Chapter 1

Introduction and Background

A proton exchange membrane (PEM) fuel cell is a transducer that converts chemical energy into electrical one without involving combustion. Recently, the PEM fuel cell has been considered as a major power source for future clean transportation in the effort to overcome both the worldwide energy reserve crisis and environmental pollution. PEM fuel cell systems are particularly well suited for vehicle applications since they feature compactness, light weight, high power densities and low operating temperature. Performances of the PEM fuel cell, however, are functions of its state of hydration: the proton conductivity drops when membrane becomes too dehydrated. This phenomenon is known as “*drying*”. Excessive water can hinder the way of reactant gases to catalyst. This phenomenon is known as “*flooding*”. Therefore, effective water management is essential to ensure high performance and long lifetime of the PEM fuel cell.

This thesis aimed to explore ways to deepen understanding about water dynamics in a PEM fuel cell. We will first provide a brief background on a PEM fuel cell structure and on its water problems. Then, we will review observation methods that will be implemented in this work. Next, we will describe the design for our PEM fuel cell under study that will define the scope of this work.

1.1 Proton Exchange Membrane Fuel Cell and Its Water Problem

Typical PEM fuel cell structure consists of end plates, current collectors, flow channels plates, gas diffusion layers (GDL), gaskets and membrane electrode assembly (MEA), as shown in Figure 1.1. The basis for the excellent suitability of fuel cells is found in their functional principles: conversion of energy in the fuel into

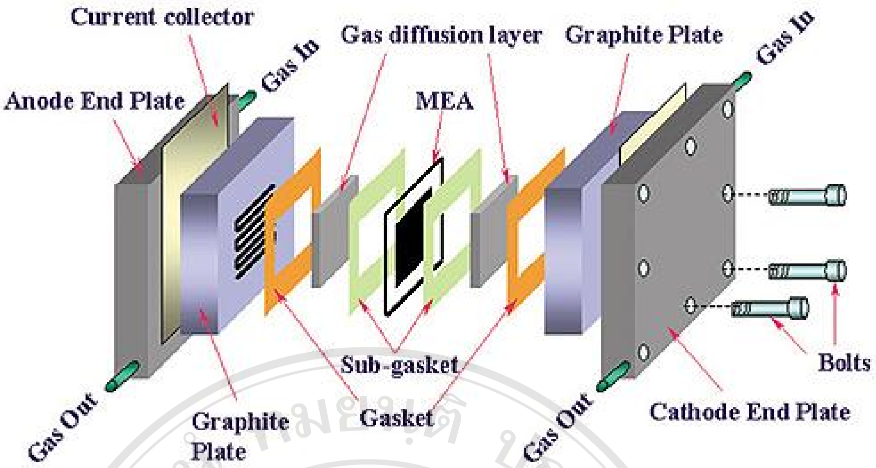

Figure 1.1: Diagram of PEM fuel cell structures [1].

electricity takes place silently, without combustion, by way of a direct electrochemical conversion. Hydrogen and oxygen react by means of a catalyst at a low temperature of about 80°C to produce only electricity and water. The PEM fuel cell uses a thin, permeable polymeric membrane as the electrolyte. Within the PEM fuel cell unit, hydrogen molecules are supplied at the anode and decomposed into its electrons and protons. The electrons are by-passed to an external circuit in order to produce electricity, while the protons cross through the membrane to the other side of the fuel cell. On the cathode, the electrons return via the cathode to re-combine with the protons, and together with the oxygen molecules to form pure water as the only reaction by-product. Pure water is formed at the cathode as a result of electric power production in the fuel cell. The polymer electrolyte membrane should be well hydrated to maintain high proton conductance and low internal resistance.

Water management is an intrinsic problem of operating PEM fuel cell. For example, when the generated water cannot be easily removed from the flow channel, it will cause flooding and prevent reactant gases to further reactions. Additionally, in order to keep MEA well-hydrated, the reactant gases usually are supplied with humidifiers. As a result, the water molecules can immigrate with proton conduction and cause drying particularly near anode. To solve the water problem, we will have to develop tools to observe water dynamics within the fuel cell, which will lead to optimization of the design and operation for PEM fuel cells.

1.2 Review of Methods for Water Dynamics Observations

Over the past few years, water formation and transport in an operating PEM fuel cell via *in situ* and *ex situ* visualization techniques are challenging phenomena to study, due to the opaque nature of traditional GDL, flow channels plate and end plate materials. Several visualization techniques [2] that have been implemented are direct optical imaging, neutron imaging, synchrotron X-ray radiography, electron microscopy and nuclear magnetic resonance (NMR) imaging. In this thesis, we explore two observation methods for our PEM fuel cell: visible and terahertz (THz) imaging. The direct visualization is the most popular observational technique for PEM fuel cells, while the THz imaging has not been reported in the literature. However, being water-sensitive, THz imaging is well worth investigated.

1.2.1 Visible Imaging

The direct optical visualization of liquid water in a transparent fuel cell has the potential to provide high resolution quantification of water distribution, but only in the flow channels. Through the visualization technique, several researchers have been carried out to investigate and compare three types of flow channels, i.e., single-serpentine, parallel and interdigitated. The study of D. Spernjak and coworkers [3] cited that in the single-serpentine channel water droplets are swept away while still small, whereas in the parallel and interdigitated channel droplets increase in number and size while adhering to the GDL and channel sidewalls. Thus, they concluded that the water accumulation in flow channel depends strongly on the flow channel design. According to the K. Sugiura and coworkers [4], cell performance with serpentine channel is better than that using a parallel channel. In previous study of the author [5], we found that serpentine flow channels with decreasing the number of bends of the channels, while keeping the active area the same, affects water accumulation drop dramatically.

1.2.2 Terahertz Imaging

"*THz band*" is an electromagnetic radiation referring to frequency 10^{12} Hz broadly from 300 GHz to 10 THz whose frequencies lie between the microwave and infrared regions of electromagnetic spectrum (see Figure 1.2). This regime has both rotational transitions from the microwave and vibration modes from the infrared. As the result of this unique location where multiple phenomena may be observed, numerous data can be extracted and interpreted. Gases will clearly present rotation transitions; liquids such as water normally have broad absorptions result to hydrogen bonding and lower-energy vibrations; and solids may either absorb broadly or have sharper-absorbing peaks due mostly to lattice phonon vibrations.

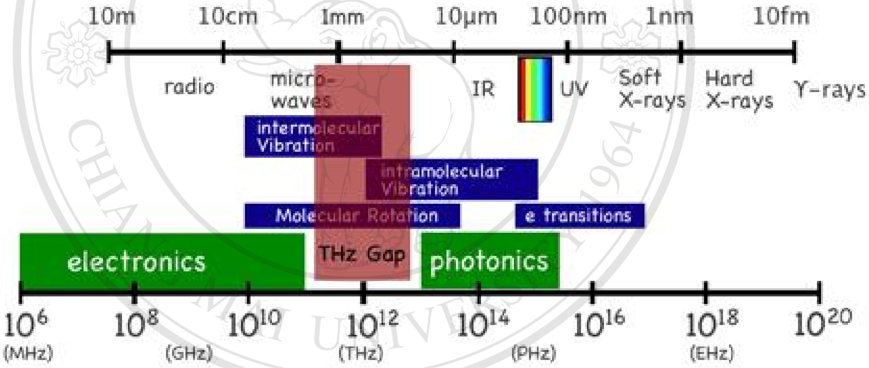

Figure 1.2: THz spectrum [6]

This band is called the "*THz gap*" as the result of the prior lack of efficient and compact THz sources and detectors. It was first detected in the 1890's by Rubens and coworkers; nevertheless, it took a long time that the first THz source was built by Auston in 1975 [7]. THz radiation has attracted increasing interest over the past twenty years because:

- The radiation is non-ionizing.
- The wavelength is shorter than microwave wavelength in order to reduce spatial resolution, while still being long enough to suffer less of the Rayleigh scattering experienced by infrared.

- THz radiation has the capability to penetrate a wide variety of non conducting materials such as clothing, papers, plastics and ceramics.
- THz radiation also is highly sensitive to the presence of polar molecules, such as water and thus hydration state, and reflected by metals.
- The universe is naturally bathed in THz radiation.

Since THz is able to penetrate many opaque materials, THz imaging is considered as a unique advantage over many other imaging systems. There are enormous applications in this field such as packaging, foam insulation, paint coating, and even security screening people. However, THz imaging typically is limited by slow capture rates and spatial resolution in the 1 mm range which is diffraction limited.

Rather than seeing the sensitivity to water as a disadvantage, one can also imagine using THz imaging to quantify the water content in biological tissue [8]. Human tissue sample is one of the most popular interest with THz imaging because of water variances in different areas and in different conditions, especially normal tissue versus cancerous tissue. Over the past few years many publications report both *in vivo* and *in vitro* methods of characterizing cancerous tissue. This idea of using THz radiation to investigation cancerous tissue was first proposed in 1997. In general, the absorption coefficient and refraction index of cancerous tissue at THz frequencies are higher than those of normal tissue. This may be considered for by higher water content in cancerous tissue and structure changing such as increased cell and protein density [9]. Figure 1.3 compares THz images between a fresh leaf and a dry leaf. The leaf on the left had been freshly cut and contained an abundance of water throughout. After being left to dry, however, much of the water evaporated with traces remaining in the stems. Water is one important material in imaging because its presence or absence severely affects both the material investigated and resulting THz image.

Figure 1.3: THz image of fresh leaf (left) and dry leaf (right) [10]

One can also imagine using THz imaging to quantify the water content in PEM fuel cells.

1.3 Proton Exchange Membrane Fuel Cell Design

In Reference [6], it has been shown that liquid in the channels is more efficiently removed by few U-turns serpentine structure than by many U-turns serpentine structure. Therefore, we design a new version of fuel cell based on this conclusion.

The PEM fuel cell for this study must allow visible and THz light to probe the flow channels. From outer to inner layers, as seen in Figure 1.4, our PEM fuel cell consists of end plates, flow channels plates and MEA. The end plates provide structure rigidity. The MEA is where the electrochemical reaction occurs. The flow channels plate of PEM fuel cell is typically made of graphite, which is machined into channel pattern that allows water and reactants to flow in and out.

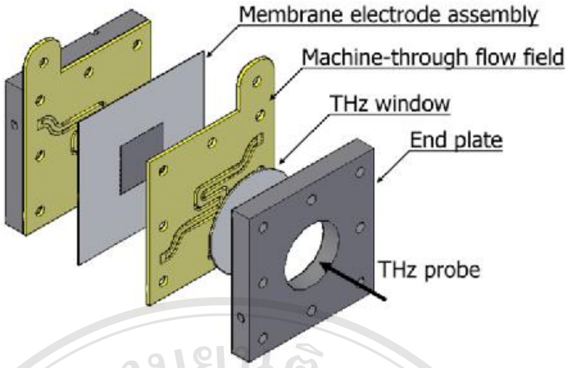

Figure 1.4: PEM fuel cell components designed with machine-through flow channel made of nickel-coated brass enclosed with THz window.

For a single cell, only one surface of the graphite is machined (called dead-end flow channel plate). Unfortunately, the dead-end flow channels plate made of graphite is not transparent to THz. As graphite is too brittle for machining through, we instead chose brass for our machine-through flow channel with 2 mm in width and 2 mm in depth. On a one side of the cell, we insert a THz window and cut a circular opening on the end plate. For the THz window, we have two candidates: one is a poly-methyl-methacrylate (PMMA) window and the other is a silicon (Si) window. Both window materials are transparent to be more specified in THz region. This PMMA material also has the advantage of being optically transparent. This allows us to visually confirm some aspects of the THz images. Si in particular has been reported to be used as a window in reflective far infrared fourier transform spectroscopy of water [11]. It is often used as a window material for THz spectroscopy of liquid samples due to its high reflectivity in this spectral regime [12].

Table 1.1 presents the detailed dimensions of our transparent PEM fuel cell. We reduce the number of bend by using two-serpentine type channel. In addition, the flow channels were directly machined into a brass plate and covered with a nickel coating. The Nafion® membrane and the carbon cloth including Pt 5 mg/cm^2 were used for the MEA. This PEM fuel cell must operate in conditions as close as possible to those prevailing in practice (especially in term of current density, gas hydration and stoichiometry).

Table 1.1: Dimensions for the transparent PEM fuel cell.

Parameter	Values
Flow channel	
Number of channel	2
Number of U-turn	2
Channel width, mm	2
Land width, mm	2
Channel depth, mm	2
Channel length, cm	7.8
Cell active area, cm^2	6.25

1.4 Scope of Thesis

Since flooding causes a threat for developing high efficiency in the PEM fuel cell, observation tools to study water management must be established. The purpose of this work is to explore a novel terahertz imaging to study water distribution in fuel cell. Intensive study also includes PEM fuel cell design that takes account the THz limitations, and visible imaging means for observing water into PEM fuel cell under operation. Since THz imaging is rather new, we will provide theoretical framework to support the application of THz measurement of water in the PEM fuel cell in Chapter 2. Chapter 3 contains the visible imaging technique setup that is applied to measurement of *in situ* fuel cell and visible image of PEM fuel cell, together with its conclusion. As point out about the complicate PEM fuel cell structure in section 2.3, the sample that was used for THz imaging is a simple model cell that consists only of flow channel plate and THz window. Both THz experimental setup and the results of *ex situ* THz imaging of PEM fuel cell are presented in Chapter 4. It also presents the result of the improvement the spatial resolution by using terahertz optics. Finally, conclusions and future work are discussed in chapter 5.