Development of Electrolyte Support for Intermediate Temperature Molten Salt Fuel Cell

By

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Abstract

Fuel cells are one of the most promising clean energy technologies under development. But a constraining factor in their further development is related to operating temperature ranges of current fuel cell systems, which is either low or high temperature. The intermediate temperature (200 ℃ to 600 °C) would be the most desirable temperature range for a fuel cell for most applications, but there is no existing mature fuel cell technology in this range, mainly because of an absence of appropriate electrolytes. An effort to develop an intermediate-temperature molten-salt electrolyte fuel cell (IT-MSFC) was undertaken in this study.

As a start, molten KOH was used as an electrolyte around 200 °C supported on a porous matrix. Tests used Pt loaded carbon cloth to be the electrode-catalyst layer, hydrogen and oxygen as fuel. The major challenge for this fuel cell was to hold electrolyte within a suitable porous support layer, without crossover of fuel gas during operation. Performance was short-lived, thus several ceramic materials were investigated in this research, including Zirconia felt, Zirconia disk, and porous NiO. To evaluate the properties of KOH molten salts working for IT-MSFCs, the performances were compared to fuel cell tests with KOH saturated solution and phosphoric acid with the same electrolyte support. KOH molten salt has large potential to work as electrolyte, with an open circuit voltage (OCV) of 1.0 V, and had linear performance curve between 1.0 V and 0.6 V, which is characteristic of fuel cells with low kinetic overpotentials. The highest performance was got by using porous NiO support in certain porosity range. Longevity of the fuel cell was a little better than the former, but still far from practical application.

The result suggested that the capillarity, permeability and compatibility of support material are essential for performance of this type of fuel cell. Besides the problem of electrolyte

retention by the support matrix, unsuitable water management, degradation of the gas diffusion layer and catalyst may also reduce the fuel cell performance. Although this work is at a preliminary stage, it has demonstrated the immense potential of IT-MSFC, and a great deal of additional work will be required to produce a practical fuel cell.

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Table of Contents

List of Figures:

List of Tables:

Chapter 1

Background and Motivation

1.1 Fuel cell back ground

Fuel cells are energy conversion devices which convert the energy of chemical reactions directly into electrical energy and heat with high efficiency. Compared to conventional electric power generating systems, fuel cell has many unparalleled advantages; therefore it was received more and more attention since the end of nineteenth century.

One of the major advantages is that the fuel cells can utilize a variety of fuels to generate power, such as hydrogen, natural gas, methanol, biomass-derived materials, and various complex hydrocarbons. It helps to reduce our reliance on fossil fuel, which is absolutely necessary for conventional power generation, as it is a limited in supply. In addition, fuel cells produce zero or near-zero toxic emissions and lower greenhouse gas emissions. Using hydrogen as the fuel, only water would be created. Although a very small quantity of NOx, SOx, CO, and CO_2 may be mixed in effluent gas result from the processing of hydrocarbon fuels into hydrogen, it is significantly lower than the emissions produced by conventional technologies.

Secondly, fuel cells have large potential for high operation efficiencies, because they convert chemical energy directly into electrical energy for which the efficiencies are not limited by the Carnot limit. Unlike the centralized thermal power generation requiring high voltage transmission wire to distribute electricity, fuel cell offer safe distributed energy generation and fast startup where it is needed, without the energy loss from the large transmission system over long distance.

Besides, the fuel cells are very scalable, which can be configured to suit a wide range of capacity, from a few watts to megawatts. Because their efficiencies are not a strong function of their operation power, they can be widely used for power supply, including portable devices, heating production, transport vehicles, or even large power plants [1, 2].

Finally, fuel cells have no moving parts during operation. It reduces the maintenance requirements and makes they work reliably with less noise.

1.2 Why intermediate temperature

Generally speaking, current fuel cells work either in the low temperature range (<200˚C), such as proton-exchange membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), phosphoric acid fuel cells (PAFC), and alkaline fuel cells (AFC) , or in the high temperature range (600˚C - 1000 ℃), such as solid oxide fuel cells (SOFC), and molten carbonate fuel cells (MCFCs). Right now, there is no mature technique for fuel cells to operate in the temperature range between 200 °C and 600 °C, because of the lack of suitable electrolytes for intermediate temperature.

However, the intermediate temperature would be the most desirable temperature range for a fuel cell for most applications, because some lingering limitations for fuel cells development are directly related to their operating temperature.

Firstly, the cost-effective catalyst is desirable for every fuel cells system. Since the pure hydrogen production, storage and delivery technology have always be an challenges for fuel cell development; if the hydrogen supply is not pure enough or fuels other than pure hydrogen are used, then the fuel cell performance is poorer and will gradually decrease over time due to catalyst degradation and electrolyte poisoning. Expensive platinum usually is the first alternative to be used as the catalyst for its high catalytic activity, especially for fuel cells those work in low temperature below 300 ℃. In contrast, nickel is a non-precious metal, is relatively inexpensive and abundant, but can be used as catalyst only if the operation temperature higher than 300 ℃ [5].

Secondly, in low temperature case, trace CO in hydrogen feed can easily poison the platinum catalyst; and significantly reduce the fuel cell performance, due to the strong adsorption of CO on Pt electro-catalysts [6]. Fortunately, the chemical binding of CO to Pt is strongly exothermic, therefore simply increasing the temperature dramatically improves CO tolerance from 10-20 ppm of CO at 80 ℃, to 1000 ppm at 130 ℃, and up to 30 000 ppm at 200 ℃ still with acceptable performance in PBI-based PEMFC [7]. This high CO tolerance offer cost advantages for hydrogen production and reduce requirements for the CO cleanup in fuel processing system. Otherwise extra steps in feed preparation are demanded by the high-purity hydrogen supply for low temperature fuel cell, because CO is the common byproduct coming from most of the processes of producing hydrogen from hydrocarbons or biofuels. There are some mature technologies that have been applied in this area. For example, more than one water gas shift reactors will be required to convert water and CO to CO_2 and hydrogen. Preferential oxidations as well as the electro-catalytic preferential oxidation by nano-particle catalysts are widely used [3]. Besides, membrane separators such as Pd-based composite membranes also have been used for hydrogen purification [4]. But any of these extra steps in feed preparation greatly increase the cost and complexity of fuel cell systems.

Thirdly, for low temperature fuel cell such as PEMFC, the overall electrochemical kinetics is determined by the slow oxygen reduction reaction (ORR). The overpotential at cathode accounts for the major voltage loss of PEMFC. In the intermediate temperature range, the reaction kinetics of hydrogen oxidation and ORR will be enhanced naturally, and the overpotential is no longer significant.

On the other hand, the high operating temperature of fuel cells that work over 600 ℃ leads to limitation of material issues. Sealing material used for intermediate temperature and low temperature fuel cell are no longer suitable for high temperature range. Brittleness need to be considered in material selection for internal components [8]. Differences in thermal expansion coefficients bring serious problems, which require expensive high temperature alloys to replace the mild steel for high temperature fuel cell stacks.

Last, but not the least, the high temperature requires bulky insulation as well as a correspondingly long period of pre-heating. For that reason, such fuel cells would better to be employed in situations where they continuously operate – particularly providing energy for buildings.

In short, the fuel cell which operates in an intermediate temperature range would circumvent most of these above-mentioned problems and bring a dramatic change in this field. The complexity and efficiency issues discussed above are shown schematically in Figure 1-1[9].

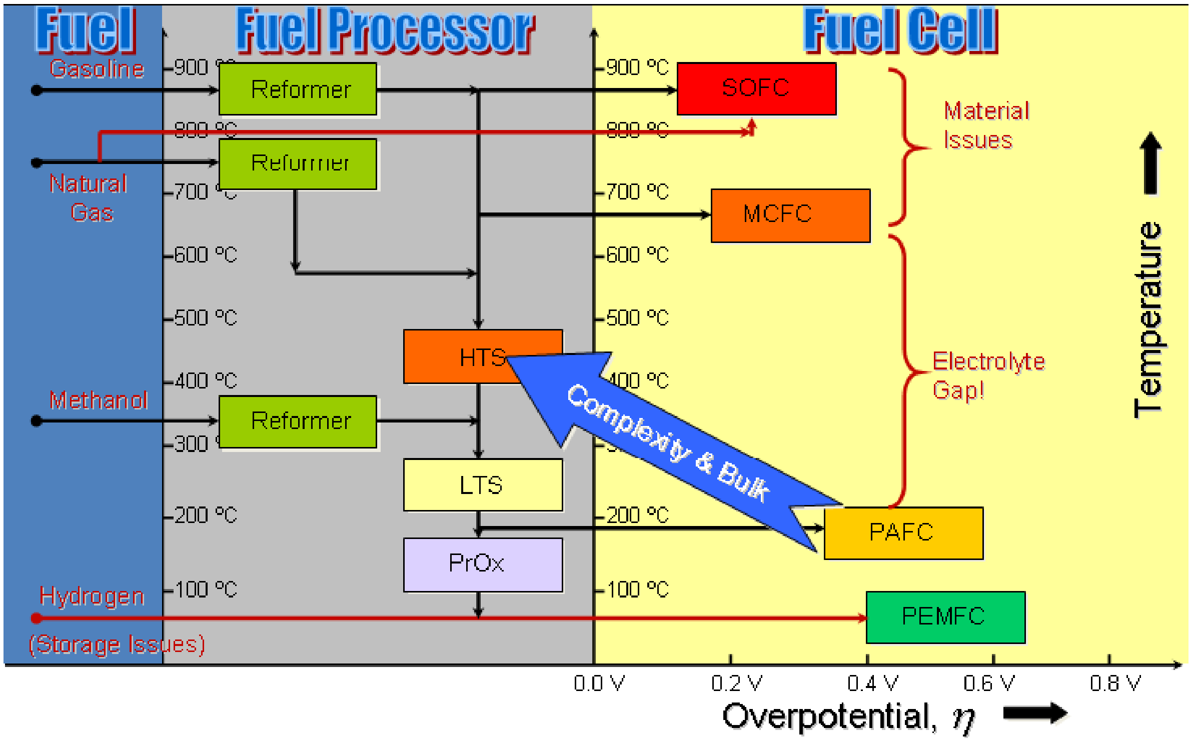


Figure 1-1: A diagrammatic representation of the temperature regimes of existing fuel cell technologies, and the associated fuel processing technologies used to produce fuel for them, as well as the overpotentials associated with the electrochemical reactions at the operating temperatures

1.3 Why molten salts

The electrolyte is the heart of any fuel cell. One of the key impediments to the development of fuel cell in the intermediate temperature range is a lack of suitable and practical electrolyte. Ideally, the component effectively separates the anode and cathode gas feeds and mediates the electrochemical reaction occurring at the electrodes through conducting a specific ion at very high rates. The transport through such electrolytes should be fast and highly selective during the operation of the fuel cell. This combination of properties limits choices of practical electrolytes.

There has been a lot work about conductive ceramic electrolytes for medium high temperature range, employing either proton or oxyanions solid-phase conduction. The conductivities however decrease dramatically when the temperature below 500 ℃, since the large activation energy of activated solid-phase ion diffusion, which suggest that these solid electrolytes could not work efficient in most of the intermediate temperature range [10, 11]. On the other hand, the liquid electrolyte supported by an inert matrix is another option for fuel cell, which has been demonstrated in PAFC, AKC and MCFC. But, the superiority of high conductivity is restrained in the intermediate temperature range either by volatility of the components in concentrated liquid electrolytes or the high melting temperatures required for conductivity.

Molten salts, however, could meet the general requirements of an intermediate fuel cell electrolyte for their high conductivity and the low volatility. And indeed, there is no other obvious option for a liquid electrolyte in this temperature range, except perhaps for ionic liquids. Since molten salts by nature have very high concentrations of ions, and they are generally not electronically conductive, they would be perfect ion conductors. Because of the strong interaction between the positive and negative ions, most of these have very low saturation vapor pressure and high boiling points.

In addition, their physical properties like viscosity and surface tension are similar in magnitude, thus the different combinations of molten salts could enlarge the liquidus range as well as the operation ranges, meanwhile, it offer a wide array of parameters which can be changed to adjust the performance and operating characteristics of the fuel cell [10]. Furthermore, the strong intermolecular forces make them to be extraordinary solvents, dissolving a wide scope of substances, such as homogeneous and heterogeneous catalyst, gases, water, even metals. It was suggested that the molten salts may directly use the homogeneous or even heterogeneous catalysts by simply dispersing them in fuel cells, as first demonstrated by Malhotra and Datta [12]. So there is no need for additional catalyst layers, which avoid many problems coming with them.

In recent decades, efforts have been made to find suitable molten salt electrolyte, which can work for intermediate temperature fuel cell. From the late1970s to the early1980s, Pier Giorgio Zambonin and his research group made thorough analysis of the chemical and electrochemical properties of alkali nitrates and nitrites, and their interactions with hydrogen and oxygen, trying to ascertain their potential use as electrolytes in a fuel cell. They demonstrated the voltammetric behavior of (Pt) H_2O/H_2, OH^- [10] system and (Pt) H_2O, CO_2/H_2, CO_3^{2-} [13] system in molten alkali nitrates. It was found that hydrogen would react with the nitrate in a nitrate melt [13-18] through the reaction $H_2+NO_3^- \leftrightarrow H_2O + NO_2^-$, and the reaction rate increased sharply along with the temperature rise above 653K. It was a relatively slow reaction process, except with the temperature rise. On the other hand, nitrite also could react with oxygen [15] through the reaction $\frac{1}{2}O_2+NO_2^- \leftrightarrow NO_3^-$, which was catalyzed strongly by the presence of superoxide ions. The reaction of oxygen with nitrite and a further investigation proved that. The results demonstrated that these reactions were indeed those which play a primary role in ionic solvents, but they didn’t build an actual fuel cell with acceptable performance. Further the nitrate melt was incompatible with the nickel catalyst for its strongly oxidizing nature. During operation, the nitrate oxidized nickel to nickel oxide which formed a solid layer on the surface of the electrode, leading to large irreversibility.

Dr. Prodyot Roy invented a novel H_2/O_2 fuel cell -- Molten Hydride Fuel Cell (MHFC) in 1990’s, which operate at 350 – 450 ℃ [19]. A solution of 10 wt % LiH in the KCl + LiCl eutectic becomes a pure hydride ion conductor act as electrolyte, while Pd-

Ag, beta-Ti and iron membrane were selected for membrane electrode. Hydrogen gas dissociates and the hydrogen atom diffuses through the cathode membrane, where hydride ion forms from hydrogen atom, and migrates through the electrolyte to the anode. Liquid lithium instead of oxygen could be used on the positive electrode to determine the discharge characteristics (voltage vs. current) of single cells under load. It was demonstrated that replacing iron with Pd alloy increased the current output up to 500 mA at 310mV, since the permeability of hydrogen through Pd-Ag is several orders of magnitude higher than iron. It indicated that the diffusion of hydrogen through the electrode membranes is the rate-controlling step for the operation of the fuel cell.

Over the past decade, a reach group led by Zhu bin in Sweden has been making a deep study about the proton conducting salts which might be able to work for intermediate temperature fuel cell (250-700℃). A large number of salts and their composites have been investigated as regards proton conductivity from both fundamental and applied aspects. They proposed the concept of molten salt oxide composites which was a two-phase composite -- there was at least one molten state for the mobile ion species within a rigid lattice framework, which was so-called average structure. The composites of salt–oxide, based on fluorides, hydrides, nitrates, sulphate and chloride-hydroxides were attempted to be used as the solid-like electrolytes with a promising outcome [20-23]. Moreover, they found that by selecting different second phase oxides, and compositions, molten salt oxide composites electrolytes had great flexibility to improve their properties for specific goals and modify their compatibility with other cell components, e.g. anode and cathode [21, 23]. The best two phase composite salts were found for gadolinia doped ceria-salt composites (GDC)-CSCs and samaria doped ceria

(SDC)-MCO_3 (M=Li, Na, K, single or mixture of carbonates) [23]. They reached power densities as high as 300-800 mW cm^{-2} at the med high temperature around 600 ℃. Although the operating temperature was higher than expected, they found addition of CaH_2 doped ceria enhanced the performance resulted from its conversion to the hydroxide [24].

In 2001, a carbon-air fuel cell using mixture molten hydroxide electrolyte was reported in a US patent [25]. They reported the use of renewable biomass (charcoal) as a source of the carbon fuel and operated at temperature varied with different combination of hydroxide electrolytes from 100 to 400 ℃. The average power output achieved was $40mW/cm^2$ at $140mA/cm^2$ over 540 h, and maximal current density achieved was greater than $250mA/cm^2$. They proposed that the ohmic control was mainly due to large electrode spacing in the carbon-air fuel cell design, while the mass transfer control is most likely due to slow oxygen diffusion to the electrode surface, which meant the performances could be substantially improved by reducing electrode spacing and increasing the cathode surface [27].

Jason C. Ganley and his group recently demonstrated that a direct ammonia/oxygen fuel cell will function at intermediate temperatures range [26]. They used a KOH–NaOH eutectic mixture to be the electrolyte and investigated the use of nickel catalysts with molten alkali. It produced approximately 50 mW cm^{-2} of power and 0.8 volts of the open circuit potential at 450 ℃ operating on a stream of pure ammonia fed to the anode and compressed ambient air fed to the cathode. These results show that molten alkali hydroxides appear to be promising electrolytes within the intermediate temperature range.

More recently, Spence M. Konde [9] has demonstrated the initial feasibility for an intermediate temperature molten salt fuel cell (IT-MSFC). He utilized Alkali hydroxide molten salts as the electrolyte. Both hydrogen and methanol acting as fuel has been investigated at temperature 200℃. Hydrogen showed better performance, up to 950mA/cm^2 at 0.4V. However, longevity of the fuel cell was very poor, though a number of experiments were undertaken to improve it, enabling extension of operating life from 5 minutes to 30 minutes, which is still far too low for practical use. The key problem was identified as the lack of electrolyte retention by the support matrix and possible degradation of the gas diffusion layer and catalyst.

All of these former works show a great potential for molten salt fuel cells operating in the intermediate temperature range. Even though these studies indicate promising results on molten salt fuel cells, there are a wide variety of unexplored possible systems that need to be investigated.

1.4 Design Goals for IT-MSFCs

The major object of this work was trying to extend the longevity of fuel cells developed by Konde [9] with an acceptable performance. Research has been conducted using alkali molten salts to be the electrolyte. Results were compared with those using alkali or acid solution as electrolyte.

To modify the electrolyte retention situation by the support matrix, three different porous materials were investigated separately under same test conditions. Around the problem of permeability and capillarity, this work would compare those results; discuss the properties of material by nature and the desirable porous structures. Research details are as follows:

1. Feasibility study of IT-MSFC using zirconia felt using different electrolytes, including the saturated KOH solution, saturated phosphoric acid solution, and KOH molten salt.

2. Zirconia disk based IT-MSFC using different electrolyte. The same electrolytes will be used in tests.

3. IT-MSFC with nickel oxide based electrolyte layer. Their inner porous structure can be changed to a certain degree via thermal oxidation. Effort has been made to find the optimal heating-up time and temperature history.

Chapter 2

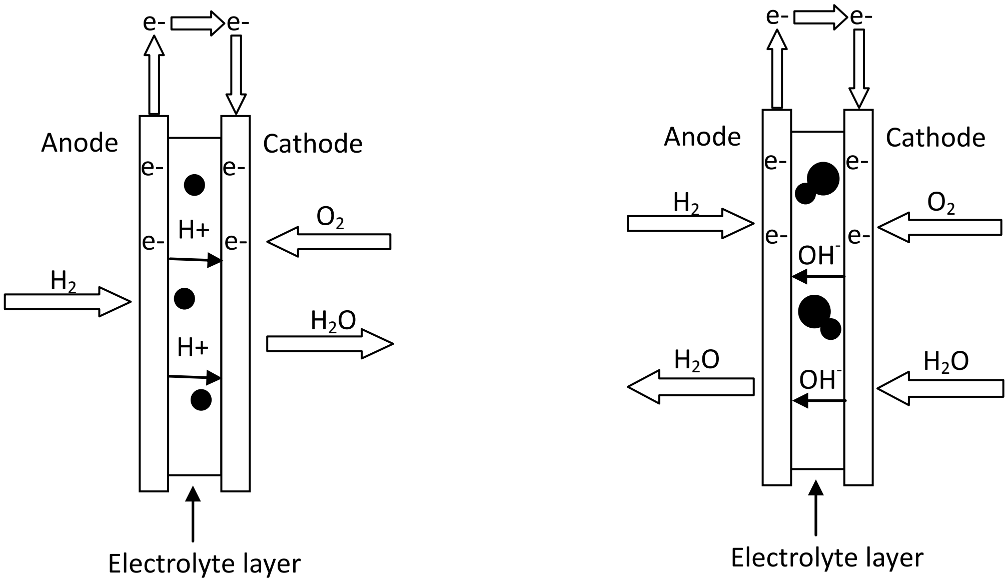
Design of Intermediate Temperature Molten-salt Fuel Cells

2.1 General design of intermediate temperature molten salt fuel cell system

Generally speaking, the physical structure of a typical fuel cell consists of an electrolyte layer (the ionic conductor) in contact with two or more electrodes. In the simplest case, a fuel cell contains two electrodes: porous anode and cathode, on either side of the electrolyte layer.

More specifically, each intermediate-temperature molten-salt fuel cell (IT-MSFC) would contain a so-called supported electrolyte layer, where the molten salt would be supported by a porous matrix. The melting point of the molten electrolyte would be just below the operation temperature range, and the porous support structure should be inert and steady. On each side of the electrolyte layer, there is an electrode layer consisting of a current collector and a catalyst layer. There may be an additional gas diffusion layer (GDL) between the electrode and the bipolar plates. But the current collector would most likely double as a GDL in existing fuel cells.

During operation, the electrode reaction will occur at a three-phase interface, between the catalyst, the electrolyte, and the gas phase on both side of fuel cell. Fuels are fed continuously to the anode (the negative electrode), where anodic electrochemical reaction take place, producing electrons carried from anode to the cathode over external circuit. On the other side, the oxidants are fed continuously to the cathode (the positive electrode), where the electrons are absorbed to reduce oxidizing agent. The anion would be generated at cathode, while proton or cation produced at anode. Charge carriers would be one of the products of the catalytic electrode reaction, and there are several options for the diffusing charge carrier depending on the choice of electrolytes, which also determine the nature of the electrode chemistry.



Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Anode: $2OH^- + H_2 \rightarrow 2H_2O + 2e^-$

Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow 2\,OH^-$

Figure 2-1: Schematic of an IT-MSFC, using a proton or hydroxide conducting electrolyte, showing the anode and cathode reactions.

As showed in the Figure 2-1, in the case of action-exchange electrolyte, usually is acid electrolyte, protons produced always exist in the form of the species $H^+ \cdot nH_2O$, and migrate toward the cathode [28]. The electrode reactions also can be written as:

At the hydrogen anode: $2H_2 + 4nH_2O \rightarrow 4H^+ \cdot nH_2O + 4e^-$ (1)

At the oxygen cathode: $O_2 + 4H^+ \cdot nH_2O + 4e^- \rightarrow (n+2)\,H_2O$ (2)

On the other hand, in base, hydroxide ions (OH^-) generated from O_2 and H_2O at cathode act as a "carrier ion", diffusing toward anode through alkali molten-salt electrolyte.

The direct mixing of the reactants in fuel cell is undesirable because it produce thermal energy, reducing the production of electrical energy. Therefore, an electronically insulating porous separator holding electrolyte between the anode and cathode used to be impervious to reactants. As a result, the electrolyte supports current transport by ions, and electrons are carried from anode to the cathode over external circuit.

The most important part in the design of an IT-MSFC is the three-phase interface, between the catalyst, the electrolyte, and the gas phase. Since gaseous fuel, the solid catalyst, and electrolyte must all make contact, which makes the three parts: the molten salt electrolyte, the porous electrolyte support, and the catalyst-GDL layer closely interrelated. Based on results of Spence's work [9], the inner structure of the porous electrolyte support plays a significant part in good performance. To improve the compatibility and retention of electrolyte in porous matrix, different material and fabrication techniques will be tested.

2.1.1 Fuel cell reversible potential and net output voltage

The maximum potential difference between the cathode and anode are achieved when the fuel cell is operated under the thermodynamically reversible condition. This maximum possible cell potential is the reversible cell potential. The net output voltage of a fuel cell at a certain current density is the reversible cell potential minus the irreversible potential which can be written as:

$$V(i) = V_{rev} - V_{irrev} \tag{3}$$

Where V_{rev} is the standard reversible potential of fuel cell, and V_{irrev} is the irreversible voltage loss which is so-called overpotential occurring at the cell.

These irreversible voltage losses are the activation overpotential (v_{act}), ohmic overpotential (v_{ohmic}), and concentration overpotential (v_{conc}). It can be written as:

$$V_{irrev} = v_{act} + v_{ohmic} + v_{conc} \tag{4}$$

Therefore:

$$V(i) = V_{rev} - v_{act\_anode} - v_{act\_cath} - v_{ohmic} - v_{conc\_anode} - v_{conc\_cath} \tag{5}$$

As showed in the above equation, activation and concentration polarization occurs at both the anode and cathode, while the resistive polarization represents ohmic losses throughout the fuel cell [2].

Activation polarization is the voltage overpotential required to overcome the activation energy of the electrochemical reaction on the catalytic surface. It dominates losses at high current density, and measure the catalyst effectiveness at a given temperature. The ohmic polarization is typically dominated by electrolyte conductivity, which is primarily a function temperature. One of the most effective methods of reducing ohmic loss is to use better ionic conductor for electrolyte layer, or a thinner electrolyte layer because the electrolyte component of a fuel cell dominates the ohmic losses. The concentration polarization is resulted from the less reactant concentration in GDL than it supplied in flow channels. It is related to the effective mass diffusion coefficient for porous electrode layer, electrode layer thickness, and current density. The higher the current density, the worse the concentration losses will be. These losses can be improved if the diffusion layer thickness is reduced, or effective diffusivity is increased.

2.2 Electrolyte

Electrolyte layer is the key part for IT-MSFCs consisting of two sub-parts: inert porous support and electrolyte. Molten salts meet the general requirements of an intermediate fuel cell electrolyte because of their high conductivity and the low volatility. The conductivity of the electrolyte is the key for high performance in any sort of fuel cell. The conductivity, σ, is given by:

$$\sigma = \frac{F^2}{RT}\sum_i z_i^2 C_i D_i \qquad (6)$$

Where F is the faraday constant, R is the gas constant and T is the temperature. For each diffusing species, z is the charge number, C is the concentration, and D is the diffusion coefficient [9]. Besides high conductivity and low volatility, ideal electrolyte should have melting point below the operating temperature range, and it should be low electronic conductivity and chemically stable. Besides, it should be compatible with the support material, preferably low-cost.

In H_2/O_2 fuel cell, the possible ionic species could be H^+, H^-, OH^-, and O_2^-. Besides, these charge carriers plus a carrier molecule may simply generate some anionic or cationic species, such as H_3O^+, NH_4^+, HPO_4^{2-}, CO_3^{2-}, NO^{3-}, and ClO_4^-, which act as the diffusing species in electrolyte. Some electrolyte that has been used in fuel cell technology could be considered [28, 29].

The molten oxide fuel cell would not be considered possible in this temperature range, because the melting points of oxides including the composites are almost universally very high. Also, in the case of a proton conducting fuel cell, some sort of acid salt, such as an acid phosphate or sulfate, have been demonstrated in the past work often aqueous-based. But due to their corrosion problem, only metals of platinum group can be used as catalysts for the electrode reaction.

On the other hand, in fuel cells using alkaline electrolyte, catalysts may be selected advantageously from a much wider range of materials, some of them relatively inexpensive. The aqueous solutions of alkali hydroxides are already widely used in AFC, and the mechanism of oxygen reduction in molten NaOH and KOH has been demonstrated [26, 30].

As an example, alkaline hydrazine fuel cell using hydrazine with alkaline electrolyte has been conducted since 2003. The electrode reactions can be written as:

Anode: $N_2H_4+4OH^- \rightarrow N_2+4H_2O+4e^-$ $E^0= -1.22V$ (7)

Cathode: $O_2+2H_2O+4e^- \rightarrow 4OH^-$ $E^0= 0.40V$ (8)

Overall: $O_2+N_2H_4 \rightarrow N_2+2H_2O$ $Er=1.62V$ (9)

Since hydrazine is toxic, and its high price, it is difficult to use widely, so it has been used only in special cases.

Molten hydroxides electrolytes offer advantages over acidic electrolytes. Firstly, oxygen reduction is considerably faster, which suggests that the working potential of the cathode electrode is more positive and larger cell voltage can be realized. In addition, apart from the advantages in catalyst selection, less severe corrosion conditions allow nickel and alloy of iron to be used as structural material in IT-MSFCs. Besides they have good mutual solubility, the electrolyte could be eutectic mixture rather than the unitary component electrolyte. The mixture of a salt containing the ion which is needed by carriers, and another salt can serves as solvent. And their melting point is still in the target temperature.

KOH, NaOH molten salts, and KOH–NaOH eutectic mixture have been used in the past [31]. All of them have suitable melting points and very high conductivity, over 1S/cm. It has been shown that KOH provides better performance than the others [9], therefore KOH molten salt will be studied in this research. The electrode reactions in alkaline electrolyte can be written as [2]:

At the hydrogen anode: $2H_2+4OH^- \rightarrow 2H_2O+4e^-$ $E^0= -0.828V$ (10)

At the oxygen cathode: $O_2+4H_2O+4e^- \rightarrow 4OH^-$ $E^0= 0.40V$ (11)

Overall: $O_2+2H_2 \rightarrow 2H_2O$ $Er=1.228V$ (12)

To compare the properties of molten hydroxides electrolytes with those of traditional electrolyte, parallel study has been conducted on alkaline solution and phosphoric acid.

2.3 Porous support layer

The ideal porous support layer would be low conductivity, and would be chemically and mechanically stable. Besides, it should be readily wet by the electrolyte, which is important, since electrolyte retention is closely related to the material compatibility and permeability. Further, it should be easy to manufacture and preferably low-cost.

2.3.1 Capillarity

Ideally, the capillary force makes the contribution of the material in retaining the electrolyte within the porous matrix, provided electrolyte can wet the support material. This relation can be expressed in terms of the contact angle, θ. This is the angle made between the surface of the liquid in a pore, and the wall of the pore. A contact angle less than 90 ℃ means the support material is readily wet by the liquid; while if the liquid does not like the support material surface, it will have a greater contact angle. Obviously, the support material with a contact angle less than 90 ℃ is required in this case.

If the liquid likes the surface, the electrolyte can be held by the capillary pressure within the porous structure. In contrast, if the contact angle is larger than 90 ℃, the capillary force actually helps to push the liquid out of the porous support. As a result of the surface interactions, the pressure in the liquid-filled pore is actually lower than external part, in the case of good material compatibility. In order to maximize the electrolyte retention, a large, negative pressure difference is desirable. This pressure serves to counteract pressure differentials and other forces which might act to push the electrolyte out of the porous support.

The pressure difference between the liquid and the gas over the curved gas-liquid interface is given by the Young-Laplace equation, which is the central equation describing capillary action [32]:

$$\Delta P = \frac{2\gamma \cos\theta}{r} \tag{13}$$

Where γ is the surface tension of the gas-liquid interface, θ is the contact angle between the liquid and the pore wall, and γ is the radius of the pore.

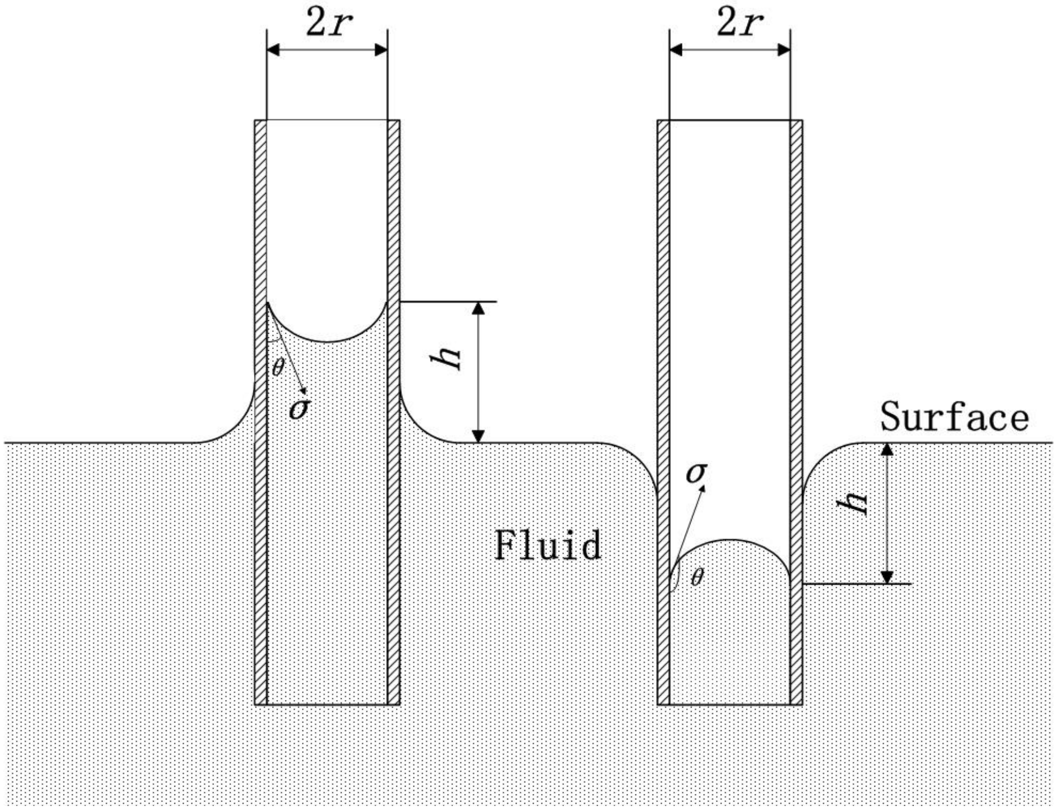


Figure 2-2: Definition of contact angle and wetting by a capillary

This gives theoretical support for the intuitive observation that a contact angle of less than 90 ° will ensure that the pressure differential is negative. Additionally, a small pore size would increase the pressure differential, which leads to better electrolyte retention. These two key factors thus determine the electrolyte retention properties of the support material. It is further described in Figure 2-2.

2.3.2 Porous material considerations

In current fuel cell technology, there are several types of commercial supported liquid electrolyte fuel cells. In AFCs, the KOH/H_2O solution is held within an asbestos matrix [30]. The electrolyte layer can be as thin as 0.05 mm; therefore ohmic polarization is not as much of an issue in this type of AFC. Though increasing the concentration of KOH enhances AFC performance, but it is not practical and feasible to use high concentrations of KOH in water due to the non-uniformity of KOH concentrations in operating fuel cell. The ORR may reduce the water concentration near the cathode and then cause to solidify the electrolyte solution, preventing reactant transport [28].

In the PAFCs, the phosphoric acid is contained in a matrix structure of silicon carbide (SiC) powder bound with a small amount of PTFE. The electrolyte is held by capillary pressure in the pores, and is typically 0.1 to 0.2mm thick [8].

In MCFC, the porous matrix γ-$LiAlO_2$ is used to hold molten carbonate in place also by the capillary effect. It typically contains about 40% γ-$LiAlO_2$ and 60% carbonate by weight. The porous matrix is usually made of ceramic powder using tape-casting or hot pressing methods. These mature techniques are simple process but usually lead to undesirable issue such as poor microstructure, and high thickness (1 to 2mm) [33, 34].

For an IT-MSFC, the requirements of the material will vary largely depending on the specific electrolyte. That means the existing material good for one electrolyte would most likely not work for other even similar electrolyte. The ceramics are the sort of materials that are most promising for use as a support, because they are chemically and mechanically stable in intermediate temperature. Besides, many ceramics have been used as the electrolyte layer for a long time; therefore there is a great amount of mature techniques and practical experience in fabricating and application of porous ceramics. For example, there is a lot study on exact control over the pore structure including the pore size, porosity, and inner structure [33, 8].

Commercial zirconia (ZrO_2) felt was used in Spence's work [9]. It is highly resistant to almost all types of chemical attack except some strong acids (particularly phosphoric acid). Some rare earth oxides, such as Titania, Ceria, would also be considered as a suitable material for a support matrix. There is a large volume of commercial products about ZrO_2 and other rare earth oxide, such as filter, sparging, dispersion and shapes of porous metal, which potentially can be used for an initial study. In addition, there is a lot knowledge and experience about producing porous ceramics and modifying the microstructure in this area, which is powerful technical support for further study.

Nickel oxide is also a sort of ceramic, usually used as glass paint. It was found that Ni and O elements in nickel oxide combine in a complex state, and there is a bound state called Zhang-Rice, which make the current difficult to pass through [35]. Therefore, nickel oxide is not electronically conductive. Besides, it is stable, not react with strong acids and bases. Some fine porous product made from nickel could be found in commerce, which could be fabricated to porous NiO in further process.

The use of porous PTFE is also possible at the low end of the temperature range; however, incorporating a molten salt into a PTFE matrix is more difficult compared to ceramic matrices. PTFE is extremely non-polar and hydrophobic, with very weak surface interactions with almost anything. This is one of the properties that lead to its excellent chemical resistance, but it would also make it difficult to ensure that the electrolyte could be retained within it.

2.3.3 Porous structure and fabrication

The selection and development of an effective support material is one of the most important considerations for IT-MSFCs. The pore structure and the surface topography govern electrolyte retention, so that they are closely interrelated to the operating life and the efficiency of the membrane.

In the ideal membrane, the porous structure would be full of electrolyte, and the amount of electrolyte would be large enough in the thin membrane to achieve the high conductivity during operation. Therefore, there are several key parameters to describe the morphology of the porous support: the porosity, pore size distribution, the surface pore size, the average pore size, and the tortuosity.

Ideally, the porosity of the matrix should be enough to contain sufficient electrolyte with high conductivity, while the pore size should be small enough that the electrolyte is effectively retained by capillary pressure. Besides, the void density distribution should be uniform to avoid the additional loss of efficiency, because the variable pore size make it difficult to fill up the porous structure by electrolyte without pinhole inside. The tortuosity describes the specific structure of the pores, measuring the twisting and turning of pores. The effective conductivity of a supported electrolyte can be calculated as [9]:

$$\sigma_{eff} = \varepsilon/\tau\ \sigma \tag{14}$$

Where σ is the conductivity of the bulk electrolyte, ε is the porosity of the support, and τ is the tortuosity.

Finally, thinner membranes are advantageous because they keep the cathode electrode saturated through “back” diffusion of water from the anode, in the case of alkaline electrolyte layer.

The electrolyte is retained in the matrix through capillary action under the premise of good compatibility, and thus, the pore size and surface interaction is the key factor to determine the electrolyte retention. The ideal structure would likely be a “honey comb” structure, where the pore was distributed homogeneously, and very thin straight through the plane of the matrix. The structure of Anodic aluminum oxide (Figure 2-3) is desired on ZrO_2 and other rare earth oxide, since aluminum oxide is not chemically inert. They are not achievable in practice in the short term, but that is what would be theoretically most desirable.

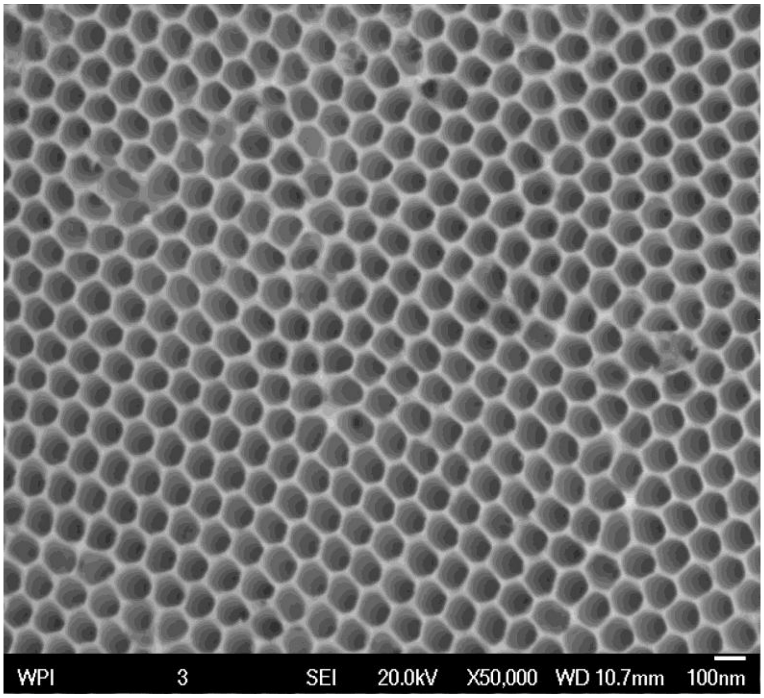


Figure 2-3: SEM of the structure of Anodic aluminum oxide

In recent decades, an increasing number of fabrication techniques of porous ceramics have appeared, especially for environments where high temperatures, extensive wear and corrosive media are involved. Such applications include high-temperature thermal insulation, support for catalytic reactions, and the filtration of molten metal, liquid, hot corrosive gases in various industrial processes [36].

The most straightforward processing preparation of porous ceramics is the partial sintering of initially porous powder compacts or the sintering of powder mixtures which undergo solid state reactions that lead to pore formation. The product usually have homogeneously pores distribution but the porosity is relatively low [8].

The industry standard process, “Tape Casting” is used to produce membranes for molten carbonate fuel cells. In this process, the green ceramic is mixed with an organic binder, and formed into a thin “tape”. It is cut to the desired size, and then fired at high temperatures, possibly followed by a calcination step. The thermal decomposition and subsequent removal of the binder leads to a pore structure, which is controlled by changing the binder used and preparation procedures [37].

Beside these traditional ways, many novel methods for the preparation of porous ceramics with controlled microstructure have been developed in response to the increasing number of new potential applications for cellular ceramics. Sol-gel synthesis widely used to prepare the porous membranes of some ceramics [38]. In this process, alkoxides (for example, silicon alkoxides for silica sols) are dissolved in an organic solvent such as PVA. They are hydrolyzed, which can be applied to a scaffold or support. Then after drying, it result in a porous layer. Control over pore size is achieved by changing the composition of the sol – additives can include chelating agents, pore formers, and yttria sources (for preparation of YSZ sol-solution).

Porous silica is widely produced by the sol-gel method (in preparation of desiccants, among other things), through hydrolysis of silicon alkoxides. The analogous process can be used to prepare yttria-stabilized zirconia and zirconia membranes with some modification [39].

The replica method is based on the impregnation of a cellular structure with a ceramic suspension or precursor solution in order to produce a macroporous ceramic exhibiting the same morphology as the original porous structure. Many synthetic and natural cellular structures can be used as templates to fabricate porous ceramics through the replica technique. A disadvantage of the replica technique is the fact that the struts of the reticulated structure are often cracked during pyrolysis of the polymeric template, markedly degrading the final mechanical strength of the porous ceramic [40, 41].

Comparing to the replica technique described above, from where the positive morphology obtained, the sacrificial template technique leads to porous materials displaying a negative replica of the original sacrificial template. It usually consists of the preparation of a biphasic composite comprising a continuous matrix of ceramic particles or ceramic precursors and a dispersed sacrificial phase. That is initially homogeneously distributed throughout the matrix and is ultimately extracted to generate pores within the microstructure. One of the main advantages of the sacrificial template method in comparison with the other fabrication routes is the possibility to deliberately tailor the porosity, pore size distribution, and pore morphology of the final ceramic component through the appropriate choice of the sacrificial material. The range of porosity and pore sizes that can be achieved with this technique is very broad (20%–90% and 1–700 µm, respectively), as they only depend on the volume fraction and size of the sacrificial template used [2, 41].

A very different form of porous ceramic with potential as a support for a molten salt fuel cell is a ceramic textile. Ceramic textiles can be made from a wide variety of ceramics, including the oxides of zirconium, aluminum, silicon, and lanthanides [37]. They have high porosities and high pore sizes, relative to ceramic matrices fabricated through other methods, the specific porosity depending on the type of weave used and the specifics of the manufacturing process. One of the advantages of these is that they are available as an off-the-shelf product from companies such as Zircar Zirconia. The high porosity and large pore size of ceramic textiles may result in poor electrolyte retention. One possible solution to this is to fill the pores in somehow, most likely with more ceramic of the same type. Suspensions of nano-particles of zirconia and other ceramics are available commercially which the textile could be soaked in and then dried and calcined. Alternatively, the particles could be produced *in situ* through a chemical reaction. Zirconia, for example, can be produced from zirconium alkoxides, and this reaction could be carried out within a sample of zirconia textile to produce zirconia which would adhere to the zirconia fibers and fill the pores [9].

Another potential porous ceramic is porous NiO. One of the advantages of this material is that they are available as a commercial product of porous Nickel plate from Mott Corporation. It has high strength, high heat tolerance with uniform porosity in a wide range. Further, it can be calcined and oxidized to NiO, but loses its porosity to a certain degree. The main problem in this case would be the increasing closed pore volume.

Because the key factors in an effective support, electrolyte retention and chemical compatibility, both depend directly on the electrolyte as well, it is likely that different support materials and/or preparation methods will be needed for different electrolytes.

2.4 Catalyst and electrode layer

The fuel cell electrode layer is the other critical component of a fuel cell. The electrode layer consists of catalyst, porous electrode or gas diffusion layer.

The catalyst layer must be very effective at breaking molecules into suitable ions and electrons. It should have high surface area, and thermally, chemically, physically interact well with the surrounding fuel cell components. The toughest requirement for electrode layer is low-cost.

In order to catalyze reactions effectively, catalyst particles must have contact to both ionic and electronic conductors. In other words, there must be passages for reactants to reach catalyst sites and for reaction products exit. The contact point of the reactants, catalyst, and electrolyte is so-called three- phase interface. Therefore, the effective area of active catalyst site usually is several times higher than the geometric area of the electrode, so as to achieve desirable reaction rate.

The catalysts used would most likely be similar to those used in existing fuel cell systems. The catalysts commonly used are platinum (at low temperatures), and at higher temperatures nickel (on anode and cathode) and silver (on the cathode) [21, 35]. Tolerance to carbon monoxide is an important issue for low temperature fuel cell. Fuel cell performance drops with very small amount of CO especially when feed gas (H_2) is supplied to the fuel cell by steam reforming. In intermediate temperature, CO tolerance will be improved because the chemical binding of CO to Pt is strongly exothermic. It makes fewer requirements for the CO cleanup in fuel. On the other hand, combining one or two other catalysts such as Pt/Ru, Pt/Mo, and Au/Pd to the base catalyst can help to prevent catalyst poisoning and deactivation, which is found by Iwase and Kawatsu [42].

For non Pt catalyst, nickel is comparatively lower price, and it can be used as catalyst throughout most of the intermediate temperature range. Raney nickel can be used to achieve very active and porous forms of nickel catalyst. They are prepared by mixing the nickel with an inactive metal such as Al. The mixing is accomplished so that the two metals are not mixed to form an alloy, but the regions and properties of both metals are maintained [35]. However, corrosion is a significant potential problem particularly on the cathode. In the case of molten salt electrolyte, their strong causticity will cause rapid corrosion of most metals. Zambonin et al [16-18] reported that molten nitrates caused corrosion of the nickel catalyst in a molten nitrate fuel cell. In molten carbonate fuel cells, a similar problem is encountered: molten carbonates are highly corrosive on the cathode; the nickel catalyst is rapidly corroded by forming a non-conductive layer of nickel oxide on the surface. In MCFCs, the problem was successfully solved by making a lithiated nickel oxide layer (NiO) on the original nickel catalyst. The one is electrically conductive, and maintains the catalytic properties of nickel. The porosity is about 55% to 65%, and the mean pore size is 5 to 7 microns. The smaller pores are filled with electrolyte, while larger pores allow for the diffusion of gas into the interior of the electrode [34, 35]. Cathode thickness causes the polarization, and the optimal cathode thickness that decreases polarization is reported from 0.4 to 0.8mm in MCFC. The experience provides reference to the similar application of catalyst for IT-MSFCs.

The gas diffusion layer is between the catalyst layer and the bipolar plates, distribute reactants homogenously to the electrodes. They also serve as current collector; provide electrical contact between the electrodes and the dipolar plates, conducting electrons. They also allow reaction product water to exit the electrode surface and permit the passage of water between the electrodes and the flow channels. Therefore, their porous structure is usually wet-proofed to insure they do not become clogged with water. So that allows the gas to spread out as it diffuses to maximize the contact surface area of the catalyzed membrane. The most common used wet-proofing agent is PTFE, for relatively low temperature. The electrode layer usually made by PTFE-treated carbon cloth or carbon paper based Pt. Being hydrophobic; it also repels most molten salts effectively. The thickness of various gas diffusion materials vary between 0.0017 to 0.04cm, and porosity between 70 and 80%. But it is suitable only for the lower end of the intermediate temperature range, because the PTFE coating that makes it hydrophobic begins decomposing in the temperature range 260 °C to 350 °C [2].

On the other hand, the GDL will prevent electrolyte to infiltrate, otherwise the electrolyte entering the GDL will destroy the three-phase interface, and prevent fuel or oxygen from reaching the catalyst. Ideally, the pore size of GDL should larger than it of electrolyte layer, causing a positive capillary pressure to electrolyte; therefore it should not wet favor to electrolyte. And idealized diagram of such a pore structure is shown in **Figure 2-4.**

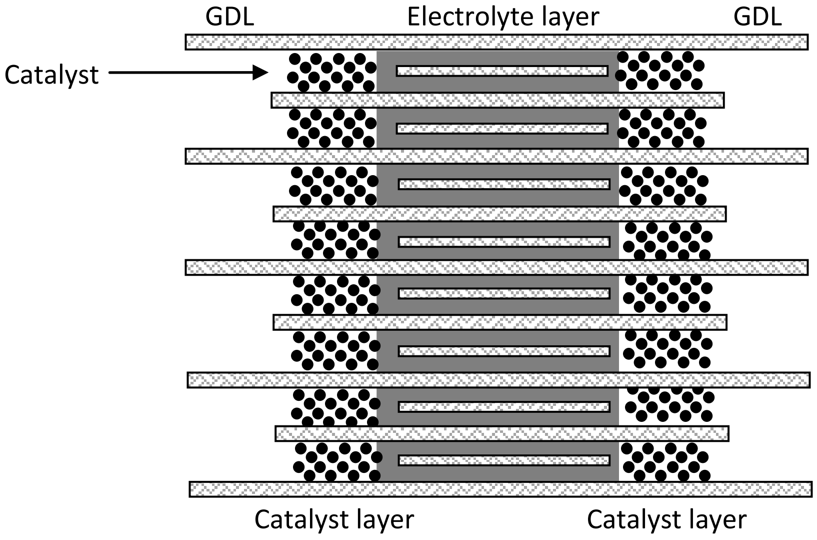


Figure 2-4: Ideal pore size structure of IT-MSFC.

Chapter 3

Experimental Results

The basic feasibility of the intermediate temperature molten salt fuel cells was studied and proved by experiments. Experiments were conducted using several different materials to be the electrolyte support, including Zirconia Cloth, porous ZrO_2-TiO_2 Disks, and porous NiO plates. Also, the results are compared with those from tests using KOH molten salts, H_3PO_4 solution, and KOH solution.

3.1 Experimental setup

The fuel cell hardware unit, we used to test, consisted of separator plates, current collector plates, membrane electrode assembly (MEA), gaskets, and insulators is shown in Figure 3-1.

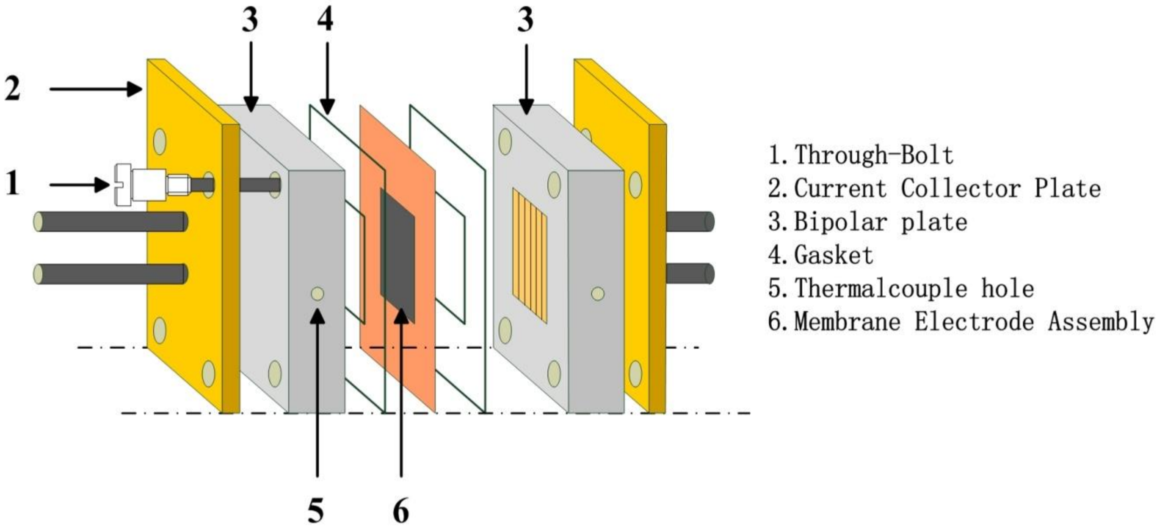


Figure 3-1: The fuel cell schematic drawing.

The separator plates included anode and cathode graphite plates, because of its low porosity, excellent chemical resistance, high electrical /thermal conductivity and mechanical strength, guaranteed a gas tight seal. The high purity graphite plates were each 3x3 inch square blocks, ½ inches thick. In the center of the side touching the MEA, each plate had 1 square inch (approximately $5cm^2$) active area cut in serpentine flow pattern. Two holes through the plate with 1/8th inch in diameter at the two corners of the flow field allowed for supply and exhaust passage. There was an additional through-hole about 1/4th inch in diameter at one edge of the flow field; this was to allow for alternate flow regimes to be investigated. But these holes were blocked with two PTFE plugs all the time; since such investigations are far beyond the scope of this study.

Current was collected by connection to copper contact plates which were on both side of the separator plates and held the graphite blocks by stainless steel inlet and outlet tubes. The two copper plates were held together by 4 1/4-20 bolts, with insulators on the cathode side so that the bolts do not short circuit the fuel cell during operation. Through-bolt assembly design required low tightening force and was more easy and fast to create uniform force distribution. The cell is shown in Figure 3-2[2].

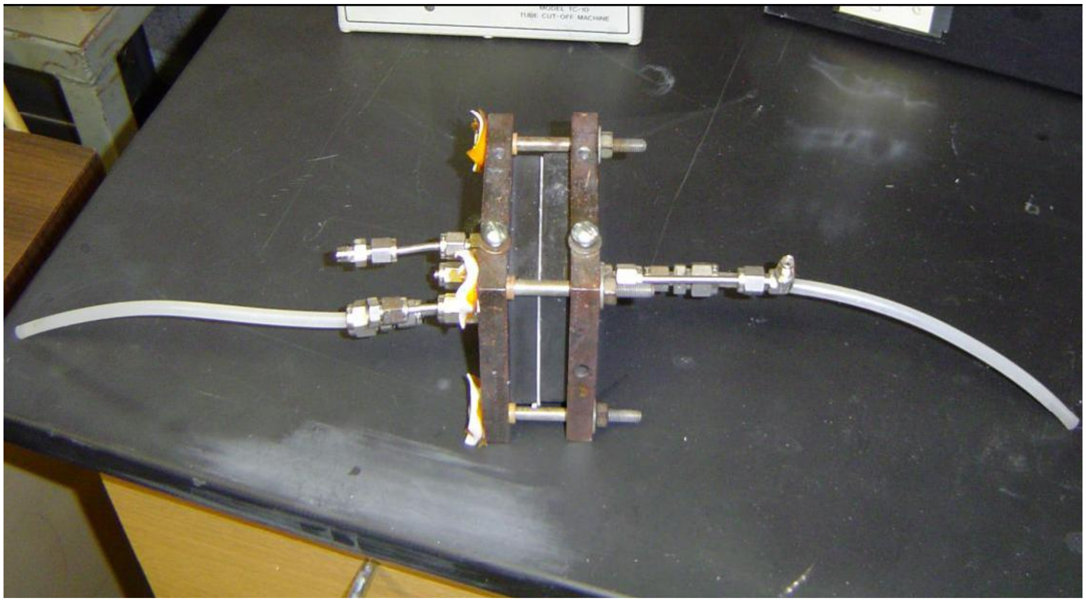


Figure 3-2: Fuel Cell, assembled without insulation.

The copper plates were 4x4 inches square and ½ inch thick, which had two heater insert holes in front, two little thermocouple insert holes for measuring internal temperature and terminals were at the top edge for connection to the load box. Each plate had two holes through it, each with a 1/8th inch stainless steel tube through it as gas inlet and outlet, protruding about 1/4th inch in diameter inside, to fit into the corresponding hole in the graphite plates. On the outside, these tubes ended in stainless steel Swagelok fittings, the inlets being 1/8th inch, and the outlets being 1/4th inch. The anode plate had two additional holes, both of which simply had a Swagelok fitting on the outside, and no fitting on the inner side, presumably used in past experiments.

In all experiments the MEA was surrounded by silicon rubber gasket or PTFE sheets, and similarly separated from the graphite plates. The gasket sheets cover all parts of the membrane except the active area.

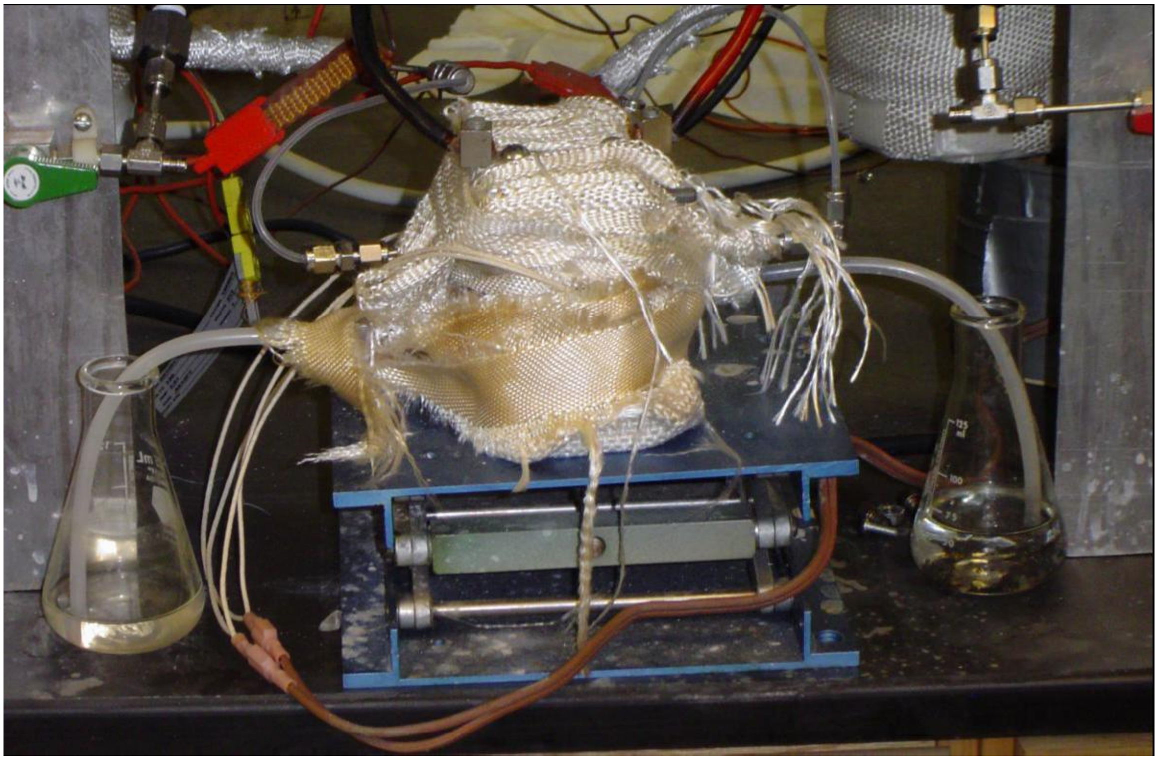


Figure 3-3: Fuel Cell, assembled with insulation

The fuel cell hardware was insulated by several layers of fiberglass insulation tape (Zetex brand), wrapped tightly around the entire fuel cell assembly, which is shown in Figure 3-3.

Heating was provided by a 120V 100 watt-maximum cartridge heater in each copper plate. The voltage supplied to the heaters was precisely controlled and monitored by the thermocouple to maintain the operating temperature waving in acceptable range

The fuel cell was controlled and monitored by a computer connecting to the Scribner Associates Series 8908 Fuel Cell Test System. This system allowed either the current or voltage to be fixed – however voltage is fixed by varying the load on the fuel cell, which results in poor performance at low current densities, or in event of rapid oscillations, as was discovered during early testing. The hydrogen and oxygen feed are controlled by the test station, and are supplied at a controlled temperature. The fuel and oxygen lines from the test station are 1/8th inch PTFE tubes with Swagelok fittings. The fuel cell, connected to the fuel cell test system, which is shown in Figure 3-4.

All of the data was taken by the computer controlled fuel cell test station. The fuel cell assembly was heated using protective gas (N_2) as the feed until the desired temperature was reached. Once the fuel cell was stable, the fuel cell test system was used in arbitrary control mode and changed into the fuel and oxygen. In this mode, a control file was used to direct the test system to fix the voltage of the cell for 10 seconds, before recording the current operating conditions of the fuel cell and moving to the next voltage. The tests started at 1.0 V, and proceeded in a decreasing direction in increments of 0.05 volts. When the minimum voltage (0.1V, 0.4V, or 0.55V) was reached, the voltage was returned to 1.0 V and the cycle repeated.

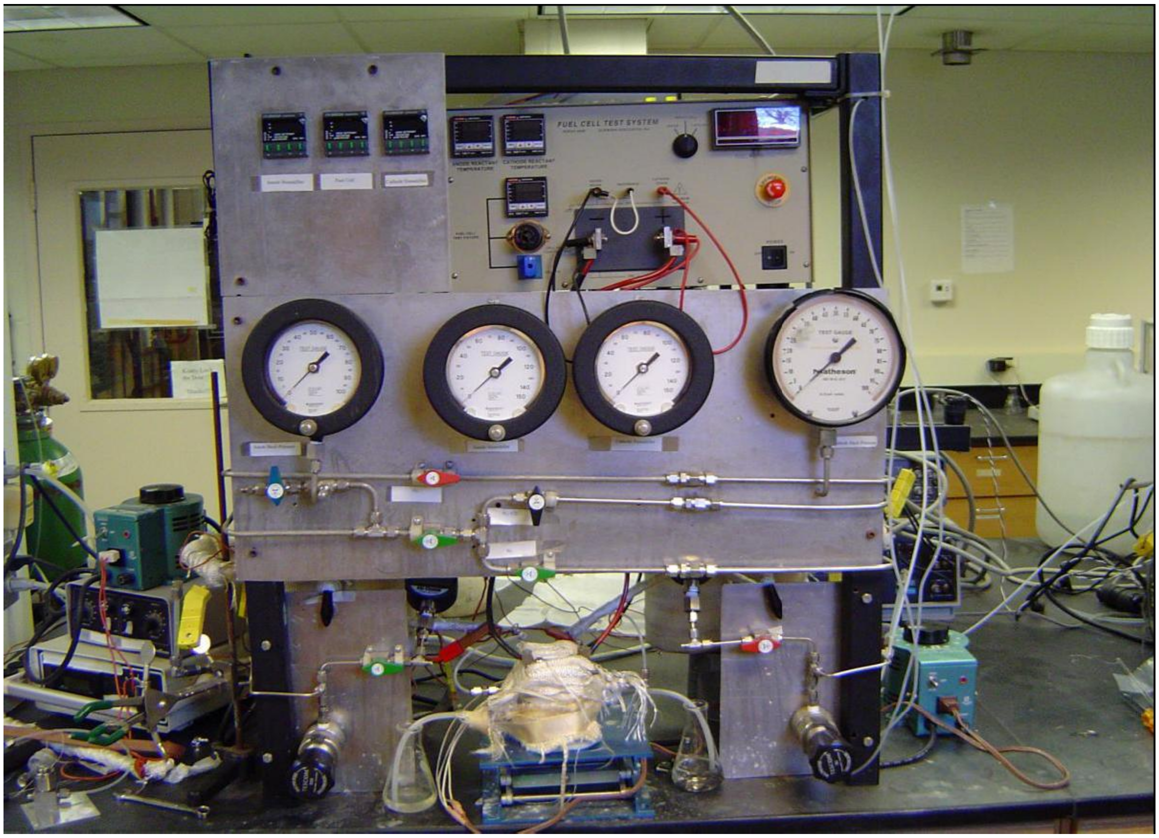


Figure 3-4: Fuel Cell, assembled with insulation, connected to test setup

3.2 Initial feasibility studies

The initial feasibility tests started from the membrane made from Zircar ZYW-30A yttria-stabilized zirconia knit cloth. The zirconia cloth membrane was cut into 2”×2” square and loaded with KOH molten salt at 200 ℃. In this case, although the reported KOH melting point is 360 ℃, commercially available KOH has up to 15% water in it, which is very difficult to remove, as a consequence, it melts at a temperature of around 180 ℃. Then it was sandwiched by two PTFE sheets and placed in an oven at 200 ℃ with a metal plate on the top of the assembly. When the electrolyte (KOH) melted, the force from the weight of the metal plate flattened it physically. Then it was cooled at room temperature, and the loaded membrane was used immediately or sealed in an airtight bag for storage because of the high hygroscopicity and CO_2-absorption of KOH salt.

The PTFE gasket was made by simple superposition of several layer of 0.005” thick PTFE sheet, which matched the loaded membrane in thickness, to create uniform force distribution. An additional piece of PTFE with an opening active area and the same thickness as electrode layer was added to each side of the loaded membrane, to prevent the electrode which included gas diffusion layer and catalyst layer from damaged by overpressure.

A commercial catalyzed GDL with a Pt loading of 0.5mg/cm^{-2} on a carbon woven web (LT140EW Low Temperature ELAT®GDE Micro porous Layer, E-TEK) was used as the electrode. It was cut into 1 inch^2 square, held by a PTFE sheet which had the same thickness sticking to the loaded membrane by PTFE tape.

Although the KOH melting point is around 180 ℃, the target operating temperature for an IT-MSFC would be above 200 ℃, and materials generally have a higher viscosity closer to their melting point, the KOH with its higher melting point might be better retained. The operating temperature was raised to 190 ℃, however, due to the manual temperature control, the temperature varied somewhat over the course of the experiments; Data was taken in the range of 185-195 ℃.

An automated testing routine was used to assess performance, and this also enabled charting of the degradation over the entire voltage range investigated, offering insights into the degradation behavior.

The results are shown in Figure 3-5 below.

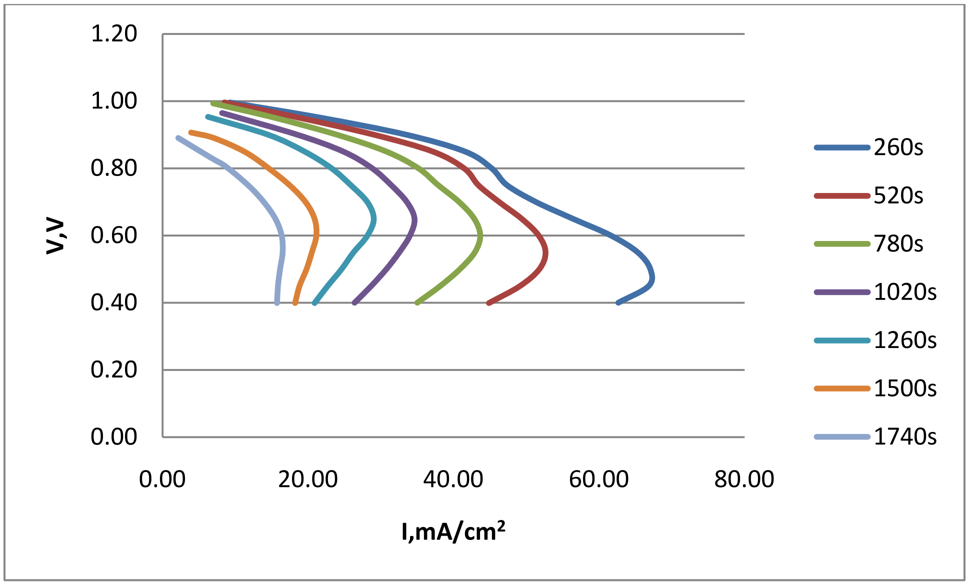


Figure 3-5: I-V curve of KOH molten salt supported by ZrO_2 felt.

These initial tests demonstrated an open circuit voltage close to 1 volt, as well as acceptable current density. Unfortunately, this was found to be very short lived. Using ZYW-30A membranes, the open circuit voltage (OCV) consistently remained stable at 1.03 volts for half an hour or longer and following an irreversible decreasing, while the performance also displayed rapid degradation of current density. The OCV decline is a clear indication of increasing crossover due to loss of electrolyte from the support layer. The performance loss was proposed to be due to a decrease in either the electrolyte conductivity (due to loss of electrolyte) or a reduction in catalytic activity caused by electrolyte leaving the support matrix and blocking the fuel gas from accessing the catalyst.

It was also observed that small pressure differences between the two sides of the fuel cell would lead to much more rapid degradation, which is consistent with degradation caused by loss of electrolyte – the electrolyte would be “blown out” of the membrane. This pressure drop effect was minimized by placing the end of each outlet tube under the surface of water in a beaker at an equal depth to carefully control the pressure on each side.

Based on close inspection of each part removed from the fuel cell assembly, it was found that part of the electrolyte was still within the membrane, but a significant portion of the electrolyte was leaving the membrane, remaining on carbon cloth, gas tubes on both side and between layers of the gasket. Some visible pinholes appeared on the loaded membrane. Electrolyte loss would lead to progressive reduction of conductivity (and accompanying loss of performance), until pores between the sides were no longer blocked by electrolyte, leading to mixing of the gases and an accompanying drop in OCV. This matched the pattern of degradation observed. This electrolyte which had escaped the membrane could also obstruct the flow of gas in the serpentine channels on the graphite plates, in addition to infiltrating the GDL and blocking access to the catalyst by the reactants.

Compared to membranes used in molten carbonate fuel cells with around 50% porosity, the ZYW-30A zirconia cloth has a high porosity of 83% and a large pore size. A large amount of electrolytes need to be supported by comparatively small amount of zirconia. Its surface topography was studied by scanning electron microscopy (SEM), shows in Figure 3-6

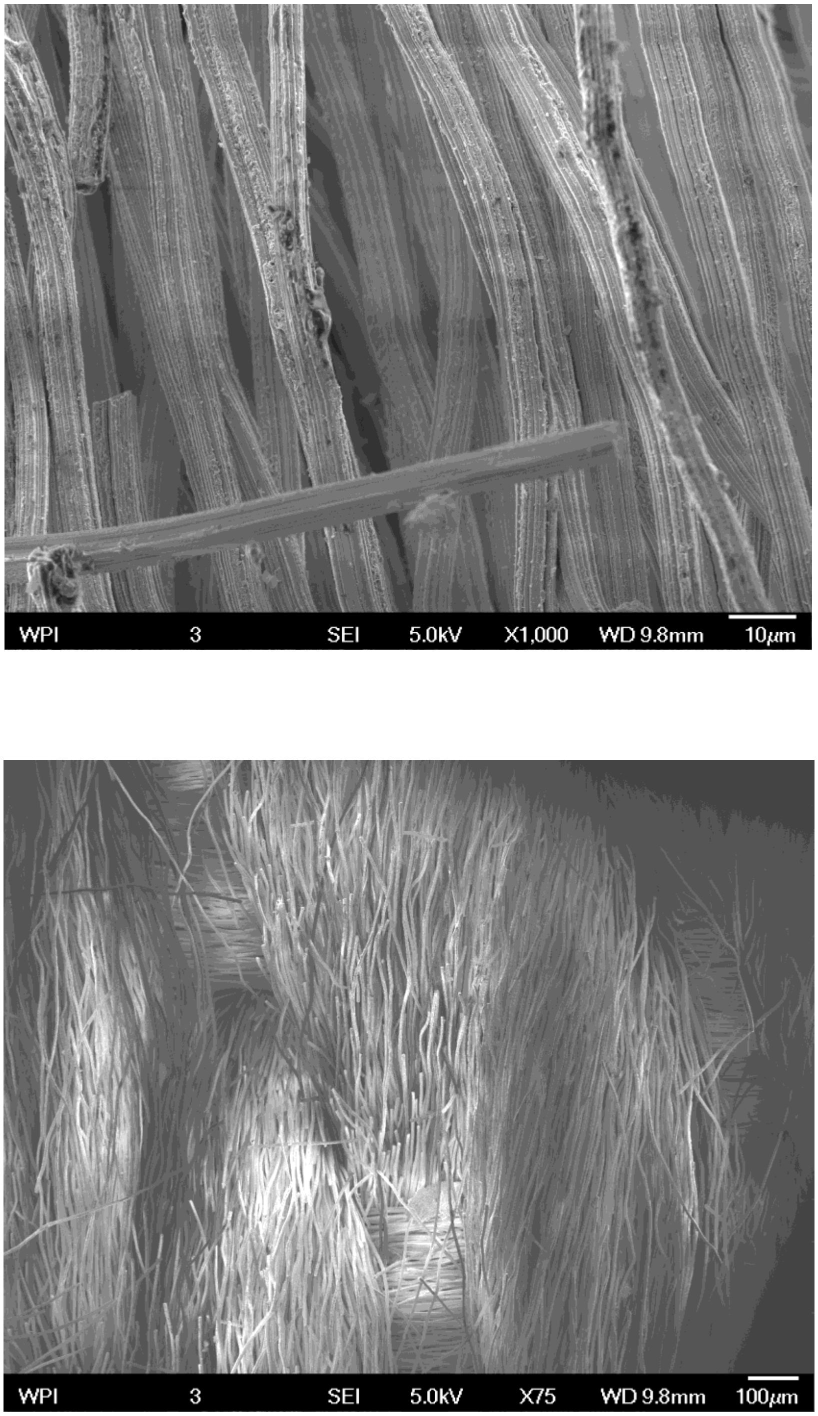


Figure 3-6: ZYW-30A zirconia cloth surface topography scanned by SEM

It was obviously that the zirconia tiny fibers were roughly and packed loosely with many fragmental fibers. And there was a distance of about 30 micrometer between each fiber.

Although the fiber might expand for absorption of KOH molten salt, the interspaces between zirconia fibers was still too large to provide sufficient capillary force to retain the electrolyte filled in the Zirconia cloth; therefore the molten salt could be easily forced out of the membrane due to gravity or a pressure difference. Increasing the outlet gas pressure could comparatively raise the open circuit voltage during operation, but it could not stop the subsequent rapid decreasing of the voltage, moreover the pressure differentials were impossible to completely avoid which also promoted the leaking of the molten electrolyte.

3.2.1 Modified Zirconia Cloth

The main problem of the initial test is the poor stability including the decreasing of the open current voltage and the degraded current density. On the basis of post morlen evidence from investigation of the fuel cells after operation, it was concluded that the main cause of the degradation was poor electrolyte retention by the matrix which due to the weak capillary action as described above. Some factors like force of gravity and the pressure differentials between the sides of the fuel cell helped to avoid the retention of the electrolyte. The viscosity of the electrolyte also plays a role; a more viscous electrolyte will more strongly resist being pushed out of a pore in the support. Moreover, even a small number of pores with large pore size will have a strong impact on the performance – once gasses begin to pass between the two sides of the fuel cell, OCV curve will drop dramatically.

Since the pressure differentials cannot be averted completely, the better promising parts to be improved are the size of the pores, the strength of surface interactions between the electrolyte and support, and the surface tension of the electrolyte. There is a commercial zirconia rigidizer, ZIR-RIG, also made by Zircar Zirconia. It is consisted of “sub-micron zirconia particles” in a solution of zirconium acetate, can be used as an adhesive to improve rigidity of the cloth. The ZYW-30A can be coated with Zirconia Rigidizer to create thin walled, rigid fibrous zirconia, which might fill the pore space, to decrease the interspaces between the zirconia fibers and the porosity of the zirconia cloth. In order to bind the zirconia particles to the zirconia cloth, the rigidizer treated ZYW-30A had to be fired at 1000-1200F (530-650 ℃) after drying.

As the procedure in the initial feasibility studies, the zirconia cloth was cut to certain size, and soaked with the solution ZIR-RIG, and then it was dried at 200 °C and fired at 550 °C for 24 hours, which removed residual moisture as well as residual acetic acid. After cooling, the membrane was loaded with KOH molten salt at 200 ℃. During all drying steps, the final firing, as well as the loading step, fine mesh stainless steel screens and the PTFE sheet were used to hold the samples flat.

The results are shown in **Figure 3-7**.

As shown in figure IV-7, current density reached 131 mA/cm^2 at 0.4 volts, which is much better than the initial test. The total test took about one hour. The degradation still occurred, but the rate of decrease was is much lower than the original one. It was obvious that the membranes treated with ZIR-RIG performed well, and were far more stable than the untreated membrane. That means the pore filling material was helpful, and multiple treatments might improve performance further. The following experiments were conducted using membrane which had been treated by ZIR-RIG twice or even three times. It was suggested that the multi treatment helped to reduce the rate of degradation slightly, improving the longevity. While the current density at the beginning was a little lower than the one-treated membrane, but both of their performance decreasing ends in the same level.

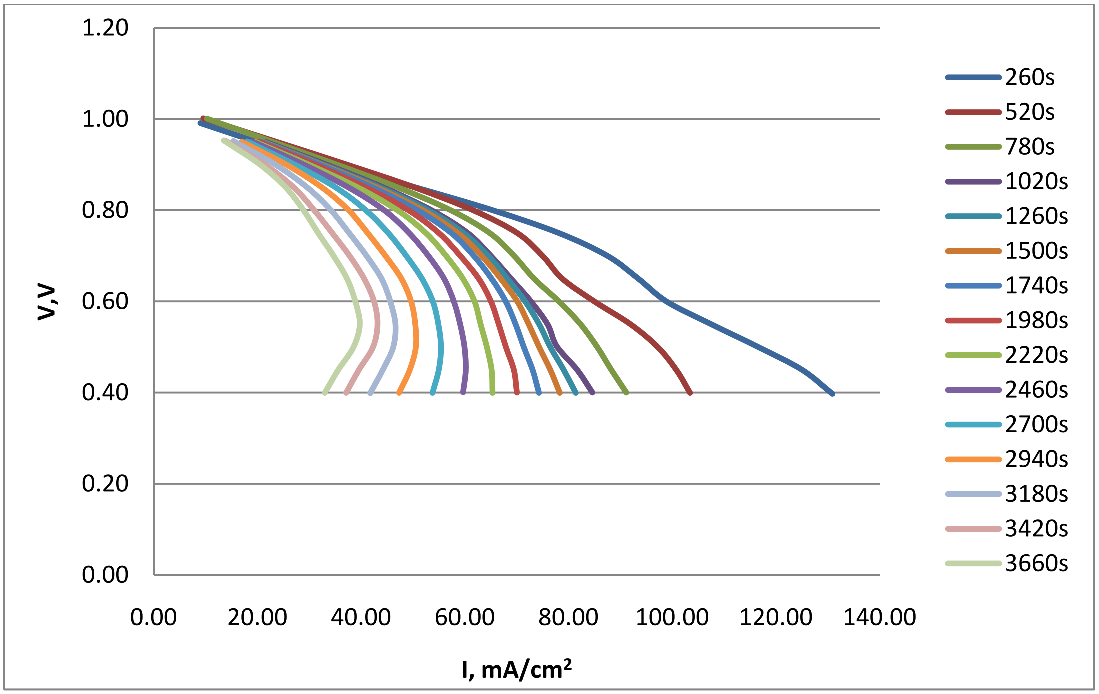


Figure 3-7: I-V curve of KOH molten salt supported by modified ZrO_2 felt.

On disassembly, it was found that there was still some electrolyte leaking through the GDL and left in the graphite channels. Small number of visible pinholes could be found on the membrane. This further suggests that electrolyte loss still occurred in this sample, albeit to a lesser extent. Although the porosity and the average pore size of the membranes have been reduced, the capillary force was still not enough to prevent the leaking of the electrolyte from the MEA.

In further tests, some new material with lower average pore size and porosity would be considered, for the purposed of improvement of the longevity and stability of the IT-MSFC.

3.3 Zirconia-Titania Disk support study

It was demonstrated as described above that due to the weakness of the capillary force, the electrolyte retention was poor in the zirconia-based cloth, which directly resulted in the short life and the degradation of the fuel cell performance. To increase the capillary action between molten salt and membrane, a commercial product, zirconia-titania porous disk by Sterlitech Corporation was considered to be the possible support material. These ceramic membranes are inorganic membrane disk designed for microfiltration, ultrafiltration and nanofiltration applications. They are 2.5 mm thick and 47mm diameters, which is too thick for a fuel cell membrane, but it can be sanded by grind machine to certain thickness we need. They meet the basic requirements of being electrolyte support: they are absolutely inert, resistant to acids and bases; the temperature they can stand high temperature up to 350℃ for a long working life. Besides, their porosity is around 25% and their average pore diameter is 3.5 μm, which is much smaller than it of zirconia felt. However, unlike the zirconia cloth, these are rigid and susceptible to cracking when clamped in a fuel cell.

The zirconia-titania disk was sanded slowly by grind machine into the thickness of 1.35mm, cut into 2”×2” square, and then cleaned following standard procedures. Allowed for the permeability of solution is definitely better than molten salts, the tests started from traditional electrolytes including KOH saturated solution used in AFC and the phosphoric acid solution used in PAFC. The disks were loaded with saturated KOH solution, whose mass fraction was around 55% and the 85% phosphoric acid separately. The loaded membrane was used immediately every time, in case they loss electrolyte and absorb CO_2 or water vapor from the air during the storage.

The silicone gasket was made by superposition of several silicon sheets with thickness of 0.4mm. The total thickness of four of them would be 1.6mm, which was a little larger than the thickness of membrane, which would be better than the exactly same thickness gasket. Because this elastomer created uniform force distribution without compression cracking of membranes and it would be good at sealing. An additional piece of silicone with an opening active area and the same thickness as electrode layer was added to each side of the loaded membrane, to prevent the electrode which included gas diffusion layer and catalyst layer from being damaged by overpressure.

The same electrode, the commercial catalyzed GDL with a Pt loading of 0.5mg/cm^{-2} on a carbon woven web (LT140EW Low Temperature ELAT®GDE Micro porous Layer, E-TEK) was used, and it was cut into the same size as reaction area in initial test, held by silicon gasket.

Although the target operating temperature for an IT-MSFC would be above 200 ℃, allowing for the electrolyte boiling points, the operating temperature was raised to certain temperature where they had the best performance.

At the first two tests for alkaline solution and phosphoric acid electrolyte, the data were taken in the temperature range of 50-155 ℃, which was selected to start at the temperature where the AFC had an acceptable performance, up to the maximum temperature for the boiling point of phosphoric acid is 158 ℃ (decomp). It was suggested that the AFC had the best performance at 75 ℃, while the PAFC had the best data at 145 ℃. Therefore, the following tests for these two electrolytes were conducted separately at this two temperature points. To compare with the initial test, there was another test using zirconia felt with phosphoric acid conducted at 145 ℃. The same automated testing routine was used to assess performance.

The results are shown in Figure 3-8, 3-9, and 3-10 below

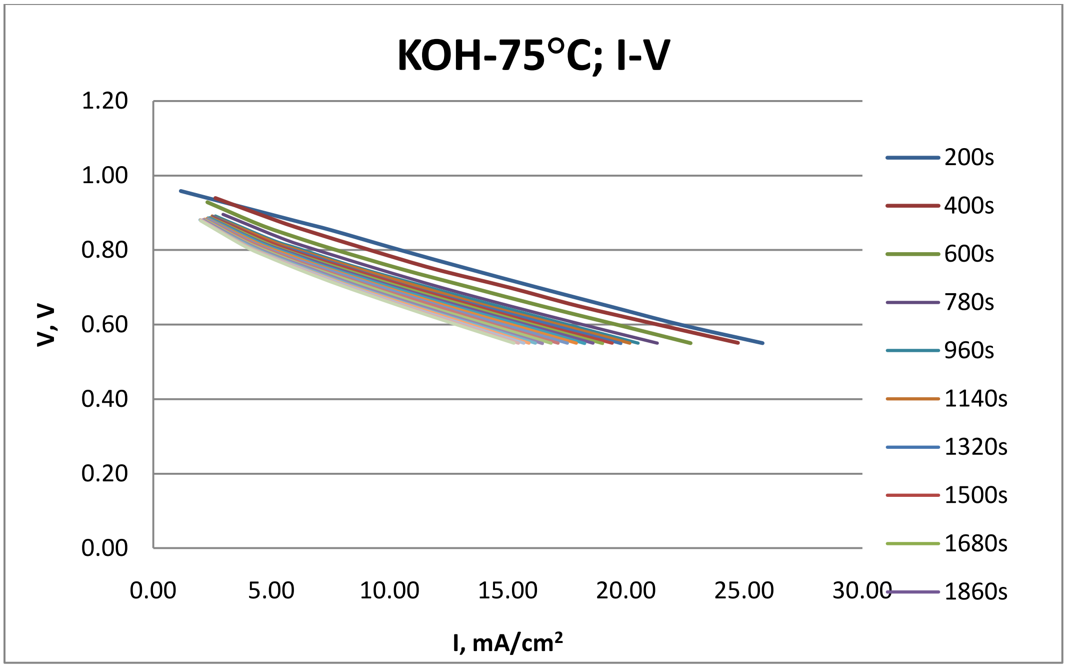


Figure 3-8: I-V curve of fuel cell with KOH saturated solution supported by ZrO_2 Disk.

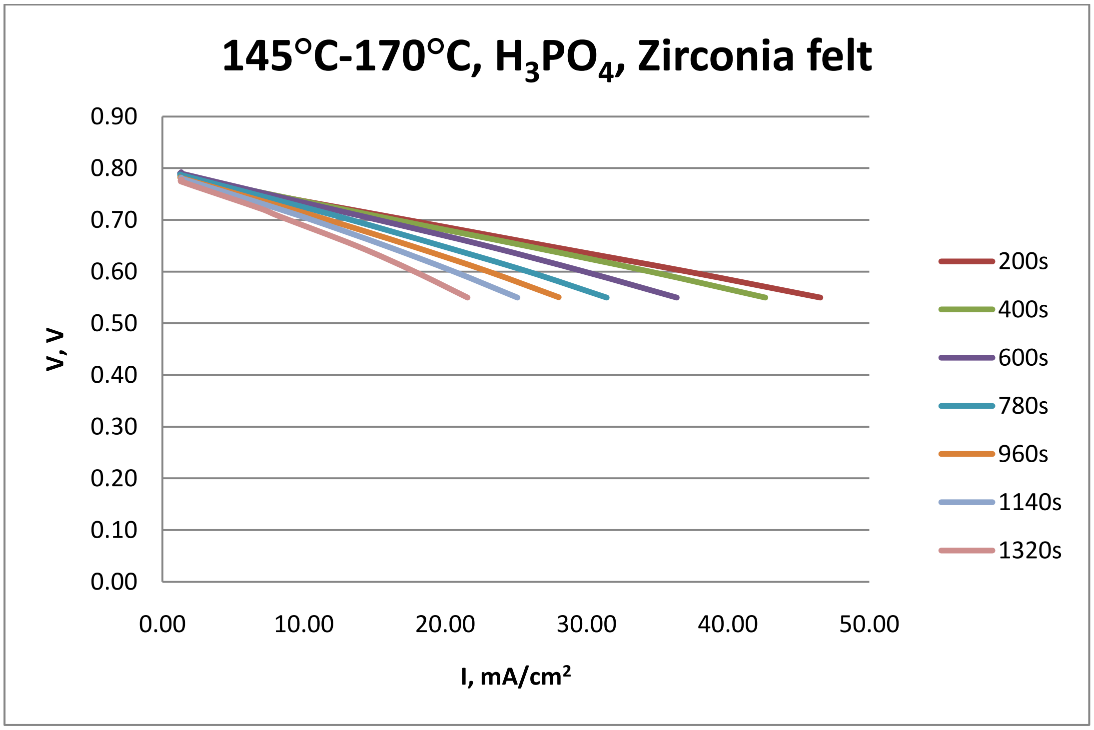


Figure 3-9: I-V curve of fuel cell with phosphoric acid solution supported by ZrO_2 felt.

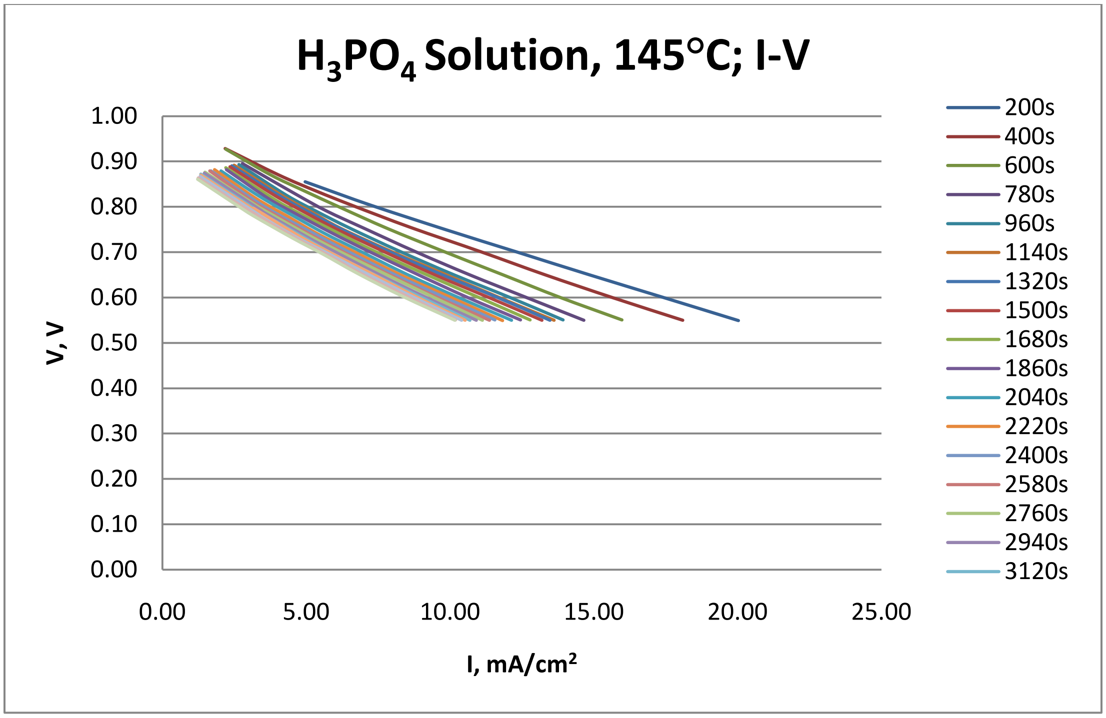


Figure 3-10: I-V curve of fuel cell with phosphoric acid solution supported by ZrO_2 Disk.

As shown in Figure 3-9, the one using zirconia felt got higher current density 46.5mA/cm^2 at 0.55 volts, than the other two. But the rapid degradation still occurred, especially in the zirconia felt. It was obvious that the degradation rates of disk-based membranes were much lower than the original one, which means the disk-based membranes were far more stable than the felt membrane. And the steady state, the AFC was a little better than the others. The bad news, however was that both of the disk membranes never got a current density higher than 30mA/cm^2, which is still much lower than the low-temperature PEM fuel cells.

It was can be concluded that although the smaller pore size reduced the degradation rate, but the lower porosity and the still relatively large pore size (3-5 μm) were unable to retain the electrolyte for extended periods.

Finally, a test using molten salt as the electrolyte in the disk was conducted at the temperature around 185 ℃. The results are shown in Figure 3-11 below.

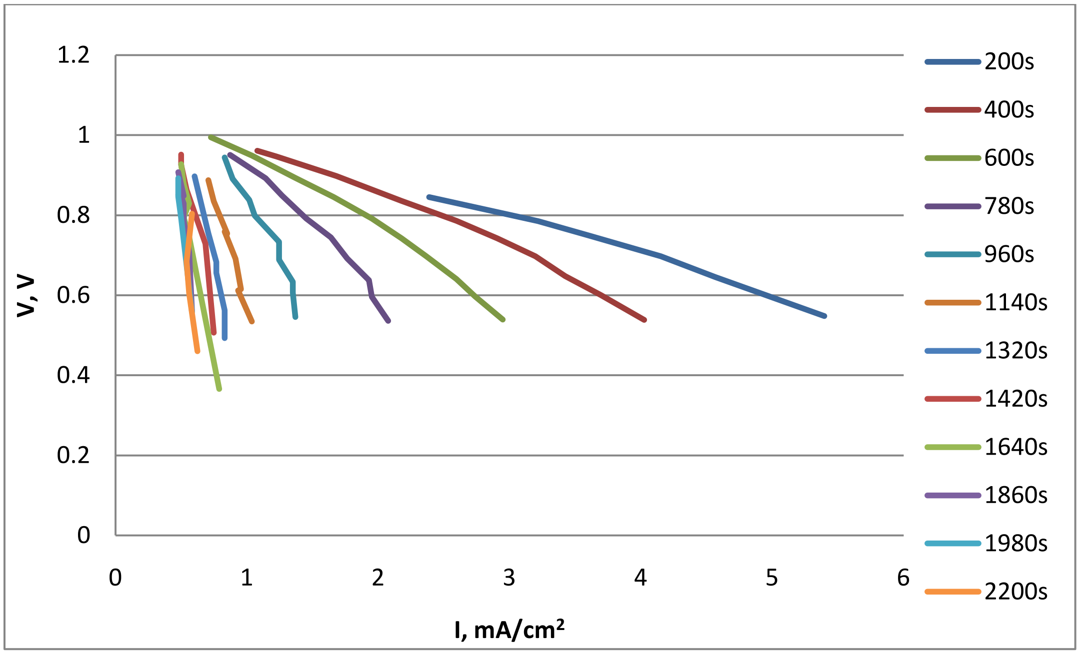


Figure 3-11: I-V curve of fuel cell with KOH molten salt supported by ZrO_2 Disk.

As shown in Figure 3-10, the one using zirconia disk with molten salt showed poor performance as well as poor stability. The main reasons would be the low porosity and large pore size. Compared to the 83% porosity of the zirconia felt, the disk just has around 25% porosity and 3-5 μm pore size, which are definitely not ideal. Another reason is the poor wettability, which magnified the poor performance and stability. It was observed that when the membrane was loaded with molten KOH at 200 ℃, it was much more difficult to absorb the molten salt, as compared to the alkaline solution and the phosphoric acid. Although the wetting angle was less than 90 ℃, the molten salt did not impregnate all the porous space according to the weight change of the membrane upon impregnation. It was very likely that the molten salt could easily infiltrate the outer layer of the disk, but it was difficult to fill of all the porous space with the molten salt simply by capillary action, because of the higher pore size inside the membrane. The way we loaded the molten salt was simply by gravity force and the capillary action between the membrane and the molten salt. This worked for the zirconia felt because it’s relatively regular inside structure, but it seems not nearly enough to impregnate all pore space of zirconia disk, resulting in a sparsely loaded membrane.

A thinner zirconia disk might be helpful, but the ceramic disk was fragile and it could be easily broken by overpressure. New techniques to help membrane being impregnated with molten salt are needed. On the other hand, some other materials with better wettability and smaller pore size are still worth a try.

3.4 Porous Nickel Oxide Plate

In the following tests, a commercial product, porous nickel plate by Mott Corporation was considered to be the possible support material following oxidation at high temperatures. These porous membranes are designed for filtration with long life, high strength, and uniform porosity in media grades ranging from 0.1 to 100 [50]. The experiment started from the nickel plate with grade of 0.5. Each sample was cut into 2”×2” square, and cleaned following standard procedures.

The samples were fired into nickel oxide in furnace separately for 2 hours, at different temperature 700 ℃, 800 ℃ and 900 ℃, in order to control the pore size changing and reduction of porosities in various degrees. After firing step, the surface of sample which was taken from 700 ℃ furnace was partial oxide, which means it cannot be able to use as support because of its electronic conductivity. For the others, although they were partial oxide according to the calculation result of the weight change, they were totally oxidized on both side surfaces and possessed no electronic conductivity, which also made them ready to test. The plates were loaded with molten KOH, and used immediately every time, in case they loss electrolyte and absorb CO_2 or water vapor from the air during the storage.

The silicone gasket was made by superposition of several silicone sheets with thickness of 0.4mm, to match the thickness of the nickel oxide plates. An additional piece of silicon with an opening active area and the same thickness as electrode layer was added to each side of the loaded membrane, to prevent the electrode which included gas diffusion layer and catalyst layer from being damaged by overpressure.

The same electrode, the commercial catalyzed GDL with a Pt loading of $0.5 mg/cm^{-2}$ on a carbon woven web (LT140EW Low Temperature ELAT®GDE Micro porous Layer, E-TEK) was used, and it was cut into the same size as reaction area in initial test, held by silicone gasket. The operating temperature was 185 ℃ in each test. The same automated testing routine was used to assess performance.

It was found that both tests demonstrated an open circuit voltage close to 0.6 volt indicating gas crossover. The sample fired at 900 ℃ and not result in any detected current density, although the sample at 800 ℃ furnace provide found very low current density (not steady and decreased rapidly). It was found that the porosity of both of the membranes had dropped lower than 10% upon oxidation. The surface topography of the one fired at 900 ℃ was studied by scanning electron microscopy (SEM), compared to the original one as shown in Figure 3-12, and 3-13.

It was obvious that the most of the open holes on the surface were closed by the oxide layer, which is the reason for the poor OCV and the zero current density. The lack of electrolyte was evidently the main reason for the lack of success of these two samples. Although the porosity of the nickel oxide was as low as 10%, the 800℃ firing sample still got a higher performance than the zirconia disk, which suggested the wettability of the nickel oxide plates was much better than the zirconia disk. Therefore, the porous nickel plates with larger pore size were considered to be the possible support for molten KOH.

The porous nickel of grade 10 has the original porosity as high as 33%. They were fired into nickel oxide in furnace separately for different time, at two different temperatures 800℃ and 900℃, in order to control the oxidation rate, the pore size changing and reduction of porosities in various degrees. The samples were tested for lack of electronic conductivity to make sure they were ready for testing, although they were only partially oxidized according to the calculation result of the weight change.

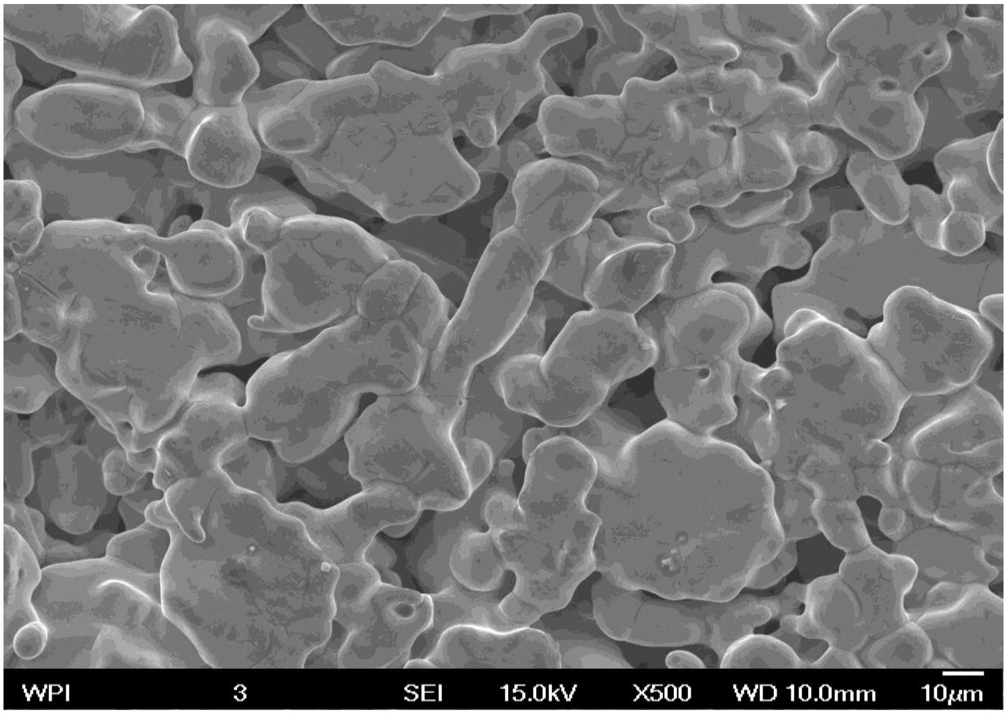


Figure 3-12: SEM of porous nickel without oxidation layer.

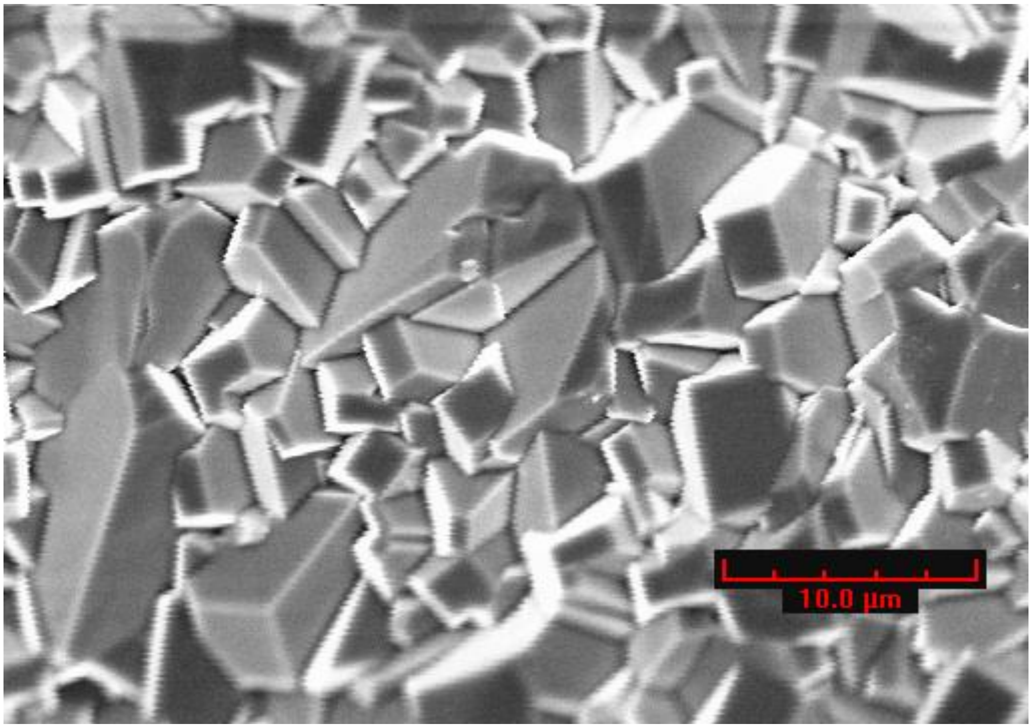


Figure 3-13: SEM of porous nickel after oxidation at 900 ℃ for 2 hours.

The porous plates were loaded with molten KOH, and used immediately every time. There are two ways to load KOH salt, which are described in some detail in Appendix A. The same silicone gasket, electrodes, and the automated testing routine were used in each test.

The experiments shown that the porous Ni plate fired at 800 ℃ for 2 hours was only partially oxidized on both sides of surface. Its electronic resistance was 0.4 Ω, which cannot to be used as support. Therefore, firing time of 5 hours and 12 hours were tried separately at temperature 800 ℃. For 900 ℃, firing time of 2 hours and 3 hours were tried. For the sample fired at 900 ℃ for 3 hours, the performance was low. The OCV would drop quickly with a very low current density, but once the load was taken away, the OCV would return to 1.03V and keep stable. It suggests that 3 hours firing time is too long at 900 ℃ to get a suitable disk, because the weak performance suggested the lack of electrolyte for the three-phase interface reaction.

The nickel oxidation rates and porosity changes for each sample were calculated by the changes of their weights and volume. The weight was measured by electronic balance, and side length of each plate was measured by vernier caliper in order to calculate the volume. For each sample, the original porosity $\emptyset_1$ and porosity after firing $\emptyset_2$ could be written as:

$$\emptyset_1 = 1 - \frac{m_1}{\rho_{Ni} \times V_1} \tag{15}$$

$$\emptyset_2 = 1 - \frac{(m_2 - m_1) \times M_{NiO}}{(M_{NiO} - M_{Ni}) \times \rho_{NiO} \times V_2} - \frac{(\frac{m_1}{M_{Ni}} - \frac{m_2 - m_1}{M_{NiO} - M_{Ni}}) \times M_{Ni}}{\rho_{Ni} \times V_2} \tag{16}$$

Where the m_1 is the original mass of nickel plate in g, m_2 is the mass after firing in g, V_1 is the original volume of the nickel plate, V_2 is the volume of the plate after firing, ρ_{Ni} is the density of nickel (g/cm^3), ρ_{NiO} is the density of nickel oxide (g/cm^3), M_{Ni} is the molar mass of nickel (g/mol), M_{NiO} is the molar mass of nickel oxide (g/mol). The nickel oxidation rate α could be written as:

$$\alpha = \frac{\frac{m_2 - m_1}{M_{NiO} - M_{Ni}}}{\frac{m_1}{M_{Ni}}} \times 100\% \tag{17}$$

The results are summarized below in Table 3-1. And the experimental results are shown following in Fig 3-12, 3-13, and 3-14.

	Ni Oxidation rate%	Porosity after firing%	Original porosity%
800 ℃-5hours	5.3	32.4	33.1
800 ℃-12hours	8.9	31.9	33.1
900 ℃-2hours	9.5	30.9	33.1
900 ℃-3hours	11.9	21.2	33.1

Table 3-1: Nickel oxidation rates and porosity changes with different firing process.

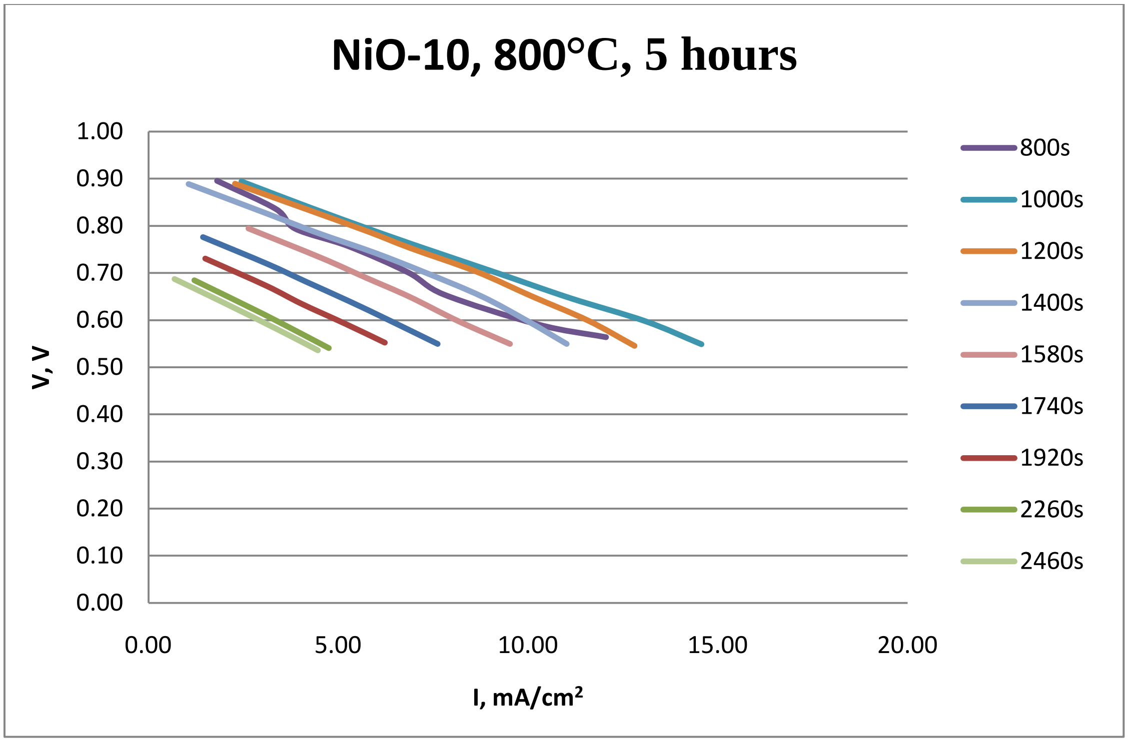


Figure 3-14: I-V curve of IT-MSFC with KOH molten salt supported by NiO-10 oxidized at 800 ℃ for 5 hours.

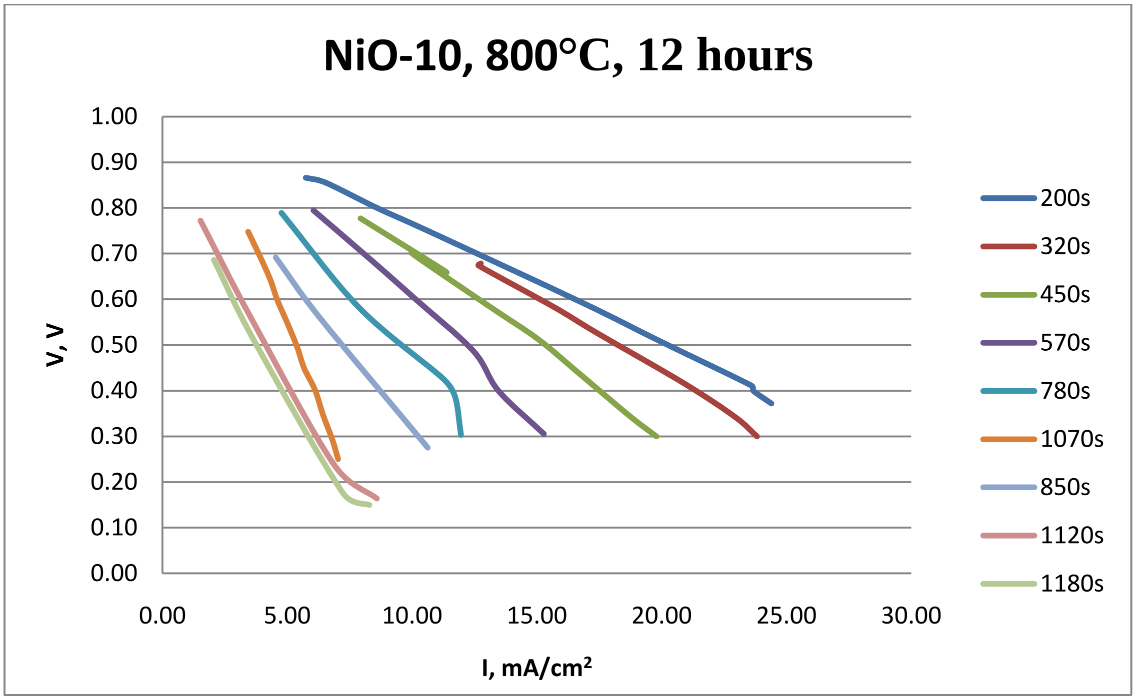


Figure 3-15: I-V curve of IT-MSFC with KOH molten salt supported by NiO-10 oxidized at 800 ℃ for 12 hours.

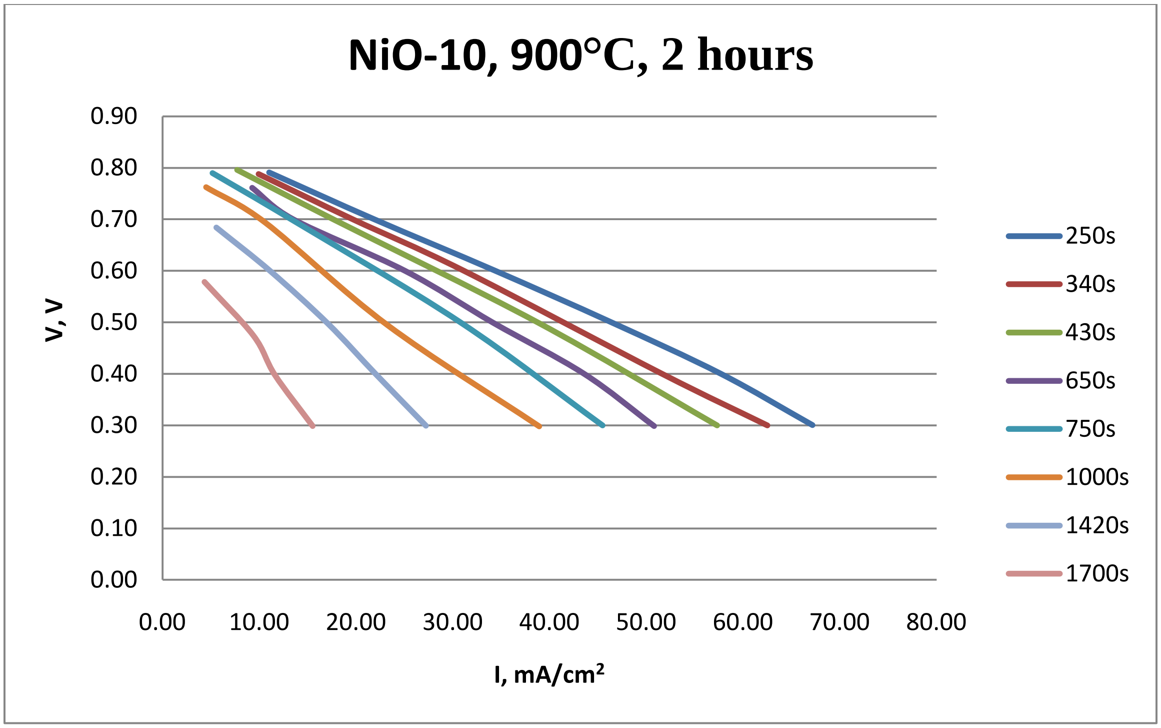


Figure 3-16: I-V curve of IT-MSFC with KOH molten salt supported by NiO-10 oxidized at 900 ℃ for 2 hours.

It was found that the disk fired at 900 ℃ for 2 hours provided the best performance, because it has relatively low pore size without losing high porosity (>30%) as shown in Table 3-1. Comparing to the zirconia-titania disk, the porous NiO plates showed a much better stability, which means the wettability of nickel oxide is better than zirconia-titania disk. Although the degradation occurred in each membrane, the lower porosity and pore size membrane provided the better performance. It further demonstrated that improvement of capillary action do as help the membranes get a better performance. However, the wettability and pore size were still not enough for preparing stable electrolyte layers.

The lower porosity and smaller pore size can be built by extending the burning time or raising their firing temperature properly. Firing at temperature of 800 ℃ seems gentle to modify the membranes; extending burning time may further improve the performance. But over firing may result in a porosity that is too low to infiltrate all the space with molten electrolyte inside the membrane.

For comparing with the traditional electrolyte, a test for the sample with 900 ℃ 2-hours firing loaded KOH saturated solution was conducted. The results are shown in Figure 3-15.

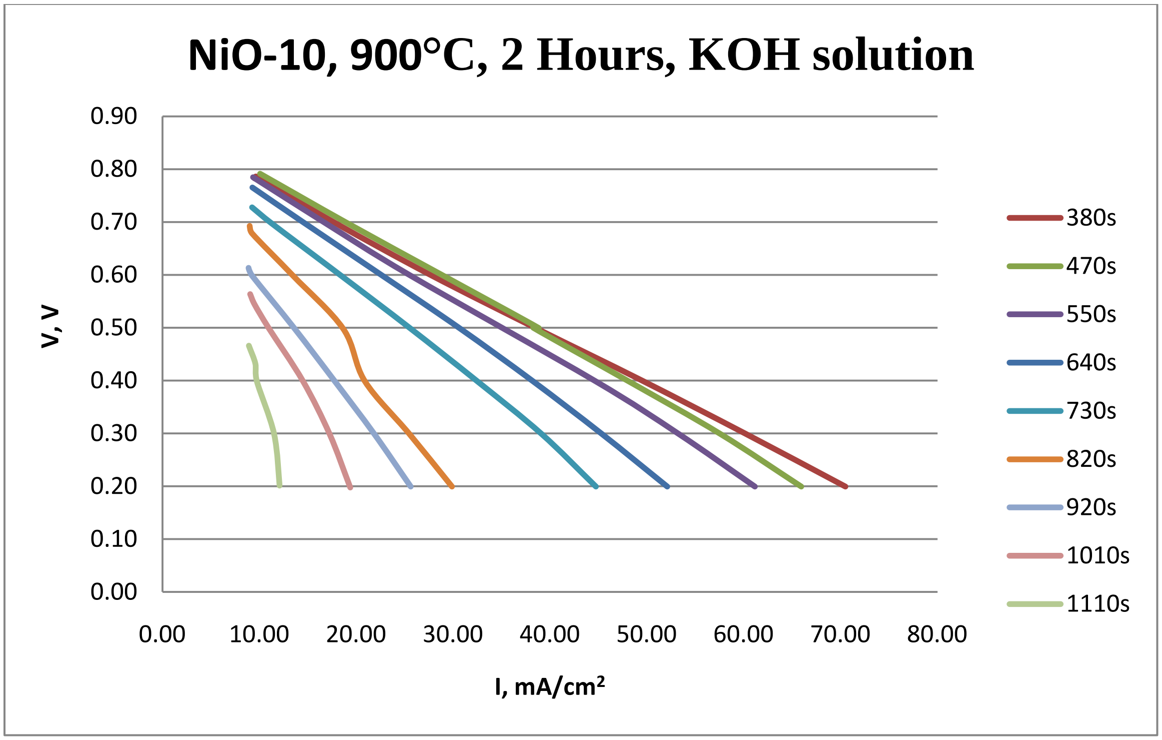


Figure 3-17: I-V curve of IT-MSFC with KOH saturated solution supported by NiO-10 oxidized at 900 ℃ for 2 hours.

At beginning, the samples had almost the same current density as KOH molten salt, with a stable OCV around 1.0, but degradation occurred more rapidly. Thus the molten salt KOH would be preferred electrolyte, although the KOH solution has a better wettability than the molten salt. In addition, all of the performance had linear performance curve between 1.0 V and 0.6 V, which is characteristic of fuel cells with low kinetic overpotentials.

On one hand, one of the main reasons for the irreversible degradation would still be the weak capillary action, which needs to be improved without sacrificing the porosity. On the other hand, wettability of electrolyte to the porous support seems not strong enough. That can be proved by the drop of OCV. The OCV were nearly 1.0V at the beginning in each NiO membranes tests, but it could not remain stable more than half an hour indicating increasing crossover. The decline might be also due to the water production, because the water will reduce the viscosity of electrolyte, making it easier for it to effuse from the porous structure.

Although the NiO support disks used have could not provide stable fuel cell, however the results are promising and it is possible that disks with lower pore size might work. None the less, lay of NiO in this manner is completely novel and promising because of good mechanical strength.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

The experiments described above have conclusively demonstrated the feasibility and the potential of using a supported molten salt electrolyte for good performance of a fuel cell within the intermediate temperature range. The primary challenge for IT-MSFC is the improvement of stability, which is directly related to the structural features and material properties of the support materials. Capillary action, wettability and the compatibility of the support material would be the three crucial factors for good performance and stability of IT-MSFC.

Several materials for support were tested as a part of this work. Because of its high porosity and the large pore size, zirconia felt showed good performance but poor stability. Zirconia-titania disks have a smaller pore size, but their poor wettability caused low uptake so that they did not work for molten salt with good results. Tests with the entirely novel porous nickel oxide plates demonstrated that the smaller pore size strengthen the capillary action, leading to improvement of performance and stability of the membrane. However the compatibility and wettability are still not good enough to allow the electrolyte to be retained within the porous matrix. Besides, it was suggested that the loss of porosity upon oxidation has a harmful effect on fuel cell operation due to the lack of electrolyte in the porous layer. Among the materials that have been tested, porous nickel oxide is still the most promising material as the electrolyte support for molten KOH-based IT-MSFC. It had linear performance curve between 1.0 V and 0.6 V, which is characteristic of fuel cells with low kinetic overpotentials.

To overcome this, a lot alternative materials can be considered as electrolyte support. Further, it is worth trying some optimization method for porous nickel oxide as well as other ceramic materials. Before the technique becomes practical, however, there is still a great amount of work required to be done on a suitable electrolyte support.

4.2 Future work

4.2.1 Modified support

According to the results from nickel oxide membrane, the performance changed significantly depending upon the preparation process. Comparatively lower firing temperature should provide better control for synthesis procedure to investigate this further. In addition, there are many other factors relative to the oxidization process, including the heating and cooling rates, firing time, and any additives. In order to increase the permeability and the compatibility of the support surface, some additives could be considered, either added in electrolyte or mixed with support matrix.

In thermal batteries, molten electrolyte needs to be retained by a binder. Few materials could be used as electrolyte binder including the SiO_2, metal oxides such as TiO_2, Y_2O_3, $LiAlO_2$, and MgO. MgO was found the most efficient material in the replacement of silica, because its solubility in molten alkali halides is considered to be low enough. For example, MgO in the LiCl-KCl eutectic, the solubility product ($pK= [Mg^{2+}][O^{2-}]$) was found to be equal to 7.2 at 450 ℃ and 8.38 at 700 ℃ [44].

The electrolyte binders are electrical insulators, but it have shown enhanced ionic conductivities and improved mechanical and thermal stability. The ceramic fillers such as Al_2O_3, CeO_2 and TiO_2 may also greatly influence the characteristic and the properties of polymer electrolyte enhancing the mechanical stability and the conductivity. A certain weight fraction of these particles is required because the liquid-phylic tendency of them may help in holding the liquid component within the membrane structure to obtain efficient electrolyte retention [43, 45].

Therefore, the amount of the binder electrolyte is one the most important parameters. If the ratio of binder is too high, it will induce an increase in the contact resistance, so that the ionic conductivity will decrease drastically. At the same time, the electrode wetting by the electrolyte may be more difficult. Further, the overall resistance of the battery would increase and the cell voltage decrease.

Numerous physical parameters influence electrolyte retention. Generally, the electrolyte and binder were fused in high temperature and then were quenched directly in the grinder, obtained by compaction of electrolyte and magnesia powders at room temperature.

In IT-MSFCs, the electrolyte binders might either added into electrolyte or replacing the porous support structure directly. Besides the materials mentioned above, some other ceramic powder could be considered as well.

4.2.2 PBI membrane

PBI membrane is well known to exhibit excellent thermochemical stability and mechanical properties. It possess excellent endurance both in alkali and acid from intermediate temperature to high temperature. Polybenzimidazole (PBI) is much cheaper and has much lower permeability for hydrogen than Nafion [46, 47].

Blank PBI is an electronic and ionic insulator, however, there are two imidazole groups (–N=, –N–) in one repeat unit of PBI. Therefore, it can become a very good ionic conductor by introducing inorganic hydroxides or acids. For instance, phosphoric acid doped PBI membrane is a very promising candidate for high temperature proton exchange membrane fuel cells (PEMFCs). Y.-L. Ma and his group demonstrated that PBI doped with high concentrations of phosphoric acid or sulphuric acid exhibited high ionic conductivity at 258 ℃. Besides, PBI fiber has been used as the matrix materials in alkaline fuel cells as well as alkaline direct ethanol fuel cell. It was found that KOH was distributed evenly in the matrix of PBI, and free or combined KOH molecules may be helpful for the ionic conductivity of PBI/KOH [48, 49].

On the other hand, high thermal stability up to 800 ℃ of the PBI/KOH has been proved, which was much higher than those of Nafion membrane and other quaternized anion exchange membrane. It means that the PBI/KOH membrane may be perfectly suitable for the temperature range of IT-MSFC [48, 49].

Currently, compared with acid or alkaline doped PBI membrane, there are no reports about molten salt doped PBI for fuel cell applications. Instead of using traditional electrolyte, molten salt may also work for PBI membrane.

4.2.3 Nickel catalyst and higher operation temperature

One of the main advantages of an IT-MSFC is the potential to use a nickel-based catalyst instead of platinum. The temperature range for nickel based catalysts will be much higher than platinum catalyst using currently. The current fuel cell assembly used in these tests uses a PTFE and silicon gasket and PTFE, kapton insulators, which limit its maximum operating temperature to approximately 260 °C. It may be possible to run at higher temperatures for brief tests, but no higher than 300 °C. This temperature range may not be high enough, and so an alternative gasket and insulator material will be necessary for experiments with nickel catalysts in this temperature range.

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Appendix A

Experimental Procedures

1. Zirconia Cloth Membrane Preparation Procedure

A. Treat membranes with zirconia solution one or more times.

B. Dry and fire treated membranes.

C. Load electrolyte into membrane.

A. Treatment of Zirconia Cloth

a. Cut 1 or more 2”×2” square of zirconia cloth type ZYW-30A.

b. Pour ZIR-RIG into clean Petri dish to a depth of approximately 1/4th inch. Ensure that the ZIR-RIG is well mixed prior to pouring, and close tightly afterwards.

c. Place a square of zirconia cloth into the Petri dish. Gently shake the dish horizontally so that the ZIR-RIG covers the zirconia cloth.

d. Using tweezers, remove the zirconia cloth from the ZIR-RIG, and lay it flat on a piece of fine-mesh stainless steel screen.

e. Using a hair-dryer on low heat, dry the top side of the membrane until it is no longer glossy. If the top is dried for too long at this stage it will stick to the screen.

f. Transfer the membrane to another piece of stainless steel screen, and dry the other side (The first piece of stainless steel screen may need to be washed before further use).

g. Continue drying the membrane, flipping frequently, until it is dry to the touch.

h. If multiple coatings are desired, repeat steps b-g.

B. Drying and Firing of treated Membranes.

a. Dry the membranes at 250 ℃ in a drying oven. They must be held flat during drying, which can be done by stacking any membranes prepared at the same time, with stainless steel screen between them, and placing a weight of some sort on top.

b. Fire the membranes in the high temperature furnace at 600 ℃ by placing them in the furnace before turning it on. As with the drying step, the membranes must be held flat, and the same methods work.

c. Turn the furnace off in 24 hours, and allow the membranes to cool without removing them from the oven.

C. Loading of Electrolyte

a. Weigh out 20-30 grams of the salts to be used into a ceramic crucible.

b. Heat in an oven at a temperature of 250 ℃. (higher than the melting point of the potassium hydroxide)

c. Wait until salt is entirely molten.

d. Set out two 3x3 pieces of aluminum, with a 3x3 piece of PTFE sheet on top of each.

e. Remove the crucible of molten salt from the oven using tongs

f. Working quickly, holds the membrane to be loaded with tweezers, and place an edge into the molten salt. The membrane will soak up the molten salt; there will be a visible change in color of areas which have soaked up the molten salt. If the molten salt does not wet the membrane, use the wet preparation method instead.

g. When about half of the membrane is wet with the molten salt, rotate the membrane 90 degrees and repeat. Do this for all 4 sides.

h. Place the membrane on top of one of the pieces of PTFE on top of an aluminum plate. Place the other plate on top of it.

i. Using tongs, place the prepared membrane and aluminum plates into the oven. Take care to ensure that the tongs do not have any of the salt on them from step g.

j. At this point, if the molten salt is still molten, another membrane may be prepared. Whether the salt stays molten long enough is dependent on ambient temperature and the temperature of the melt.

k. When the molten salt in the membrane has melted, the aluminum plates will be seen to be closer together and parallel. When this occurs, remove them from the oven, and place them on a flat surface, with a small weight of some sort on top of them to hold the membrane flat as the salt hardens.

l. When the aluminum plates are cool enough to touch, but still hot, take off the upper aluminum plate and PTFE sheet, and transfer the membrane directly and immediately to an airtight plastic bag. Ensure that there is no air in the bag before sealing it.

m. Allow crucible to cool to room temperature and wash. When working with molten hydroxides, the crucibles can only be used once in most cases.

n. Membranes prepared in this manner, and immediately sealed in a plastic bag will keep 2-4 weeks or more before use.

2. Zirconia-Titania Disk Membrane Preparation Procedure

A. Sanding.

B. Clean and dry membranes.

C. Load electrolyte into membrane.

A. Sanding.

a. Turn on the grind machine; hold the disk on the sand paper.

b. Measure the thickness by vernier caliper at least four points.

c. Stop grinding until the thickness match the target thickness.

d. Sanding the edges

When the aluminum plates are cool enough to touch, but still hot, take off the upper aluminum plate and PTFE

B. Cleaning and Drying Membranes.

a. Wash membrane with a 15-20g/L alkaline cleaning solution of sodium hydroxide (NaOH) at a temperature of 85 °C for 30 minutes in ultrasonic tank.

b. Rinse membrane with water until pH returns to neutral.

c. Wash membrane with a 5ml/L acid solution of nitric acid (HNO_3) or solution of 75% phosphoric acid (H_3PO_4) at a temperature of 50 °C for 15 min.

d. Rinse membrane with water until pH returns to neutral. They are now ready to be used.

e. Dry the membranes at 150 ℃ in a drying oven.

C. Loading KOH Molten-salt Electrolyte Into Membrane.

a. Put the membrane into a clean Petri dish.

b. Put enough KOH pellets on the top surface of the membrane. Heat them in an oven at a temperature of 250 ℃.

c. Wait until salt is entirely molten, turn-over the membrane, repeat the step b.

d. Take out the membrane and turn off the oven.

D. Loading Alkaline and Acid Solution Into Membrane.

a. Put membrane into solution and take them into ultrasonic tank for 30minutes.

b. Take it out, which is ready to test.

3. NiO Membrane Preparation Procedure

A. Cut the Ni plate into square by cutting machine.

B. Clean and dry membrane

a. Clean the membrane by DI water in ultrasonic machine for 30 minutes.

b. Clean the membrane by acetone solution in ultrasonic machine for 30 minutes.

c. Dry the membrane by hair dryer

C. Fire membranes in furnace with certain program – the rate of temperature increasing and decreasing are 10 ℃ per minute.

D. Loading of electrolyte is the same as the zirconia-titania disk

E. Or loading the electrolyte by vacuum bottle.

a. Put the membrane on the bottom of bottle with an inlet and an outlet.

b. Inlet connects to the concentrated KOH solution, and outlet pipe connect to the vacuum pump.

c. Close the inlet, Open the outlet and vacuum pump, until the pressure in bottle is no longer change.

d. Close the outlet, and Open the inlet, letting the membrane immersed in concentrated solution.

e. Take out the membrane and dry it in oven at 120 ℃.

f. Take out the membrane and weight its mass change by electronic balance.

g. Repeat the step a to step f until the weight change less than 0.5% and make sure the total weight is more than the porous membrane being pregnant with KOH molten salt.

4. Assembling Fuel Cell

a. Ensure that all components of the fuel cell assembly are present: Two graphite plates, two copper blocks, the two PTFE inserts for the graphite plates, the four bolts with insulators in good condition, the PTFE gasket, and the membrane itself.

b. Secure the cathode copper block in the vise. Place the cathode graphite plate on it, so that the tubes on the copper block engage the holes in the graphite plate. The plate will only fit one way, and the graphite plates are not interchangeable. Place one of the PTFE inserts in the hole in the graphite plate.

c. Put the four bolts with insulators on them through the holes in the anode copper block.

d. Cut two pieces of GDE, 0.875”x0.875”.

e. Place the large half of the PTFE gasket on the graphite plate.

f. Place a piece of GDE in the hole in the gasket, catalyst side up.

g. Wearing gloves, remove the membrane from the plastic bag. Once it has been removed from the bag, until it is covered in step k, work must be done quickly because the electrolyte is hygroscopic.

h. Place the membrane in the gasket. If it does not fit, quickly trim it using a sharp utility knife. It is best to score the gasket and then break it, rather than trying to cut through it entirely.

i. Place the other piece of GDE in the middle of the membrane, catalyst side down.

j. Place the other part of the gasket on top of the membrane, with the hole aligned with the GDE.

k. Place the graphite anode plate on top of the gasket/membrane/GDE assembly. Press down on it to ensure that there is no gap between the two parts of the PTFE gasket. If there is, remove the second part of the gasket, and place a thin PTFE gasket to fill the gap, and replace the top part of the gasket as in step j.

l. Lower the copper anode block onto the graphite plate. Ensure that the terminal screws are on the same side.

m. Hand-tighten the nuts on the four bolts, with a washer between the nut and the copper cathode block.

n. Tighten the bolts with 70 inch-pounds of torque using the torque wrench. Tighten the bolts in a diagonal pattern, to minimize chance of damage to the membrane due to uneven pressure.

o. Remove fuel cell assembly from the vice.

p. Place the two cartridge heaters into the holes on the sides of the copper blocks.

q. Insert the end of the yellow thermocouple into the thermocouple holes (located opposite one of the holes for the cartridge heater.

r. Wrap the cell tightly with insulation tape, such that the heaters and thermocouple are held in place by the heating tape.

s. Wrap both outlet tubes with a short length of insulation tape, and place a folded piece of insulation tape on the top side, directly on top of the graphite plates.

5. Operating Fuel Cell

a. Connect the inlet tubes from the fuel cell station to the fuel cell assembly. The anode (fuel) side is the one with an extra, sealed, tube coming from it. The fuel line is on the left side of the fuel cell test station, the oxygen line is on the right.

b. Connect the power cables from the fuel cell test unit to the fuel cell. Black wire is negative, and goes to the anode; red wire goes to the cathode.

c. Plug the thermocouple into the thermocouple plug behind the fuel cell assembly.

d. Plug the wires from the cartridge heater into the cord from the Variac. Do not turn on the Variac.

e. Turn on the power to the fuel cell station at the power strip and the switch on the front of the fuel cell test unit. If the voltage is reading a constant 0.000 volts, the cell is shorted out due to insulator failure. Disassemble cell, and replace or repair insulators if this is the case.

f. Place both outlet tubes into an Erlenmeyer flask partly filled with water, such that the ends are just submerged.

g. Start the fuel cell test program on the computer. Set the operating parameters.

h. Ensure that all valves on hydrogen, oxygen and nitrogen cylinders are closed.

i. Connect the end of the fuel and oxygen lines going to the fuel cell test station to the T on the end of the line from the nitrogen cylinder. Open the valves on the nitrogen cylinder.

j. On the computer console, start the fuel flow. This will of course only supply nitrogen. This helps to prevent clogs and establish a stable flow pattern. Verify that bubbles can be seen coming from both outlet tubes.

k. Turn the power switch on the Variac to the 120v position, and set the dial to 75.

l. Monitor the temperature of the fuel cell until it approaches the target operating temperature (within 10-15 degrees)

m. Stop the fuel flow at the computer console.

n. Working very quickly, turn off the valves at the nitrogen tank, and disconnect the fuel and oxygen lines from the T, and connect them to the oxygen and hydrogen tanks. Turn on the valves on the hydrogen and oxygen cylinder. Note that, like on the nitrogen cylinder, there are two valves on the hydrogen cylinder.

o. Restart the fuel flow.

p. When operating temperature is reached, turn the dial on the Variac to 55-65 (adjust as needed in this range to maintain operating temperature)

q. Begin tests from the computer console. The standard method for testing has been an Arbitrary Control test, using the IVCurve3.fcc control file. This is optimized for obtaining data over the whole voltage range in a fuel cell with rapidly changing (degrading) performance, and may not be appropriate once stability concerns have been addressed.

r. After the planned tests are completed, the fuel cell may be shut down. When working with fuel cells experiencing rapid degradation, the experiments have been terminated once the performance has degraded to the point where there it is felt that no more useful data will be obtained.

s. Stop the fuel supply at the computer console and close the fuel cell testing program.

t. Remove the outlet tubes from the flasks of water (if this is not done, when the power to the fuel cell test station is shut off, and the feed lines start to cool, a vacuum will be created and will suck water up into the fuel cell assembly).

u. Turn off power to the fuel cell test station at the power strip.

v. Allow assembly to cool.

w. Disconnect the fuel cell assembly from the test station and begin disassembly and cleaning.

6. Disassembly and Cleaning of Fuel Cell Assembly

a. When assembly is cool, unwrap the insulation tape, and remove the cartridge heaters and thermocouple.

b. Remove the nuts from all four bolts.

c. Separate the halves of the fuel cell by pulling on the copper blocks. Often times, one or both of the graphite plates will be stuck to the copper blocks Ċ this occurs due to electrolyte blowout, and is a sign of poor electrolyte retention during the test.

d. Separate the PTFE gasket, with the membrane inside it, from the two plates. In cases of severe electrolyte blowout, this may be difficult.

e. Peel off the sheet of PTFE gasket which is not stuck to the middle portion of the gasket with PTFE tape. Remove the membrane electrode assembly, and immediately store it in an airtight plastic bag for future investigation.

f. Rinse the surface of the graphite plates and both sides of the gasket with water to remove traces of the electrolyte.

g. If the graphite plates are stuck to the copper blocks, remove the terminal screw from the copper block, and soak it in water overnight. Other methods have been tried, but they do not work consistently.

h. Ensure that none of the inlet or outlet tubes are clogged. If they are, soak the tube (or the whole copper block assembly) in water overnight. Again, the terminal screw must be removed. If it is not, it will corrode significantly overnight by galvanic corrosion. In cases of severe clogs, it is sometimes necessary to replace the tube.

i. Dry all components thoroughly before they are used again.

7. Making New Insulators

From time to time, the insulators on the four bolts of the fuel cell assembly will wear through. They must be replaced. Rulon flange bearings available from Small Parts inc (part number U-FBP-4/8) offer an off-the-shelf solution, but they deform rapidly, and soon fail to provide insulation. In the absence of a permanent solution, insulators may be prepared expediently through this procedure.

a. Cut a 1 inch square of the 0.030 inch thick PTFE sheet for each insulator being made.

b. Cut a 2 inch length of 1 inch wide Kapton insulation tape for each insulator.

c. Wrap each piece of PTFE with Kapton.

d. Stack the insulators being produced atop each other.

e. Use a 1/4th inch diameter drill bit to bore a hole in the middle of each square. Because PTFE and Kapton are soft, no drill is needed ˙C it has been found to be easiest to simply work the drill bit by hand.

f. Place on bolt as shown below

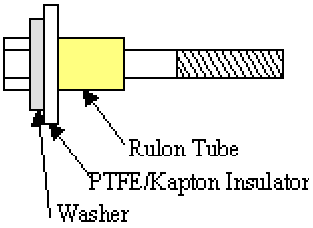

Figure A-1: Proper assembly of bolt and insulator