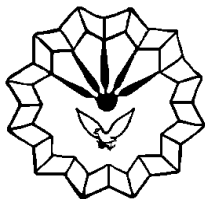


In the name of God

کلیه حقوق مادی مترتب بر نتایج مطالعات، ابتکارات و
نوآوری های ناشی از تحقیق موضوع این پایان نامه
متعلق به دانشگاه رازی است.



Razi University

Faculty of Engineering

Department of Chemical Engineering

Ph.D. Thesis

**Preparation and Characterization of Organic-Inorganic
Nanocomposite Membrane for Intermediate Temperatures
Application in PEM Fuel Cells**

Supervisor:

Prof. Sayed Siavash Madaeni

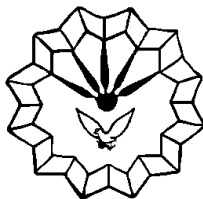
Advisor:

Dr. Ezzat Rafiee

By:

Mehdi Amirinejad

March 2011



Razi University

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Department of Chemical Engineering

Ph.D. Thesis

Preparation and Characterization of Organic-Inorganic Nanocomposite Membrane for High Temperatures Application in PEM Fuel Cells

By:

Mehdi Amirinejad

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March 2011

Acknowledgements

I would like to take this opportunity to express my sincere gratitude to my supervisor, Prof. Sayed S. Madaeni, for his encouragement, guidance and inspiration throughout my graduate career. His teachings and expertise have allowed me to grow as a person and a professional. I am grateful for all the years that I have shared with him.

I would also like to extend my thanks to my research advisor, Dr. Ezzat Rafiee, for her effort and guidance, without her this work would never be possible.

I would also like to thank the members of the thesis committee for their time and technical guidance.

I send my thanks to Prof. Bruno Scrosati and Prof. Jae-Suk Lee for accepting me as a researcher and providing facilities to perform experiments at University of Rome "La Sapienza" and Gwangju Institute of Science and Technology (GIST). The graduate students and researchers of these two institutes especially Dr. Maria Assunta Navarra for their kind help in both my research and personal life are gratefully acknowledged.

I would also like to thank all of my colleagues and friends at Razi University for their friendship and help with various tasks. Mr. Naser Tavajohi helped me to accomplish Neural Network modeling.

Nothing can be accomplished without family support. I would like to extend my special gratitude to my parents, wife's parents, my brothers and sisters for their neverending love, support and encouragement.

Many thanks are due to my wife Soudeh for understanding, her support, encouragement and patience especially during my stay in overseas when we are far from each other for long times without which I would not have succeeded this far. I am forever grateful for her.

Finally we are grateful to God, Prophet Muhammad and Ahlol-beit who continue to be our refuge and our guiding light.

Abstract

Heteropolyacids (HPAs) are nanosized metal–oxygen cluster anion acids stronger than the conventional solid acids. In this thesis, a series of organic-inorganic nanocomposite membranes for operation of proton exchange membrane fuel cells (PEMFCs) at high temperature/low humidity were prepared. Cesium hydrogen salt of heteropolyacids (CsHP) including $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ (CsPMo) and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) were incorporated into Nafion. The addition of hygroscopic and conductive CsHP enhances the water content but limits the activity of the sulfonic group of polymer matrix. Particles agglomeration and Nafion active sites (sulfonic groups) covering are seen in the nanocomposite membranes. The insoluble and high surface area solid acids CsPW and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (PWS) with different loadings are incorporated into end-group cross-linkable, sulfonated fluorinated biphenol (ESF-BP) copolymer. Thermal analyses, water uptake, ion exchange capacity (IEC), oxidative stability, mechanical property, proton conductivity in different condition and the single PEMFC performance are conducted to investigate the influence of HPAs additive on the prepared PEMs. Proton conductivity values were measured at different humidity and temperature conditions. The conductivity for nanocomposite membranes at anhydrous and high-temperatures condition (110 °C and 120 °C) is higher than the plain polymer due to the additional water retention or additional surface functional sites provided by HPAs. The fuel cell responses show that in the fully hydrated state and at the higher current densities, the prepared MEAs with nanocomposite membranes possess better response compared with the plain Nafion. In partially hydrated cell, at both low and high current densities, the superior performance of the MEA prepared by nanocomposite membranes was observed. The stability of single cells under a constant load demonstrates that the decay rate for recast Nafion membrane is rapid due to the dehydration. The covering effect for the CsPW particle is stronger than that for the CsPMo particle results in higher water uptake, IEC, the conductivity and the fuel cell performance and lower voltage decay for CsPMo/Nafion membrane rather than CsPW/Nafion membrane. The results of oxidative stability of membranes show that the CsPW/Nafion composite membrane has superior stability against oxidative agents due to the CsPW in lowering H_2O_2 diffusion and/or catalyzing the peroxide decomposition.

The FT-IR measurement of the prepared CsPW, CsPMo and PWS inorganic powders show that the primary Keggin structure remains almost unaltered. The molecular structure of ESF-BP copolymer is identified by ^1H NMR spectra. The addition of HPAs to the ESF-BP

polymer matrix increases glass transition temperature, tensile strength, oxidative stability, water uptake (slightly) and conductivity and decreases the IEC (slightly), membrane density and elongation at break.

The results of modeling of PEMFCs by multi-layer perceptron (MLP) and radial basis function (RBF) artificial neural networks and the adaptive network based on fuzzy interface system (ANFIS) show that the MLPNN can model the system with higher accuracy than the RBFNN but the required time for developing the RBFNN model is lower than the MLPNN due to the learning procedure. The ANFIS learning time and the accuracy are noticeably lower and higher than the RBFNN and the MLPNN, respectively. Novel nanocomposite membranes were prepared using polymer blend of polyethylene oxide (PEO) and polyvinylidene fluoride-chloro tetrafluoro ethylene (PVDF-CTFE) copolymer with CsPW as proton conductor by solvent-free procedure. The alteration of the conductivity in the range of temperatures in dry condition may be attributed to segmental motion of polymer which resulted in proton hopping from one site to another or increasing free volume for proton motion. In fully hydrated state, dynamic equilibrium between different proton moieties determines the mode of proton conductivity which can be described by Grotthuss mechanism. In the presence of water molecule, the free proton may be formed.

Keywords: Heteropolyacid; Nanocomposite membrane; Nafion; Proton exchange membrane fuel cell; Poly(arylene ether); Artificial neural network; Polyethylene oxide

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Chapter One

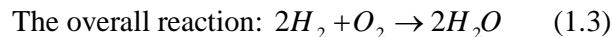
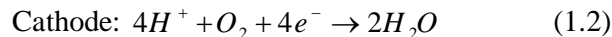
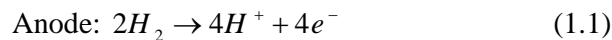
An Overview of Proton Exchange Membrane Fuel Cells

1.1. Introduction

Fossil fuels have provided a convenient and plentiful energy source, and have been used profitably in all sectors of the global economy. However, continued reliance on fossil resources causes several problems. First, worldwide oil demand continues to increase, and replacing the produced oil is technically and politically demanding and very capital intensive. Second, known fossil reserves are concentrated in only a few regions of the world. Oil and natural gas reserves, in particular, are in regions geographically separate from those undergoing the most rapid economic growth. Third, the widespread use of fossil fuels contributes to environmental disturbances, such as air pollutants and CO₂ [1].

Fuel cells will contribute to reducing the demands for fossil fuels [2]. A fuel cell directly converts chemical energy into electricity thereby eliminating the mechanical process steps that limit thermodynamic efficiency. It can be two to three times as efficient as the internal combustion engine with little or no emission of primary pollutants (CO, HC and NO_x) or greenhouse gas CO₂ [3].

The basic principle of a fuel cell is as follows. Hydrogen enters the pores of the anode and reaches the reaction zone and dissociates to H⁺ (see Fig. 1.1). The protons pass through the proton exchange membrane and electrochemically react with the reduced oxygen (from air) at the cathode, produce water:



There is a significant difference between a battery and a fuel cell. A battery has to store its chemical energy and the output will be depleted over time until eventually, the battery is totally discharged. If it is a rechargeable (secondary) battery it can be used again after charging, otherwise it has to be exchanged by a new battery (primary battery). A fuel cell, on the other hand, is continuously fed with a fuel, e.g. hydrogen which is stored outside of the cell. The process producing the electrical current continues for as long as there is a supply of reactants [4].

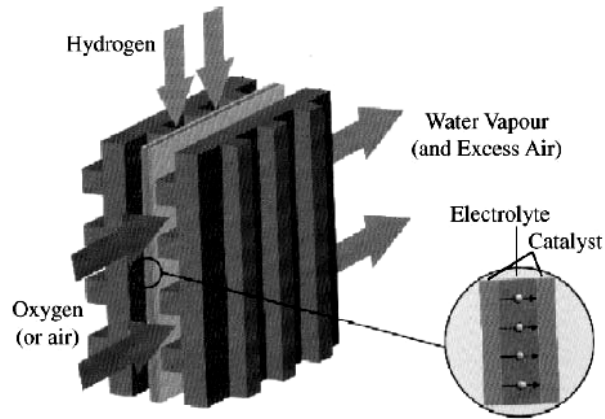
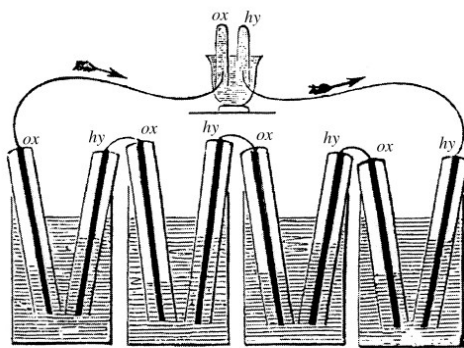
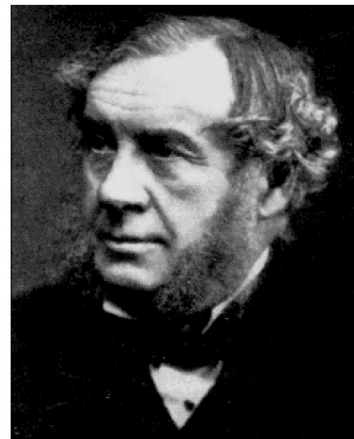


Fig. (1.1): The operating principle of a fuel cell [4]

The first fuel cell was demonstrated by Sir William Grove (Fig. 1.2) at the Royal Society of Chemistry in London in 1839 [5]. The catalysis pioneer Wilhelm Ostwald (1853-1932) was also involved in the early days of fuel cell development. Other important work in the late 19th century was performed by Walther Nernst (1864-1941) and Fritz Haber (1868-1934). All of these three German scientists were later together with Carl Bosch (1874-1940) involved in the development of the ammonia process, which would revolutionize the chemical industry in general and large-scale high pressure manufacture of chemicals in particular. The first practical alkaline fuel cell was developed by Francis T. Bacon (1904-1992) and co-workers at Cambridge University.



(a)



(b)

Fig. (1.2): (a) Grove's fuel cell, (b) Sir William Grove (1811-1896) [5].

1.2. Fuel cell benefits and limitations [6]

- Energy security: reduce oil consumption, and increase the amount of the country's available electricity supply.
- Reliability
- Low operating cost
- Constant power production: generates power continuously unlike backup generators, diesel engines or Uninterrupted Power Supply (UPS).
- Choice of fuel: allows fuel selection, hydrogen may be extracted from natural gas, propane, butane, methanol and diesel fuel.
- Clean emissions
- Quiet operations: quiet enough to be installed indoors, normal conversation possible near to fuel cell, and hearing protection is not required as for the combustion engines.
- High efficiency: converts up to 50–70% of available fuel to electricity and reduces fuel costs and conserves natural resources.

1.3. Types of fuel cells

Fuel cells are usually classified by the electrolyte employed in the cell [7]. A second grouping can be done by looking at the operating temperature for each of the fuel cells. There are, thus, low-temperature and high-temperature fuel cells. Low-temperature fuel cells are the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Membrane Fuel Cell (PEMFC), the Direct Methanol Fuel Cell (DMFC) and the Phosphoric Acid Fuel Cell (PAFC). The high-temperature fuel cells operate at temperatures approx. 600-1000 °C and two different types have been developed, the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). The electrolyte used in DMFCs, in most cases, is the same kind of membrane used in a PEMFC which is commonly referred to the fuel cell that uses hydrogen or hydrogen-rich gas (i.e., production from hydrocarbon reformers) as fuel.

Table (1.1) provides a summary of fuel cell types [8]. The electrolyte is provided in the first column. Selected operating parameters appear in the second column. The fuel listed is the crudest possible. AFCs, for example, require pure hydrogen, whereas the PAFC can tolerate hydrogen-rich gas from a hydrocarbon reformer. The reformat typically contains some impurities, such as CO, which can poison some fuel cells.

Table (1.1): Summary of fuel cell types [8]

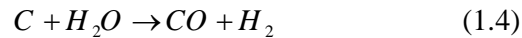
Fuel cell Electrolyte	Fuel oxidant T_{op} , η	Electrochemical reactions	Applications	Advantages	Disadvantages
<i>Alkaline</i> KOH (e.g.)	H ₂ Air <100 °C, <70%	Anode: $H_2 + 2(OH)^- \rightarrow 2 H_2O + 2e^-$ Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Space	Efficiency is highest of all fuel cells. Low operation capability reduces startup time. Technology has been successfully used in space	CO can poison the fuel cell so reformers are not yet suitable for delivery of H ₂ . CO ₂ in the reactants causes carbonation of the electrolyte
<i>PAFC</i> Phosphoric acid	H ₂ or Ref-H ₂ Air ~ 190 °C, <45%	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2O_2 + 2H^+ \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Electric utilities transportation	PAFCs contribute >90% of fuel cell electricity generation currently. Waste heat utilization increases system efficiency	Typically limited to >100 kW applications. Heat required for startup
<i>MCFC</i> Molten carbonate	Many Air ~ 650 °C, <60%	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ Cell ^a : $H_2 + 1/2O_2 + CO_2 \rightarrow H_2O + CO_2$	Electric utilities	High quality waste heat suitable for Brayton or Rankine combined cycle to boost system efficiency. Internal reforming allows fuels from H ₂ to diesel	High operating temperature leads to greater parasitic losses in small (kW) scale stacks. CO ₂ must be added to the air side. Heat required for startup. Special materials required
<i>SOFc</i> Solid oxide (yttria-stabilized zirconia)	Many Air ~ 1000 °C, <60%	Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Cathode: $1/2O_2 + 2e^- \rightarrow O^{2-}$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Electric utilities	High quality waste heat suitable for Brayton or Rankine combined cycle to boost system efficiency. Internal reforming allows fuels from H ₂ to diesel	High operating temperature leads to greater parasitic losses in small (kW) scale stacks. Heat required for startup. Special materials required
<i>PEMFC</i> Proton exchange membrane	H ₂ or Ref-H ₂ Air <100 °C, <55%	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2O_2 \rightarrow H_2O$	Transportation Portable power Electric utilities	Low temperature leads to short startup time. Receiving most attention for mW–100 kW applications. Operating temperature is increasing for better waste heat utilization	Water management (Nafion hydration) is a major issue. CO poisoning is a problem with reformat
<i>DMFC</i> Proton exchange membrane	Methanol Air <100 °C, <55%	Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Cathode: $O_2 + 4H^+ + 4e^- \rightarrow H_2O$ Cell: $CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$	Portable power	Same as PEMFC. DMFC has additional advantages such as liquid fuel increasing power density per system volume and convenient refueling	Direct methanol fuel cell is less efficient and has less power density. Liquid methanol crossover reduces efficiency

^a CO₂ is produced at anode and circulated to cathode.

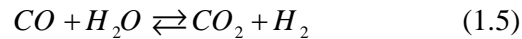
1.4. Hydrogen production [9-11]

Of the present, world-wide production of hydrogen (around 50 million tonnes per annum), over 90% comes from raw fossil materials. In energy terms, hydrogen equates to around 5% of the world's oil consumption.

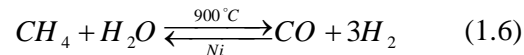
The gasification of coal is the oldest means of obtaining hydrogen from fossil fuels. When heated in a restricted supply of air (so-called 'destructive distillation' or 'pyrolysis'), coal is converted to mixture of hydrogen, methane and carbon monoxide (typically, 50, 35 and 8%, respectively), together with coal tar and coke. Alternatively, when heated coal is reacted with steam the 'water-gas reaction' occurs:



The water-gas reaction is highly endothermic. Conversely, the combustion of coal or coke in air is highly exothermic. It is, therefore, usual to pair off the two reactions so as to balance the heat evolved with that absorbed. The two reactions may be conducted consecutively in short bursts or, more usually, simultaneously by feeding a mixture of air and steam to the heated bed. The resulting gas is a mixture of CO, H₂, CO₂, and N₂. This may be upgraded in terms of hydrogen content by the 'water-gas shift reaction'. The gas is reacted with steam over a catalyst that converts carbon monoxide to carbon dioxide and increases the amount of hydrogen:



The steam reforming of natural gas is the most efficient and widely used process for making hydrogen. At present, it is also the cheapest route. The methane is reacted with steam and air over a nickel-based catalyst:



The resulting product is known as 'synthesis gas' (or 'syngas'). As with the gasification of coal, steam reforming can be combined with the water-gas shift reaction (reaction 1.5) to increase the yield of hydrogen. Steam reforming is very energy-intensive since it operates at high temperatures (850–950 °C) and high pressure (3.5 MPa). The thermal efficiency can reach 60–70%.

A third method is 'partial oxidation' in which fuel and oxygen are combined in proportions such that the fuel is converted into a mixture of hydrogen and carbon monoxide. The amount of hydrogen is only about 75% of that produced by steam reforming (but of course the content can be increased via the water-gas shift reaction). The