بسم الله الرحمن الرحيم

Development of Polymer Polyelectrolyte Membranes for Direct Methanol Fuel Cell Application

A Thesis

SUBMITTED

BY

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B.Sc. Chemistry (2006)

M.Sc. Chemistry (2013)

TO

FACULTY OF SCIENCE

Ain Shams University

FOR THE DEGREE OF Ph.D

(Chemistry)

2017

APPROVAL SHEET FOR SUBMISSION

Title of Ph.D. Thesis:

‘Development of Polymer Polyelectrolyte Membranes for Direct Methanol Fuel Cell Application’

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Acknowledgment

I thank **"Allah"** for supporting me in everything in my life.

Actually there are many people to whom I owe a great deal of thanks for helping me achieve this degree. First, I would like to express my deepest sincere gratitude and appreciation to ***Prof. Dr. Ahmed Ismail Hashem*** Professor of Organic Chemistry, Faculty of Science, Ain Shams University, for his Interest in the work, guidance, revising the work, and correcting the thesis till it reached its present form. ***Prof. Dr. Mohamed Samir Mohy Eldin***, Head of Polymeric Material Department, Advanced Technology and New Materials Research Institute, City for Scientific Research and Technological Applications (SARTA city). ***Prof. Dr. Mohamed El sayed Youssef,*** Acting vice dean of Information Research Institute, City for Scientific Research and Technological Applications (SARTA city) and ***Dr. Ahmed Omer***, Assistant professor at Advanced Technology and New Materials Research Institute, Polymeric Material Department, SARTA city for their strong support and encouragement me. Special thanks for my husband ***Dr. Tamer Mahmoud,*** Assistant professor at Advanced Technology and New Materials Research Institute, Polymeric Material Department, SARTA city for his unlimited helpful assistance and continuous guidance to perform this work.

Also, I would like to thank my family : specifically my father, my aunt, my aunt's husband and my grandmother for their continuous support and encouragement. I also want to thank my sisters *Heba* and *Walaa* and my lovely kids *Rodina, Mahmoud* and *Mohamed.*

I wish to recognize my staff friends in City of Scientific Research and Technological applications (SARTA- city). Finally, my thanks are also due to everyone who presented me any help, advice, service and assistance in this work.

Maysa

Abstract

Fuel cells are environmental friendly devices for energy conversion, power generation, and one of the most promising candidates as zero-emission power sources. One of the main drawbacks of the fuel cells is related to the use of the liquid electrolyte. Using a polymer membrane as an electrolyte can solve some limiting requirements of fuel cells. In the resent study, new cheaper polyelectrolyte complex membranes based on renewable natural polymer (chitosan and alginate) was prepared by physically and chemically crosslinking for direct methanol fuel cell (DMFC). Four sets of membranes were prepared. Two of them based on physically crosslinking of chitosan/alginate and sulfonated chitosan/ alginate, and the others based on chemically crosslinking of the same pairs using glutaraldehyde. The membranes were characterized by FTIR to verify complex formation, XRD to observe the effects of modification on crystallinity, TGA to assess the thermal stability, SEM for morphological structure and tensile testing for mechanical stability. Absorption studies were carried out to evaluate the interaction with water and methanol. Finally, methanol permeability of membranes was tested and compared with that published for commercial fuel cell membrane (i.e.; Nafion)

Keywords: Fuel cells; Polyelectrolyte membranes; Ion exchange capacity; Chitosan; Alginate; Methanol permeability.

SUMMARY

Direct methanol fuel cells (DMFCs), which use methanol as the fuel, have many advantages over other fuel cell systems because methanol has a high energy density and is liquid at room temperature. DMFC has paid the considerable attention and developed very quickly because of the abundance source, low price, safe transportation and storage of methanol, and, therefore, it is attractive for portable application such as laptop and mobile phone. However, DMFC still has some problems that need to be solved. One is the methanol crossover from the anode side to the cathode through the mostly used Nafion membranes. That led to lowering the efficiency of the cells as a result of fuel losses at the anode and mixed potential formed by methanol oxidation at the cathode.

The polymer electrolyte membranes (PEM) for direct methanol fuel cell application must have essential characters such as improved methanol barriers, and proton transportation, cost effectiveness, and adequate mechanical and chemical stability for prolonged DMFC operation. Accordingly to the growing needs for PEM, a new polymer electrolyte membrane (PEM) based on new polyelectrolyte complex membranes of chitosan and alginate prepared by physically and chemically crosslinking for direct methanol fuel cell (DMFC) was investigated. To achieve this goal this study was divided into three parts:

Firstly, Chitosan–sodium alginate membranes were prepared by solution casting-solvent evaporation technique. The chitosan and low molecular weight sodium alginate (or activated alginate) blend solutions were prepared.

Secondly, preparation of a water-soluble chitosan derivative with highly ion exchange capacity based on N-alkyl sulfonation process. Various sulfonation degrees of sulfonated chitosan (SC) were obtained via chemical reaction of chitosan (Ch) with1, 3-propane sultone, where alkyl sulfonic groups hanging the side chain of chitosan through a ring-opening reaction.

Thirdly, preparation of alginate sulfonated chitosan membranes physically and chemically as PEMFC. Proton exchange membrane was

produced with four variations of sulfonated chitosan substitutions (0, 0.5, 1 and 2) without and with glutaraldhyde.

The Physico-chemical changes in poly ion complex membranes structure and properties as a result of modification investigated in this task. Infrared spectroscopic analysis (FTIR) along with thermal gravimetric analysis (TGA), morphological characterization (SEM) and X-Ray diffraction analysis (XRD) were used to provide evidence for the occurrence of functionalizations. The structure of sulfonated chitosan was verified also with using the elemental analysis.

Also, the effect of the water/methanol uptake behaviour, optical properties, wettability, IEC, mechanical stability properties and methanol permeability were studied.

The study revealed the following points:

There are many membranes used in PEM fuel cell.

- **Nafion** is the most common and commercialized used as PEM for DMFC. Nafion has sulfonic groups which can transfer hydrogen ion.
- Disadvantages of Nafion
    1. High methanol permeability.
    2. High cost of membrane. It costs about 700 $ US per square meter.

In this thesis, the work is focused on development of polyelectrolyte membranes based on natural polysaccharides such as chitosan and alginate to replace Nafion. These membranes might have the following advantages:

1. low cost of membrane which extract from crab shells
2. Low methanol crossover.

- The methanol permeability for all modified membranes was found to be less than that of Nafion® 117 membranes.

The study has succeeded to introduce solutions for both problems that decrease the efficiency of DMFCs and produce cheaper and cleaner PEM to be used in fuel cell.

List of abbreviation

Abbreviations

AFC	Alkaline fuel cell
Alg	Alginate
AMCA	Aminated cellulose acetate
CO_2	Carbon dioxide
Cs	Chitosan
CD	Cyclo dextrins
DCAA	dichloroacetic acid
DMFC	Direct methanol fuel cell
DMSO	dimethyl sulfoxide
FC	Fuel cell
FT-IR	Fourier Transform Infrared Spectroscopy
GA	Glutaraldehyde
GDLs	Gas diffusion layers
GRAS	Generally Recognized as Safe
IEC	Ion exchange capacity
IMFC	Indirect methanol fuel cell
NOCC	N,O-carboxymethyl chitosan
PECs	Polyelectrolyte complexes
PEMFCs	Polymer electrolyte membrane fuel cells
PEMs	Polymer electrolyte membranes
PGA	Propylene glycol alginate
SC	Sulfonated Chitosan
SEM	Scan Electron Microscope
TBAF	tetrabutylammonium fluoride
TGA	Thermal Gravimetric Analysis
TS	Tensile strength
XRD	X-Ray Diffraction Analysis

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