Polymers for Energy Storage and Conversion
Polymer Science and Plastics Engineering

The "Polymer Science and Plastics Engineering" series publishes both short and standard length monographs, textbooks, edited volumes, practical guides, and reference works related to all aspects of polymer science and plastics engineering including, but not limited to, renewable and synthetic polymer chemistry and physics, compositions (e.g. blends, composites, additives), processing, characterization, testing, design, and applications. The books will serve a variety of industries such as automotive, food packaging, medical, and plastics as well as academia.

Series Editor: Srikanth Pilla, PhD
Wisconsin Institute for Discovery
University of Wisconsin-Madison
pilla@wid.wise.edu

Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)
1 High Performance Polymer Hydrogel Based Materials for Fuel Cells
Yogeshwar Sahai and Jia Ma
1.1 Introduction 1
1.2 Hydrogel Electrolyte 3
1.3 Poly(vinyl alcohol) Hydrogel 4
  1.3.1 Chitosan-based Hydrogel in Fuel Cells 9
  1.3.2 Chitosan Membrane for Polymer Electrolyte Membrane Fuel Cell 10
  1.3.3 Chitosan Membrane for Alkaline Polymer Electrolyte Fuel Cell 17
  1.3.4 Chitosan for Fuel Cell Electrode 18
Summary 19
References 20

2 PVAc Based Polymer Blend Electrolytes for Lithium Batteries
M. Ulaganathan, R. Nithya and S. Rajendran
2.1 Introduction 27
  2.1.1 Polymer Electrolytes 29
  2.1.2 Role of Polymers in Electrolyte 32
  2.1.3 Polymers 33
  2.1.4 Advantages of Polymer Electrolytes in Battery 39
  2.1.5 Poly Vinyl Acetate (PVAc) 39
  2.1.6 PVAc Based Polymer Electrolytes 40
  2.1.7 Surface and Structural Analysis 47
Conclusion 49
References 49
3 Lithium Polymer Batteries Based on Ionic Liquids 53
S. Passerini, M. Montanino and G.B. Appetecchi

3.1 Lithium Batteries 54
3.1.1 Introduction 54
3.1.2 Lithium Polymer Batteries 57

3.2 Lithium Polymer Batteries Containing Ionic Liquids 61
3.2.1 Ionic Liquids 61
3.2.2 Ionic Liquid-Based Polymer Electrolytes 62
3.2.3 Ionic Liquid-Based, Lithium Polymer Battery Performance 88

Glossary 94
References 96

4 Organic Quantum Dots Grown by Molecular Layer Deposition for Photovoltaics 103
Tetsuzo Yoshimura

4.1 Introduction 104
4.2 Molecular Layer Deposition 105
4.3 Concept of Solar Cells with Organic Quantum Dots 107

4.4 Polymer Multiple Quantum Dots 110
4.4.1 Fabrication Process and Structures 110
4.4.2 Structural Confirmation of Polymer MQDs 115
4.4.3 Photocurrent Spectra 118
4.4.4 MLD on TiO₂ Layer 119

4.5 Molecular Multiple Quantum Dots 120
4.5.1 Fabrication Process and Structures 120
4.5.2 Structural Confirmation of Molecular MQDs 123
4.5.3 Photocurrent Spectra 124

4.6 Waveguide-Type Solar Cells 127
4.6.1 Proposed Structures 127
4.6.2 Photocurrent Enhancement by Guided Lights 129
4.6.3 Film-Based Integrated Solar Cells 130

4.7 Summary 135
References 135

5 Solvent Effects in Polymer Based Organic Photovoltaics 137
Matthias A. Ruderer and Peter Müller-Buschbaum

5.1 Introduction 137
5.2 Solar Cell Device Structure and Preparation
5.3 Spin-Coating of Active Layer
5.4 Influence of Solvent on Morphology
  5.4.1 Crystallization Process and Cluster Formation
  5.4.2 Lateral Structures
  5.4.3 Vertical Material Composition
  5.4.4 Mesoscopic Morphology
5.5 Residual Solvent
  5.5.1 Absolute Solvent Content in Homopolymer Films
  5.5.2 Lateral Solvent Distribution
5.6 Summary
Acknowledgment
References

6 Polymer-Inorganic Hybrid Solar Cells
Ashish Dubey and Qiquan Qiao
6.1 Introduction
  6.1.1 Hybrid Solar Cell
  6.1.2 Semiconducting Conjugated Polymers
  6.1.3 Inorganic Semiconductors
  6.1.4 Solar Cell Device Characterization
6.2 Hybrid Conjugated Polymer-Inorganic Semiconductor Composites
  6.2.1 Inorganic Semiconductor in a Bilayer Structure
  6.2.2 Inorganic Semiconductor as a Blend with Conjugated Polymer
  6.2.3 Inorganic Metal Oxide as Charge Transport Layer
6.3 Conclusion
References

7 Semiconducting Polymer-based Bulk Heterojunction Solar Cells
Matthew Schuette White and Niyazi Serdar Sariciftci
7.1 Introduction
7.2 Optical Properties of Semiconducting Polymers
7.3 Electrical Properties of Semiconducting Polymers
7.4 Mechanical Properties Polymer Solar Cells 208
7.5 Processing of Polymers 210
7.6 State-of-the-art of the Technology 212
References 213

8 Energy Gas Storage in Porous Polymers 215
Joel Fawaz, Kean Wang and Ali Almansoori
8.1 Introduction 216
8.2 Microporous Organic Polymers 217
  8.2.1 Polymer of Intrinsic Microporosity 218
  8.2.2 Conjugated Microporous Polymers 222
  8.2.3 Hypercrosslinked Polymer 231
  8.2.4 Covalent Organic Frameworks 238
8.3 Characterization of MOPs 239
Conclusion 242
List of Abbreviation 242
References 243

Index 249
Preface

Polymers are increasingly finding applications in the areas of energy storage and conversion. A number of recent advances in the control of the polymer molecular structure control which allows the polymer properties to be more finely tuned, have led to these advances and new applications. This book is an attempt to assimilate these advances in the form of a comprehensive text which includes the synthesis and properties of a large number of polymer systems for applications in the areas such as lithium batteries, photovoltaics, solar cells.

Chapter 1 introduces the structure and properties of polymer hydrogel with respect to its applications for low to intermediate temperature polymer electrolyte-based fuel cells. In recent years, there has been extensive research on the development of high performance electrochemical devices which can generate and store energy at low cost. Fuel cells have been receiving attention due to their potential applicability as a good alternative power source. Chapter 2 describes PVAc-based polymer blend electrolytes for lithium batteries. Among the different kinds of batteries, Li-ion secondary batteries play a key role in the development of modern technologies especially in the portable electronic devices and in heavy electrical vehicles because of advantages such as high theoretical capacity, improved safety, lower material costs, ease of fabrication into flexible geometries, and the absence of electrolyte leakage. Chapter 3 reviews the lithium polymer batteries based on ionic liquids. A very promising approach for overcoming the existing drawback is represented by the addition of ionic liquids, as co-salts, into the polymer electrolytes. Ionic liquids, molten salts at room temperature, have very interesting properties such as high chemical, thermal and electrochemical stability, high conductivity, no measurable vapor pressure and non-flammability. In Chapter 4, the concept of the solar cell with the organic multiple quantum dots (MQDs) is proposed. Next, molecular layer deposition (MLD)
processes for the polymer MQDs and the molecular MQDs are described, and experimental results of absorption spectra and surface potential are presented to confirm that designed MQD structures are constructed by MLD actually. In Chapter 5, solvent effects in polymer-based organic photovoltaic devices are discussed. The example of using solvents with different boiling points (choice of solvent) to control the morphology and crystallinity due to the evaporation rate and interaction with the polymers are discussed. Moreover, solvent molecules remaining inside the active layer are presented. Chapter 6 suggests that conjugated polymer-inorganic semiconductor composite has come a long way and still remains a matter of research interest, so as to exploit unique properties of conjugated polymers and inorganic semiconductors in single and tandem devices. Numerous challenges still exist to obtain device performance matching to polymer-fullerene counterpart cells. However, with further engineering of polymer and inorganic materials, followed by effective device design and processing steps, there is still room to raise device performance with new breakthroughs. Chapter 7 provides an overview of the properties of the polymers which factor into their use for solar power, whether for niche applications or for large scale harvesting. Chapter 8 reviews the use of macroporous organic polymers as promising materials for energy gas storage with the distinguished advantage in the diversity in synthetic chemistry and versatility in post-modifications.

Vikas MITTAL
Abu Dhabi
February 20, 2013
List of Contributors

Ali Almansoori holds a PhD in chemical engineering from Imperial College, London. He is currently an Associate Professor and Chairman of the Chemical Engineering Department at the Petroleum Institute in Abu Dhabi. His main research interest is the area of process systems engineering. He also conducts general research in the area of hydrogen systems and storage. He has published 15 refereed journal articles, 2 book chapters, and more than 20 conference presentations.

Giovanni Battista Appetecchi graduated in industrial chemistry in 1993 and has been working since 1992 on basic and applied research devoted to electrochemical energy storage systems. He is author/co-author of about 120 publications in peer reviewed international scientific journals, 2 book chapters, 103 communications, 2 invited lectures and 2 patents.

Ashish Dubey is a graduate student in the Department of Electrical Engineering at South Dakota State University. He received his Master degree in nanotechnology from Amity University, India. His research interests include, organic-inorganic hybrid solar cells, morphological studies of donor-acceptor blend films, and their optical and electrical characterization.

Joel Fawaz graduated with a BS in chemical engineering (Honors with Distinction) from the Petroleum Institute, Abu Dhabi, U.A.E. She was in the Provost’s list during all her student years (2008-2011). She completed her internship at the University of Minnesota, U.S. Currently, Ms. Fawaz is pursuing a Master of Science in chemical engineering at the Petroleum Institute. Her research interests include polymers, catalysis and reaction engineering.
Jia Ma received her PhD in materials science and engineering from the Ohio State University under the supervision of Dr. Yogeshwar Sahai. Dr. Ma is working as a postdoctoral researcher on the development of polymer membrane and electrode for fuel cells. She is the first author of eight journal papers.

Maria Montanino obtained her doctorate degree in chemical science in 2007. As a researcher at ENEA, she is working on the research and development of electrochemical storage systems based on ionic liquids. She is the co-author of 30 manuscripts in peer reviewed international scientific journals and 2 book chapters.

Peter Müller-Buschbaum is full university professor at Technische Universität München, heading the Chair of Functional Materials in replacement for Professor Petry, and heads TUM Solar and the network ‘Renewable Energies’ of the Munich School of Engineering. He has 211 peer-reviewed publications to his credit and his research focus is on polymer and hybrid nanostructures.

R. Nithya is working as a lecturer in the Department of Physics, Shanmuganathan Engineering College, Pudukkottai, Tamil Nadu, India. The author has completed her MSc in physics during the year of 2008 where she was awarded University 1st Rank (Gold medallist). She has also completed her M.Phil in physics at the Alagappa University in 2009. The author has also published many research articles in various reputed international journals.

Stefano Passerini is a professor in the Institute of Physical Chemistry and co-founder of the MEET battery research centre at the University of Muenster, Germany. His research activities are focused on electrochemical energy storage in batteries and supercapacitors. He is the co-author of more than 200 scientific papers, a few book chapters and several international patents. In 2012 he was awarded the Research Award of the Electrochemical Society Battery Division. Since 2013 he has been appointed has European Editor of Journal of Power Sources.

Qiquan Qiao is an assistant professor in the Department of Electrical Engineering and Computer Sciences at South Dakota State University. He was a recipient of the 2011 College of Engineering Young Investigator Award. Dr. Qiao was granted an Early Career Award from the National Science Foundation, and in
2009 he received the Bergmann Memorial Award from the US-Israel Bi-national Science Foundation.

S. Rajendran is a professor and has been associated with the research in the field of solid state Ionics for more than 32 years. He has guided 12 scholars for PhD programme and 48 scholars for M.Phil programme. At present, he is guiding 7 PhD scholars. He has been awarded various fellowships like INSA, KOSEF, and has published 103 research articles in various international journals and presented more than 100 papers at many national and international conferences.

Matthias A. Ruderer received his Doctorate Degree in Physics from the Technische Universität München (TUM) in 2012 with the highest distinction. His main research interest is the investigation of the structure-function relationship of polymer-based photoactive films. To date Matthias A. Ruderer has published 24 peer-reviewed publications in the field of polymer physics.

Yogeshwar Sahai is a Professor in the Materials Science & Engineering Department at The Ohio State University, Columbus, USA. He obtained his PhD from Imperial College of Science and Technology, University of London, England in 1979. His research is in clean energy areas, including fuel cells, batteries, polymeric electrolyte membranes, and catalysts for electrochemical applications. Dr. Sahai has published over 140 technical papers in peer reviewed journals and refereed proceedings, and has published 5 books and 5 patents.

Niyazi Serdar Sariciftci is a full professor in the Institute for Physical Chemistry at the Johannes Kepler University in Linz, Austria. He is the founder and head of the Linz Institute for Organic Solar Cells (LIOS). In 2010, he was ranked 14th of the top 100 material scientists by ISI. In 2012 he received the highest Austrian award for science, the Wittgenstein Prize.

M. Ulaganathan is currently working as a Research Fellow in the Energy Research Institute at the Nanyang Technological University, Singapore. The author has published many research articles in the fields of polymer electrolytes, fuel cells in many international journals. One of his research articles published in Materials Chemistry and Physics was placed in the hottest top-25 articles list during the
period of July-September 2011. Nowadays, the author is mainly concentrating in the field of redox flow batteries especially in vanadium redox flow batteries, flexible Li-ion full cell batteries, ion exchange membranes, gel electrolytes for Li-ion batteries.

Kean Wang is an associate professor in the Department of Chemical Engineering at the Petroleum Institute, Abu Dhabi. His research areas include membrane separation and adsorption science. He has published 4 book chapters, more than 70 research papers and has been awarded one patent. Energy gases (CH$_4$ and H$_2$) storage in nanoporous adsorbents is one of his key research interests.

Matthew White is an assistant professor in the Institute for Physical Chemistry at the Johannes Kepler University in Linz, Austria. He received his Bachelor’s degree in physics and mathematics from the University of Washington in 2003, and his PhD in Physics from the University of Colorado, Boulder in 2009.

Tetsuzo Yoshimura received BSc from Tohoku University and MSc and PhD in physics from Kyoto University. He then joined Fujitsu Laboratories and Fujitsu Computer Packaging Technologies, Inc., San Jose, California. He is a professor in Tokyo University of Technology and studies molecular layer deposition and self-organized optical circuits for photovoltaics and optical interconnects.
High Performance Polymer Hydrogel Based Materials for Fuel Cells

Yogeshwar Sahai and Jia Ma

Department of Materials Science & Engineering, The Ohio State University, Columbus OH USA

Abstract
In recent years, there has been extensive research on the development of high performance electrochemical devices which can generate and store energy at low cost. Fuel cells have been receiving attention due to its potential applicability as a good alternative power source. Polymer hydrogel electrolyte is prospective material to deliver high performance at low cost in fuel cells which use polymer membrane as electrolyte and separator. This chapter introduces structure and properties of polymer hydrogel with respect to its applications for low to intermediate temperature polymer electrolyte-based fuel cells.

Keywords: Fuel cell, polymer hydrogel, electrolyte

1.1 Introduction

A fuel cell is an electrochemical device that produces electrical energy via electrochemical reactions between the fuel and the oxidant. Unlike a battery, which stores a finite amount of energy, a fuel cell continues to produce energy as long as the oxidant and the fuel are fed into it. Energy generation from combustion in a heat engine is intrinsically inefficient and also causes environmental problems. On the contrary, a fuel cell is inherently energy efficient, environmentally friendly, and silent.

The polymer electrolyte-based fuel cell employs a polymer membrane as the electrolyte. Compared to other types of fuel cells, it
is capable of achieving reasonably high power performance at relatively low working temperatures, and thus is considered a promising power supply for transport, stationary, and portable applications. The major component of a fuel cell is the membrane electrode assembly (MEA) which consists of solid polymer electrolyte membrane (either a cation exchange membrane (CEM) or an anion exchange membrane (AEM)) sandwiched between an anode and a cathode. An electrode generally consists of a catalyst layer and a diffusion layer. The catalyst layer must have facile transport of reactants and products as well as good ionic and electronic conductivity. Therefore, the catalyst layer should have high porosity and large electrochemically active surface area. The solid polymer electrolyte membrane should have good ionic conductivity and no electronic conductivity. For such an application, an ideal solid electrolyte membrane should fulfill a number of requirements including high ionic proton conductivity, long-term chemical and mechanical durability under heated and humidified conditions. A primary goal is to find stable polymer-based materials with ionic conductivities within the range of $mS \text{ cm}^{-1}$ at temperatures up to 100°C [1]. Ionic conductivity of many polymeric membranes, increases with its water content, and thus hydration is of significance to achieve high conductivity, especially at high temperatures. Perfluorinated ionomers, such as Nafion, with fluoroalkyl ether side chains and sulphonylic acid end groups on polytetrafluoroethylene backbones, have been the most commonly used polymer electrolyte membrane so far. Nafion material is also used as an electrode binder which facilitates ionic conduction, provides mechanical support for catalyst particles, and enhances dispersion of catalyst particles in the catalyst layer. Nafion possesses many desirable properties as a polymer electrolyte, and yet it is very expensive and loses ionic conductivity if not sufficiently hydrated. For application in a polymer electrolyte-based fuel cell using methanol as the fuel or direct methanol fuel cell, solid polymer electrolyte membrane also needs to have low methanol permeability. However, Nafion membrane has relatively high methanol crossover.

Research has been going on in the development of high-performance, cost-effective polymer-based membrane electrolyte as an alternative to Nafion for use in polymer electrolyte-based fuel cells. Hydrogel polymer electrolyte has high potential for applications in fuel cells. This chapter introduces structure and properties of polymer hydrogel electrolyte with respect to its applications in fuel cells.
1.2 Hydrogel Electrolyte

Hydrogel is macromolecular network that is capable of trapping large amount of water or biological fluids [2]. The three-dimensional network of hydrogel is insoluble in the precursor solution due to the presence of chemical cross-links, and/or physical entanglements [3]. Chemical hydrogels are formed by covalent cross-linking reaction between the polymer and a cross-linking reagent, whereas physical hydrogels are stabilized by physical entanglements, electrostatic attractive forces, and hydrogen bonding. The schematic diagram of a chemical hydrogel with point cross-links and a physical hydrogel with multiple junction zones are shown in Figure 1 (a) and (b), respectively. In Figure 1(a) the solid lines represent polymer chains that constitute the hydrogel matrix. The solid dots in the cross-link points of the polymer helices represent the cross-links formed by chemical reaction between the polymer and cross-linker. In Figure 1(b) the solid lines represent the polymer helices aligning themselves laterally in extended junction zones.

Many hydrogels have been found to possess the ability of easy film making, good ionic conductivity, and ionic exchange property [5], which have led to their applications in many electrochemical energy devices. Gel electrolytes based on poly (ethylene oxide), poly (acrylonitrile), poly (methyl methacrylate), and poly (vinylidene fluoride) have been employed in solid-state lithium-ion batteries [6, 7]. One way of producing hydrogel membranes is entrapping

![Figure 1.1](image-url)  
**Figure 1.1** Schematic diagram of (a) a chemical hydrogel with point cross-links, and (b) a physical hydrogel with multiple-junction zones [4].
of an aqueous solution of strong electrolyte with a polymeric matrix. It was found that polyacrylamide-based hydrogels doped with \( \text{H}_3\text{PO}_4 \) exhibited ionic conductivities in the range of \( 10^{-3} \text{--} 10^{-2} \text{ S} \cdot \text{cm}^{-1} \) at room temperature [8]. Another method to produce polymeric hydrogel membranes is introduction of copolymers based on highly conducting monomers. Hydrogel electrolyte membranes containing highly conducting sulpho group was prepared by radical copolymerization of sodium styrenesulphonate or potassium sulphopropyl acrylate with acrylamide and acrylonitrile [9]. These membranes are capable of holding water at temperatures 70--90\(^\circ\)C and have an ion exchange capacity of \( 0.8\text{--}1.4 \text{ mg-equiv/g} \).

A number of polymeric materials are employed to produce hydrogel electrolyte. This chapter does not intend to review all reported polymer hydrogel materials for fuel cell applications, but concentrates on poly(vinyl alcohol) and chitosan since they are cost-effective materials which have been intensively investigated for fuel cell applications.

### 1.3 Poly(vinyl alcohol) Hydrogel

Poly(vinyl alcohol) (PVA) discovered in 1924, is one of the most widely investigated polymers for hydrogels [10]. It is a cheap, nontoxic, and chemically stable synthetic polymer used in a wide range of industrial, commercial, medical, and food applications [11]. General chemical and physical properties of PVA are summarized in Table 1. PVA is prepared by hydrolysis or partial hydrolysis of

| **Table 1.1** General chemical identity and physical properties of polyvinyl alcohol. |
|----------------------------------|---------------------------------|
| **Molecular weight**             | 30,000--200,000                 |
| **Structural formula**           | \((\text{-CH}2\text{CHOH})_n\cdot\text{-CH}2\text{CHOCHCH}_3\)\_m            |
| **Physical appearance**          | Odorless, white to cream colored granular powder |
| **Specific gravity**             | 1.19--1.31                      |
| **Solubility**                   | Insoluble in aliphatic and aromatic hydrocarbons, esters, ketones, and oils, water soluble |
polyvinyl acetate. Different length of the initial vinyl acetate polymer and the degree of hydrolysis under alkaline or acidic conditions yield PVA of differing physical properties.

Pure PVA does not possess intrinsic protonic conductivity. However, several organic functional groups, such as sulfonate, hydroxyl, amine, carboxylate, phenolic, and quaternary ammonium salts can be incorporated into PVA to enhance its proton conductivity and hydrophilicity. Some of the sulfonating agents for modification of PVA are shown in Figure 2 [12]. Cross-linking is one way to modify the polymer properties, such as degree of swelling, thermal, chemical, and mechanical stability, methodology adopted

![Diagram](image_url)

Figure 1.2 Chemical modification of PVA to introduce sulfonate groups [12].
to impart proton conductivity. For instance, cross-linking decreases water solubility or swelling, and yet excessive cross-linking leads to brittleness of polymer membrane. PVA can be cross-linked in a variety of ways like freezing, heat treatment, irradiation, and chemical treatment. Some typical examples are shown in Figure 3.

The -OH groups of PVA react with -CHO groups of certain aldehydes to form acetal or hemiacetal linkages under acidic conditions [13]. The resultant polymeric entity is water insoluble and gel like in nature. The cross-linking reaction between PVA and glutaraldehyde leading to the formation of PVA chemical hydrogel is schematically depicted in Figure 4. PVA chemical hydrogel was employed as electrode binders for an alkaline fuel cell using borohydride as the fuel or a direct borohydride fuel cell (DBFC) [14, 15]. As indicated in Figure 5, a high power density of PVA binder-based DBFC was achieved. The PVA chemical hydrogel in an inverted glass beaker is shown in Figure 6, where a Teflon-coated magnetic stirring bar that was used to mix solutions of PVA and glutaraldehyde is seen stuck within the hydrogel at the bottom of the beaker. This figure clearly shows the solid nature of PVA chemical hydrogel, and it also makes it easier to understand how the electrode materials are held within the hydrogel and bound to the carbon cloth substrate in the
Figure 1.4 Reaction between glutaraldehyde and PVA leading to the formation of PVA chemical hydrogel.

Figure 1.5 Plots of cell voltage and power density versus current density for DBFCs with PVA chemical hydrogel binder-based electrodes at different operating cell temperatures [15].
actual electrode while allowing transport of any water-soluble species such as ion, fuel or oxidant to the catalyst. In addition to the electrode binder, a PVA hydrogel was used to cast as electrolyte membrane by a solution casting method. Sahu et al. characterized the PVA membrane using different techniques [16]. The scanning electron micrograph reveals a smooth surface of the PVA membrane with no defects. The X-ray diffraction pattern of PVA membrane exhibits broad peaks at 2θ values of 11°, 20° and 41°, respectively. The broad peaks in the XRD pattern indicate a partially amorphous nature of the PVA membrane. The thermogravimetric analysis of acidic PVA membrane shows a weight loss of about 10% in the temperature range between 30 and 150°C due to evaporation of surface and moderately bound water. The PVA membrane undergoes total thermal oxidation at temperature between 150 and 470°C due to the decomposition of its polymer chains. The midpoint ASTM glass transition temperature for PVA membrane is 108.26°C. The Young’s modulus and proportional limit stress values for PVA membrane are 3.24 and 0.977 MPa, respectively. The water uptake value for PVA membrane is about 1.3 g H₂O/g PVA hydrogel membrane. A PVA hydrogel membrane was employed in a DBFC and delivered peak power densities comparable to the Nafion membrane (Figure 7) [17]. For membrane application in direct methanol fuel cells for which proton conductivity and methanol crossover are of significance, PVA membranes are becoming competitive with respect to the state of art Nafion membranes [12].
Figure 1.7 Curves of cell polarization and power density of a DBFC using a PVA hydrogel membrane electrolyte (PHME) or a Nafion membrane electrolyte (NME) with oxygen as the oxidant at 60°C [17].

1.3.1 Chitosan-based Hydrogel in Fuel Cells

Cost-effective and eco-friendly polymer electrolytes from renewable sources can become a promising substitute for synthetic polymers for use in fuel cells [18]. Chitosan (CS), a polysaccharide bioresource, has been attracting considerable interest as solid polymer electrolyte and binder material in low and intermediate temperature polymer electrolyte-based fuel cells. Chitosan (Figure 8) is a hydrophilic, inexpensive, biodegradable, and non-toxic natural polymer that is derived by deacetylation of chitin [poly(N-acetyl-d-glucosamine)] [19]. Chitin, which is present in the exoskeleton of arthropods, is the second most abundant natural biopolymer next to cellulose. Characteristics of CS are influenced by a number of parameters such as its molecular weight and degree of acetylation [19]. CS contains hydroxyl (–OH), primary amine (–NH₂), and ether (C–O–C) groups, and due to the presence of these functional groups, CS has high water attracting capacity. The –OH and –NH₂ functional groups in
CS enable various chemical modification of CS to tailor it for specific applications [20–23]. Chemical modifications, such as sulfonation [24–26], phosphorylation [27–30], and quaternization [31, 32] possibly generate ion exchange sites and improve ionic conductivity. However these chemical modifications also increase swelling of chitosan and as a result have negative effect on its mechanical strength. CS membranes are normally cross-linked before being employed in fuel cells. Cross-linking is a common chemical modification to ensure good mechanical and chemical stability of CS. In cross-linked CS, polymer chains are interconnected by cross-linkers to form three dimensional networks. Main interactions forming the network are covalent or ionic bonds. In addition, some secondary interactions, such as hydrogen bridges and hydrophobic interactions, also occur in CS networks [33]. Dialdehydes, such as glyoxal and glutaraldehyde [34], diethylene glycol diglycidyl ether [35], and epichlorohydrin are used to form covalent linkage in CS chains [36]. CS dissolved in weak organic acid solution becomes polycationic which can form ionic cross-links with a number of cross-linking reagents, such as acids of sulfate ions, phosphate ions, and sulfosuccinic ions.

1.3.2 Chitosan Membrane for Polymer Electrolyte Membrane Fuel Cell

Various CS-based membranes, both anionic and cationic, have been extensively examined for fuel cell applications. Table 2 lists some properties of CS-based polymer membrane for applications in fuel cells. These CS-based membranes generally do not offer significant
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionic conductivity, S cm(^{-1})</th>
<th>Methanol permeability, cm(^{2}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO(_{4})</td>
<td>2 x 10(^{-2}), hydrated, 60°C</td>
<td>8.0 x 10(^{-7}) to 1.2 x 10(^{-7}) mol L(^{-1}) MeOH, 20°C</td>
</tr>
<tr>
<td>CS-glutaraldehyde-sulfosuccinic acid</td>
<td>4.52 x 10(^{-2}), hydrated, 25°C</td>
<td>9.6 x 10(^{-7}), hydrated, 25°C</td>
</tr>
<tr>
<td>CS/PAA</td>
<td>2.49 x 10(^{-2}), hydrated, RT</td>
<td>0.49 to 1.03 x 10(^{-2}), 30% MeOH</td>
</tr>
<tr>
<td>CS/Sodium alginate</td>
<td>4.2 x 10(^{-2}), hydrated, RT</td>
<td>3.9 x 10(^{-2}), 30% MeOH</td>
</tr>
<tr>
<td>CS/(AA-AMPS)</td>
<td>3.59 x 10(^{-3}), hydrated, 30°C</td>
<td>4.6 x 10(^{-2}), 30-32°C, 50% MeOH</td>
</tr>
<tr>
<td>CS/PVP</td>
<td>2.4 x 10(^{-2}), hydrated, RT</td>
<td>2.41 x 10(^{-2}), 50% MeOH</td>
</tr>
<tr>
<td>CS/phosphorylated titanate nanotube</td>
<td>1.58 to 1.75 x 10(^{-2}), hydrated, 20°C</td>
<td>7.3 x 10(^{-3}), hydrated, 30°C</td>
</tr>
<tr>
<td>CS/Beta Zeolite-SO(_{4})</td>
<td>1.17 x 10(^{-2}), 1.49 x 10(^{-2}), hydrated, 20°C</td>
<td>5.8 to 9.55 x 10(^{-2}), 2M MeOH</td>
</tr>
<tr>
<td>CS/polyacrylic acid</td>
<td>1.14 x 10(^{-2}), 1.86 x 10(^{-2}), hydrated, 30°C</td>
<td>2.7 x 10(^{-2}), hydrated, 25°C, 1M</td>
</tr>
<tr>
<td>CS/SPAEEK</td>
<td>3.9 to 4.4 x 10(^{-2}), hydrated, 25°C</td>
<td>2.81 to 9.79 x 10(^{-7}), 25°C</td>
</tr>
<tr>
<td>CS/Nafion triple layer</td>
<td>8.8 x 10(^{-2}), 95% RH, 25°C</td>
<td>2.52 x 10(^{-7}), hydrated, 25°C</td>
</tr>
<tr>
<td>CS-Adenosine triphosphate/Nafion</td>
<td>1.58 x 10(^{-1})</td>
<td>1.58 x 10(^{-1})</td>
</tr>
</tbody>
</table>

Ref: 39, 40, 41, 43, 45, 46, 47, 44, 52, 55, 56, 58, 61, 64, 67
advantages over traditional Nafion membrane, as far as proton conductivity is concerned. In its dry state, CS has a very low electrical conductivity. However, CS can be used as a polymer matrix for ionic conduction. It was found that when solvated with lithium salt or proton donor salts such as ammonium salts [37, 38], ionic conductivity of CS membrane was enhanced. Due to intrinsic hydrophilic nature of CS, it is able to significantly reduce methanol crossover, which makes CS a suitable material for use in a DMFC. For instance, sulfuric acid cross-linked CS membrane was found to have methanol permeability almost three times lower than that for Nafion 117 membrane [39, 40].

Cross-linking reagent has impact on properties of CS membrane electrolyte. It was found that introducing sulfosuccinic acid as crosslinker in addition to glutaraldehyde improved proton conductivity, and yet also increased methanol permeability as compared to using glutaraldehyde alone. Chemical structure of sulfosuccinic acid and glutaraldehyde cross-linked CS is shown Figure 9. A peak power density of 41 mWcm$^{-2}$ was achieved by a sulfosuccinic acid and

![Figure 1.9 Structure of cross-linked CS, I: amino and aldehyde groups reaction; II: ionic interaction of sulfosuccinic acid and CS [41].](image)