By using this N-DMFC, the price of other parts of the DMFC can be reduced to a very low price, less than 10% of the total price. It can be claimed from the cost estimation that the N-DMFC has a simple structure which saves the cost. However, more studies have to focus on improving the efficiency of the catalyst to make the system commercially available.

Experiments have been designed and operated for testing the flexibility of the DMFC manufacturing. The results were discussed, and basically, it is possible to have an automatic DMFC production line. Performance evaluations and further developments that were not done within the scope of this feasibility study need to be explored.

4.3. Future work and limitations

Even though the N-DMFC has its advantages, it is not perfect. The present aim "commercial feasibility" was not reached. The performance 621 €/W was due to problems of low power output and high crossover rate. There are several things that can be done to improve its performance.

In the future, the efficiency of the catalyst in N-DMFC has to be a more prominent problem. More studies have to focus on this aspect. In the future research, it could

be the key point to further enhances the N-DMFC performance. It has been reported that in some other research, carbonized TiO_2 nanotubes have showed over 700% increase in the catalytic activity for methanol oxidation with the same Pt/Ru load, compared to untreated nanotubes. This could be tested with the N-DMFC structure. Hopefully, it will also increase the performance of N-DMFC. For further development, a thicker membrane could be tested in order to decrease the crossover rate. Also some other membranes which we have not tested with N-DMFC should be tested, such as Nafion.

For the assembly process, more specific tests concerning ultrasonic welding quality such as the influence of welding parameters on welding results and DMFC performance should be considered. Probably a Six Sigma method could be applied into managing the manufacturing process. At last, a small-scale N-DMFC production line should also be built and tested.

The work is limited by the project time and project funding. It is also limited by the current FC catalyst research status. In the future, with development of the catalyst and FC technology, hopefully, our N-DMFC design could be a practical solution for PFC and will be available in the market.

References

Abdelkareem MA, Tsujiguchi T, and Nakagawa N. "Effect of black catalyst ionomer content on the performance of passive DMFC." Journal of Power Sources 195 (2010): 6287-6293.

Achmad F, Kamarudi SK, Daud WRW, and Majlan EH. "Passive direct methanol fuel cells next term for previous termportable electronic devices." Applied Energy 88 (2011): 1681-1689.

Agnolucci P. "Economics and market prospects of portable fuel cells." International Journal of Hydrogen Energy 32 (2007): 4319-4328.

Alexandre H. Improving and Understanding Direct Methanol Fuel Cell (DMFC) Performance. Worcester: Worcester polytechnic institute, 2005.

Ali Abdelkareem M, and Nakagawa N. "DMFC employing a porous plate for an efficient operation at high methanol concentrations." Journal of Power Sources 162 (2006).

Ascoli A, Pandya JD, and Redaelli G. "Electrical characterization of a 2.5 kW phosphoric acid fuel cell stack operating on simulated reformed biogas." Energy 14 (1989): 875-878.

Bae BC, Kho BK, Lim TH, Oh IH, Hong SA, and Ha HY. "Performance evaluation of passive DMFC single cells." Journal of Power Sources 158 (2006): 1256-1261.

Baglio V, Stassi A, Matera FV, Antonucci V, and Arico AS. "Investigation of passive DMFC mini-stacks at ambient temperature." Electrochimica Acta 54 (2009): 200-209.

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

Cheekatamarla PK, Finnerty CM, Robinson CR, Andrews SM, Brodie JA, Lu Y, and DeWald PG. "Design, integration and demonstration of a 50 W JP8/kerosene fueled portable SOFC power generator." Journal of Power Sources 193 (2009): 797-803.

Chen CY, Shiu JY, and Lee YS. "Development of a small DMFC bipolar plate stack for portable applications." Journal of Power Sources 159 (2006): 1042-1047.

Chen R, and Zhao TS. "A novel electrode architecture for passive direct methanol fuel cells." Electrochemistry Communications 9 (2007): 718-724.

Cindrella L, Kannan AM, Lin JF, Saminathan K, Ho Y, Lin CW, and Wertz J. "Gas diffusion layer for proton exchange membrane fuel cells-A review." Journal of Power sources 194 (2009): 146-160.

Coutanceau C, Koffi RK, Léger JM, Marestin K, Mercier R, Nayoze C, and Capron P. "Development of materials for mini DMFC working at room temperature for portable applications." Journal of power sources 160 (2006): 334-339.

Cowey K, Green KJ, Mepsted GO, and Reeve R. "Portable and military fuel cells." Current Opinion in Solid State and Materials Science 8 (2004): 367-371.

Dillon R, Srinivasan S, Aricò AS, and Antonucci V. "International activities in DMFC R&D: status of technologies and potential applications." Journal of Power Sources 127 (2004): 112-126.

Ding J, Liu J, and Yin GQ. "Fabrication and characterization of low-temperature SOFC stack based on GDC electrolyte membrane." Journal of Membrane Science 371 (2011): 219-225.

Dyer C. "Fuel cells for portable applications." Journal of Power Sources 106 (2002): 31-34.

Eccarius S, Krause F, Beard K, and Agert C. "Passively operated vapor-fed direct methanol fuel cells for portable applications." Journal of Power Sources 182 (2008): 565-579.

Eckfeld S, Manders JE, and Stevenson MW. "The Asian battery market—a decade of change." Journal of Power Sources 116 (2003): 32-39.

Farhad S, and Hamdullahpur F. "Conceptual design of a novel ammonia-fuelled portable solid oxide fuel cell system." Journal of Power Sources 195 (2010): 3084-3090.

Frano B. PEM Fuel Cells: Theory and Practice. Connecticut Global Fuel Cell Center, University of Connecticut, Storrs, USA: ACADEMIC PRESS, 2005.

Gandy D. Carbon Steel Handbook. Palo Altro: EPRI, 2007.

Guo Z, and Y Cao. "A passive fuel delivery system for portable direct methanol fuel cells." Journal of Power Sources 132 (2004): 86-91.

Hou HY, Wang S, Jin W, Jiang Q, Sun L, Jiang L, and Sun G. "KOH modified Nafion112 membrane for high performance alkaline direct ethanol fuel cell." International Journal of Hydrogen Energy 36 (2011): 5104-5109.

Hu MG, Sui S, Zhu X, Yu Q, Cao G, Hong X, and Tu H. "A 10 kW class PEM fuel cell stack based on the catalyst-coated membrane (CCM) method." International Journal of Hydrogen Energy 31 (2006): 1010-1018.

Jain SL, Nabae Y, Lakeman BJ, Pointon KD, and Irvine JT. "Solid state electrochemistry of direct carbon/air fuel cells." Solid State Ionics 179 (2008): 1417-1421.

Kamarudin S, Achmad F, and Daud W. "Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices." International Journal of Hydrogen Energy 34, no. 16 (2009): 6902-6916.

Kim CH, Kim KJ, and Ha MY. "Investigation of the characteristics of a stacked direct borohydride fuel cell for portable applications." Journal of Power Sources 180 (2008): 114-121.

Kuhn M, Napporn T, Meunier M, Therriault Dl, and Vengallatore S. "Fabrication and testing of coplanar single-chamber micro solid oxide fuel cells with geometrically complex electrodes." Journal of Power Sources 177 (2008): 148-153.

Kundu A, Jang JH, Gil JH, Jung CR, Lee HR, Kim SH, Ku B, and Oh YS. "Micro-fuel cells--Current development and applications." Journal of Power Sources 170 (2007): 67-78.

Lai QZ, Yin GP, Zhang J, Wang ZB, Cai KD, and Liu P. "Influence of cathode oxygen transport on the discharging time of passive DMFC." Journal of Power Sources 175 (2008): 458-463.

Lan R, Xu XX, Tao SW, and Irvine JT. "A fuel cell operating between room temperature and 250 °C based on a new phosphoric acid based composite electrolyte." Journal of Power Sources 195 (2010): 6983-6987.

Li YS, Zhao TS, and Liang ZX. "Effect of polymer binders in anode catalyst layer on performance of alkaline direct ethanol fuel cells." Journal of Power Sources 190 (2009): 223-229.

Liu BH, Li ZP, and Suda S. "Development of high-performance planar borohydride fuel cell modules for portable applications." Journal of Power Sources 175 (2008): 226-231.

Liu H, Song CJ, Zhang L, Zhang JJ, Wang HJ, and Wilkinson DP. "A review of anode catalysis in the direct methanol fuel cell." Journal of Power Sources 155 (2006): 95-110.

Liu JG, Zhao TS, Chen R, and Wong CW. "The effect of methanol concentration on the performance of a passive DMFC." Electrochemistry Communications 7 (2005): 288-294.

Liu JG, Zhao TS, Liang ZX, and Chen R. "Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cell." Journal of Power sources 153 (2006): 61-67.

Martin JJ, Qian W, Wang H, Neburchilov V, Zhang J, Wilkinson DP, and Chang Z. "Design and testing of a passive planar three-cell DMFC." Journal of Power Sources 164 (2007): 287-292.

McLean G. "Small Fuel Cells." The Knowledge Foundation's Seventh Annual International Symposium. Washington DC, USA: The Knowledge Foundation's Seventh Annual International Symposium, 2005.

Mehta V, and Cooper JS. "Review and analysis of PEM fuel cell design and manufacturing." Journal of Power Sources 114 (2003): 32-53.

Michel B, and Graham A. "Li-ion batteries and portable power source prospects for the next 5–10 years." Journal of Power Sources 136 (2004): 386-394.

Miesse CM, Jung WS, Jeong KJ, Lee JK, Lee J, Han J, Yoon SP, Nam SW, Lim TH, and Hong SA. "Direct formic acid fuel cell portable power system for the operation of a laptop computer." Journal of Power Sources 162 (2006): 532-540.

Modestov AD, Tarasevich MR, Leykin AY, and Filimonov VY. "MEA for alkaline direct ethanol fuel cell with alkali doped PBI membrane and non-platinum electrodes." Journal of Power Sources 188 (2009): 502-506.

Neburchilov V, Martin J, Wang HJ, and Zhang JJ. "A review of polymer electrolyte membranes for direct methanol fuel cells." Journal of Power sources 169 (2007): 221-238.

Oszcipok M, Zedda M, Hesselmann J, Huppmann M, Wodrich M, Junghardt M, and Hebling C. "Portable proton exchange membrane fuel-cell systems for outdoor applications." Journal of Power Sources 157 (2006): 666-673.

Oszcipok M, Zedda M, Riemann D, and Geckeler D. "Low temperature operation and influence parameters on the cold start ability of portable PEMFCs." Journal of Power Sources 154 (2006): 404-411.

Pan YH. "Advanced air-breathing direct methanol fuel cells for portable applications." Journal of Power Sources 161 (2006): 282-289.

Park YC, Kim DH, Lim S, Kim SK, Peck DH, and Jung DH. "Design of a MEA with multi-layer electrodes for high concentration methanol DMFCs." International Journal of Hydrogen, 2011.

Peighambardousta SJ, Rowshanzamir S, and Amjadi M. "Review of the proton exchange membranes for fuel cell applications." International Journal of Hydrogen Energy 35 (2010): 9349-9384.

Qian WM, Wilkinson DP, Shen J, Wang HJ, and Zhang JJ. "Architecture for portable direct liquid fuel cells." Journal of power sources 154 (2006): 202-213.

Raman RK, Prashant SK, and Shukla AK. "A 28-W portable direct borohydride-hydrogen peroxide fuel-cell stack." Journal of Power Sources 162 (2006): 1073-1076.

Rayment C, and Sherwin S. Introduction to Fuel Cell Technology. Notre Dame: University of Notre Dame, 2003.

Shewhart WA. Economic Quality Control of Manufactured Products. Bell Telephone Laboratories, 1930.

Shimizu T, Momma T, Mohamedi M, Osaka T, and Sarangapani S. "Design and fabrication of pumpless small direct methanol fuel cells for portable applications." Journal of Power Sources 137 (2004): 277-283.

Shimpalee S, Ohashi M, Van Zee JW, Ziegler C, Stoeckmann C, Sadeler C, and Hebling C. "Experimental and numerical studies of portable PEMFC stack." Electrochimica Acta 54 (2009): 2899-2911.

Sollogoub C, Guinault A, Bonnebat C, Bennjima M, Akrour L, Fauvarque JF, and Ogier L. "Formation and characterization of crosslinked membranes for alkaline fuel cells." Journal of Membrane Science 335 (2009): 37-42.

Steven D, and Pratt RJ. USA Patent US006127058A. 2000.

Sung W, and Choi JW. "A membraneless microscale fuel cell using non-noble catalysts in alkaline solution." Journal of Power Sources 172 (2007): 198-208.

Suominen A, and Tuominen A. "Analyzing the Direct Methanol Fuel Cell technology in portable applications by a historical and biliometric analysis." The Journal of Business Chemistry 7 (2010): 117-130.

Taber K, Zobel M, Schmidt H, and Hebling C. "A polymer electrolyte membrane fuel cell system for powering portable computers." Journal of Power Sources 122 (2003): 1-8.

Tang HL, Wang SL, Pan M, Jiang SP, and Ruan YZ. "Performance of direct methanol fuel cells prepared by hot-pressed MEA and catalyst-coated membrane (CCM)." Electrochimica Acta 52 (2007): 3714-3718.

Urbani F, Squadrito G, Barbera O, Giacoppo G, Passalacqua E, and Zerbinati O. "Polymer electrolyte fuel cell mini power unit for portable application." Journal of Power Sources 169 (2007): 334-337.

Wang Z, Liu Y, and Linkov V. "The influence of catalyst layer morphology on the electrochemical performance of DMFC anode." Journal of Power Sources 160 (2006): 326-333.

Ward CA, Stanga D, Pataki L, and Venter RD. "Design for the cold start-up of a man-portable fuel cell and hydrogen storage system." Journal of Power Sources 41 (1993): 335-352.

Wee J. "Which type of fuel cell is more competitive for portable application: Direct methanol fuel cells or direct borohydride fuel cells?" Journal of Power Sources 161 (2006): 1-10.

Wee JH. "Applications of proton exchange membrane fuel cell systems." Renewable and Sustainable Energy Reviews 11 (2007): 1720-1738.

Wheeler DJ. Advanced Topics in Statistical Process Control. SPC Press, Inc, 1995.

Wolf W, Arnold L, and Hubert AG. Handbook of Fuel Cells. Vol. 3. Chichester: Wiley, 2003.

Yalcinoz T, and Alam MS. "Dynamic modeling and simulation of air-breathing proton exchange membrane fuel cell." Journal of power sources 182 (2008): 168-174.

Yang CC, Lin CT, and Chiu SJ. "Preparation of the PVA/HAP composite polymer membrane for alkaline DMFC application." Desalination 233 (2008): 137-146.

Yang WM, Chou SK, and Shu C. "Effect of current-collector structure on performance of passive micro direct methanol fuel cell." Journal of power sources 164 (2007): 549-554.

Zervas PL, Tatsis A, Sarimveis H, and Markatos NC. "Development of a novel computational tool for optimizing the operation of fuel cells systems: Application for phosphoric acid fuel cells." Journal of Power Sources 185 (2008): 345-355.

Zhao TS, Chen R, Yang WW, and Xu C. "Small direct methanol fuel cells with passive supply of reactants." Journal of Power Sources 191 (2009): 185-202.

Appendix I[11]

Appleby AJ. Fuel Cell Handbook. New York: Van Reinhold Co., 1989.

Blomen L, and Michael M. Fuel Cell Systems. New York: Plenum Press, 1993.

Breeze P. Power Generation Technologies: Evaluating the Cost of Electricity. London: Financial Times Energy, 1998.

Hacker BC, and James MG. On the Shoulders of Titans: a history of Project Gemini. NASA: Washington, DC, 1977.

Kordesch K, and Günter S. Fuel Cells and Their Applications. New York: VCH, 1996.

Linden D. Handbook of Batteries and Fuel Cells. New York: McGraw-Hill, about 1984.

Lischka JR, Ludwig M and the British alkali industry. New York: Garland, 1985.

Norbeck J. Hydrogen Fuel for Surface Transportation. Warrendale, PA: Society of Automotive Engineers, about 1996.

Ostwald W. Electrochemistry: History and Theory. Translated by N. P. Date. New Delhi: Amerind for the Smithsonian Institution and the National Science Foundation, 1980.

Young GJ. Fuel Cells, 2 volumes. New York: Reinhold Publishing Corp., Vol.1 - 1959, Vol.2 - 1961). Both volumes reprint papers given at symposia in 1959 and 1961, respectively.

U.S. Department of Energy. Fuel Cells for the 21st Century: Collaboration for a Leap in Efficiency and Cost Reduction. Morgantown, WV: US DoE, 1999.

Wendel CH. The Allis-Chalmers Story. Sarasota, Florida: Crestline Publishing Co., 1988.

Alder W, Charles R and Thompson C. "Note on the Development of Voltaic Electricity by Atmospheric Oxidation of Combustible Gasses and other Substances." Proceedings of the Royal Society of London, Vol.46, 1889.

[11] This Appendix is used for Figure 1-2.

American Gas Journal. “Guide to Fuel Cell Technology", pp.29, May, 1961

Appleby AJ. “The Electrochemical Engine for Vehicles”, Scientific American, pp.74, July 1999.

Bacon FT, and Fry TM. "Review Lecture: The Development and Practical Application of Fuel Cells." Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences, Vol.334, pp.431, September, 1973

Baur E, and Preis H. Zeitschrift für Elektrochemie, Vol.43, pp.727, 1937

Baur E, and Tobler J. Zeitschrift für Elektrochemie, Vol.39, pp.169, 1933

Borchers W. "Direct production of electricity from coal and combustible gasses." Translation, Electrical Review, Vol.35, pp.887, November, 1894

Dornheim MA. "Helios breakup review." Aviation Week & Space Technology. pp.59. September, 2004

Douglas DL. “Advances in Basic Sciences: 1. Fuel Cells.” Electrical Engineering, September, 1959.

Douglas DL. and Herman A. Liebhafsky. “Fuel Cells: History, Operation and Applications.” Physics Today, pp.26, June, 1960

Dyer CK. “Replacing the Battery in Portable Electronics.” Scientific American, pp.88, July, 1999

Editor, "The Jacques Carbon Generator." The Electrical Review, Vol.38, pp.826, June, 1896

Elmore GV, and Tanner HA. "Intermediate Temperature Fuel Cells." Journal of the Electrochemical Society, 1961.

Fairley P, and Alex S. "Competing to Fuel the Fuel Cells." Chemical Week. New York, 5 May 1999.

Fellows L. "British Fuel Cell Runs a Lift Truck" The New York Times. pp.6. August, 1959

Grove WR. “On a Gas Voltaic Battery.” Proceedings of the Royal Society, pp.268-78, 346-54, 422-432, 1843

Grove WR. “On a Gaseous Voltaic Battery.” Philosophical Magazine and Journal of Science, Vol.21, pp.417-20, 1842

Grove WR. “On Voltaic Series and the Combination of Gases by Platinum.” Philosophical Magazine and Journal of Science, Vol.14, pp.127, 1839

Grove WR. “On a new Voltaic Combination.” Philosophical Magazine and Journal of Science, Vol.13, pp.430, 1838

Hunt LB. “The first fuel cell.” Platinum Metals Review, 1978

Jacoby M. "New Fuel Cells Run Directly on Methane." Chemical & Engineering News, Washington, 1999.

Ketelaar JAA. "History." Leo J. M. J. Blomen and Michael N. Mugerwa, ed. Fuel Cell Systems. New York: Plenum Press, pp.24. 1993

Kordesch KV. "25 Years of Fuel Cell Development (1951-1976)." Journal of the Electrochemical Society, pp.77, 1978

Kragh H. "Confusion and Controversy: Nineteenth-Century Theories of the Voltaic Pile." F. Bevilacqua and L. Fregonese, eds. Nuova Voltiana: Studies on Volta and his Times, Vol.1, pp.133, 2000.

Liebhafsky HA. “Fuel Cells.” International Science and Technology, pp.54, January, 1962

Liebhafsky HA, and Cairns EJ. “Hydrocarbon Fuel Cells: A Survey.” Presentation to the American Institute of Electrical Engineers 1962 Pacific Energy Conversion Conference. 12-16 August, 1962

Lloyd AC. “The Power Plant in Your Basement.” Scientific American, pp.80, July 1999

Maio P. "Driving Force." Wall Street Journal (Eastern Edition), Vol.234. pp.13 September, 1999

Mond L, and Carl L. Proceedings of the Royal Society, Vol.46, pp.296, 1889

Nixon W. "Back to the future." Amicus Journal, Vol. 21, pp.17, 1999

Ostwald W. Zeitschrift für Elektrochemie, Vol.1, pp.122, 1894

Reed CJ. "Gas Batteries." Electrical World, Vol.25, pp.419, and pp.482, 1895

Rhodin JGA. "Can the heat of combustion of coal be turned directly into electric energy?" The Engineer. Vol.142, pp.80, 1926

Service RF. "New Tigers in the Fuel Cell Tank." Science, Vol.288, pp.1955, 2000

Srinivasan S. "Fuel Cells for Extraterrestrial and Terrestrial Applications." Journal of the Electrochemical Society, pp.41c, 1989

Staff. "Cleaner and Quieter Electrical Generator Seen in Five Years" Wall Street Journal, pp.8, 1959

Warshay M, and Paul RP. The fuel cell in space: yesterday, today and tomorrow. NASA-TM-102366 E-5084 NAS 1.15:102366.

Williams KR. “Francis Thomas Bacon, 21 December 1904-24 May 1992.” Biographical Memoirs of the Fellows of the Royal Society. 1994.

W.T.C. “The Union Carbide Fuel Cell System: A Brief Description.” Union Carbide Corporation, 1966

Yaeger E. "Fuel Cells." Science. New Series, Vol.134, pp.1178, 1961

National Museum of American History, Smithsonian Institution. Fuel Cell History Project, 2011, http://americanhistory.si.edu/fuelcells/index.htm