RADIATION GRAFTED BI-FUNCTIONAL CATION EXCHANGE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

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Choose an item.

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DEDICATION

This thesis is dedicated to my late father, Hamzah bin Jaafar who taught me that the best kind of knowledge to have is learned for its own sake. It is also dedicated to my mother, husband and son, who taught me that even the largest task could be accomplished if it is done one step at a time.

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ABSTRACT

Vanadium redox flow battery (VRFB) utilizing cation exchange membrane (CEM) has the potential as a non-degradable large-scale energy storage for sustainable energy. Nafion with PTFE backbone with the acidic sulfonic groups is the most common membrane for VRFB. However, Nafion is expensive, and suffers from vanadium ion crossover, produces low ion selectivity results in severe capacity decay and voltage declination in an open circuit, and these drawbacks lead to self-discharge. Polymer-based radiation grafted membrane with two-functional groups of monomer collaborated cells is considered as one alternative to overcome the weakness of Nafion. This research produced a reduced-crossover vanadium ion membrane that has commercial value through one-step pre-irradiation grafting of two functional groups of monomers onto the ETFE polymer backbone. The modification of ETFE membrane was completed by one-step radiation grafting polymerization process. The manipulation of the two types of monomers, types of solvents used, reaction time and temperature were optimized to obtain the targeted degree of grafting. The targeted grafting yield of <180% poly (ethylene tetrafluoroethylene)-g-styrene sulfonic acid-g-N-Vinyl formamide (ETFE-SSS-VNF) was successfully achieved. Characterization analysis of the membranes using FTIR and XPS analyses showed the new peaks from SSS and NVF monomers marked the attachment of C=O, O-H, N-H stretching and S=O functional groups onto ETFE film. The cross-section of modified membrane through FESEM-EDS and mapping displayed the monomers were well distributed through ETFE membrane. The modified ETFE membrane exhibited extremely low vanadium crossover while sustaining high conductivity. In the single-cell VRFB test, the modified membrane provided higher coulombic efficiencies up to 96%, and energy efficiencies (EE: 81-84%) higher than commercial membrane N117(EE: 59.7-60.8%) at a current density of 40 mA/cm^2. Incorporating -SO$_3$ group from SSS monomers and -N-C=O group from NVF monomers provided high proton conductivity and hindered vanadium ion crossover, demonstrating their high performance as a potential ion exchange membrane for VRFB application. The modification of ETFE membrane with low vanadium ion crossover is a promising new CEM for VRFB application.

ABSTRAK

Bateri aliran redox vanadium (VRFB) menggunakan membran penukaran kation (CEM) mempunyai potensi sebagai penyimpanan tenaga berskala besar yang tidak terdegradasi untuk tenaga lestari. Nafion dengan tulang belakang PTFE dengan kumpulan sulfonik berasid adalah membran yang paling biasa untuk VRFB. Walau bagaimanapun, Nafion adalah mahal, dan mengalami lintasan ion vanadium, menghasilkan selektiviti ion yang rendah, mengakibatkan pereputan kapasiti yang teruk dan penolakan voltan dalam litar terbuka, dan kelemahan ini membawa kepada nyahcas sendiri. Membran cantuman sinaran berasaskan polimer dengan dua kumpulan berfungsi monomer sel bekerjasama dianggap sebagai satu alternatif untuk mengatasi kelemahan Nafion. Penyelidikan ini menghasilkan membran ion vanadium terkurang ketelapan yang mempunyai nilai komersial melalui cantuman pra-penyinaran satu langkah dua kumpulan berfungsi monomer pada tulang belakang polimer ETFE. Pengubahsuaian membran ETFE telah diselesaikan dengan proses pempolimeran cantuman sinaran satu langkah. Manipulasi kedua-dua jenis monomer, jenis pelarut yang digunakan, masa tindak balas dan suhu telah dioptimumkan untuk mendapatkan tahap cantuman yang disasarkan. Sasaran untuk darjah penggrafan di bawah 180% oleh ETFE membran yang telah diubahsuai berjaya dicapai. Analisis FTIR dan XPS menunjukkan kumpulan fungsi dari monomer seperti C=O, O=H dan N=H serta S=O telah berjaya dilampirkan di permukaan ETFE. Membran ETFE ynag diubahsuai mempamerkan ketelapan vanadium ion yang rendah serta mengekalkan konduktiviti proton yang tinggi. Di dalam ujian satu sel bateri VRFB, membran yang diubahsuai mempamerkan kecekapan coulumbic yang tinggi sehingga 96 % dan kecekapan tenaga membran pada 81- 84 % lebih tinggi berbanding membran komersial N117 pada skala 40 mA/cm^2 ketumpatan aliran. Pemerbadanan fungi kumpulan -SO^3 dari monomer SSS dan -N-C=O dari kumpulan monomer NVF mempamerkan ketahanan proton yang tinggi serta ketelapan vanadium yang rendah. Mengubahsuai polimer ETFE kepada CEM menjanjikan membran yang berkualiti dan bagus untuk aplikasi VRFB. Proses mengubah suai ETFE membrane yang bercirikan ketelapan vanadium yang rendah merupakan CEM baharu yang telah dihasilkan serta berpotensi dan sesuai untuk aplikasi VRFB.

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LIST OF ABBREVIATIONS

AIEM	-	Amphoteric Ion Exchange Membrane
AIBM	-	azoisobutylronitrile
AEM	-	Anion Exchange membrane
ATRP	-	Atom transfer radical polymerization
BPO	-	Benzoyl peroxide
CEM	-	Cation exchange membrane
EES	-	Electrical Energy Storage
VRFB	-	Vanadium Redox Flow Battery
SSS	-	Styrene Sulfonic Acid
NVF	-	N-vinyl Formamide
PEM	-	Proton Exchange Membrane
RFB	-	Redox Flow Batteries
RIGP	-	Radiation-induced Graft Polymerization
PTFE	-	Polytetrafluoro-ethylene
ETFE	-	Polyethylene-tetrafluoroethylene
DMSO	-	Dimethyl sulfoxide
DMF	-	Dimethylformamide
FTIR	-	Fourier-transform Infrared spectroscopy
TGA	-	Thermogravimetric
FESEM	-	Field emission scanning electron microscope
EDS	-	Energy Dispersive X-ray Spectroscopy
XRD	-	X-ray Diffraction
IEC	-	Ion-Exchange Capacity
WU	-	Water uptake
PC	-	Proton conductivity
CE	-	Coulumbic Efficiency
VE	-	Voltage Efficiency
EE	-	Energy Efficiency

LIST OF SYMBOLS

σ - Proton conductivity

Ω - resistance

L - Thickness

A - Area

P - Permeability

C_R (t) - Vanadium ion concentration in right reservoir

C_L - Vanadium ion concentration in left reservoir

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CHAPTER 1

INTRODUCTION

1.1 Research Background

High demand for large scale energy storage has become the first concern to integrate renewable energy sources into the electricity grid. Electrical energy storage (EES) can make the electricity market more efficient, cleaner and sturdy. By making these power resources more stable and disposable, the EES system can significantly strengthen the power quality and reliability of the electricity supply system.

The commercialised viable power plant needs uninterrupted fuel sources such as burning coal, using natural gas, or adopting uranium isotopes as nuclear energy. Conventional energy is non-renewable, high emission of greenhouse gas and is hazardous to a living organism. Pointing to providing power into important areas like electricity generation, water heating and cooling, transportation and rural, non-conventional, renewable energy storage is needed to meet the demand of the increasing population. Using alternative and sustainable energy storage proves that it is relatively safer for the environment and cost-efficient. Even the auto industry now is towards zero-emission technology to protect the ecosystem by using a 100% electric power system and genially adopting solar and wind energy technology to charge the car. Redox flow battery is one of the renewable energy storage system.

Among all redox flow batteries available, vanadium redox flow batteries (VRFB) are the high potential alternative devices for energy storage systems. It has become more attractive since Skyllas-Kazacos proposed it in 1985 due to its good long life and low maintenance cost compared to other redox flow batteries. VRFB is suitable for large scale energy storage systems due to its broad range of energy capacity with proven performance and fast response time. It is the most promising energy storage device with reliability, durability and safety. VRFBs possessed a long cycle-life and high efficiencies due to the truancy of electrode intercalation/deintercalation, and the electrolytes are not cross-contaminated with each other and straightforward heat management (Wang *et al.* 2020b; Zhang *et al.* 2021; Xu *et al.* 2022). Prudent Energy in the United States is a company that has to widen its market in Asia and Canada, offers VRFB-energy storage systems. They have installed 50 VRFB systems at utility and commercial customer sites in 12 countries worldwide. The aggressive use of VRFB as an energy storage system shows the demand for an energy storage solution has increased. Despite these advantages and information, VRFB systems are relatively high in cost. Fundamental changes to VRFB cell design are required to enable intrusive improvement of the operating power system. Figure 1.1 below is the vanadium redox flow battery.

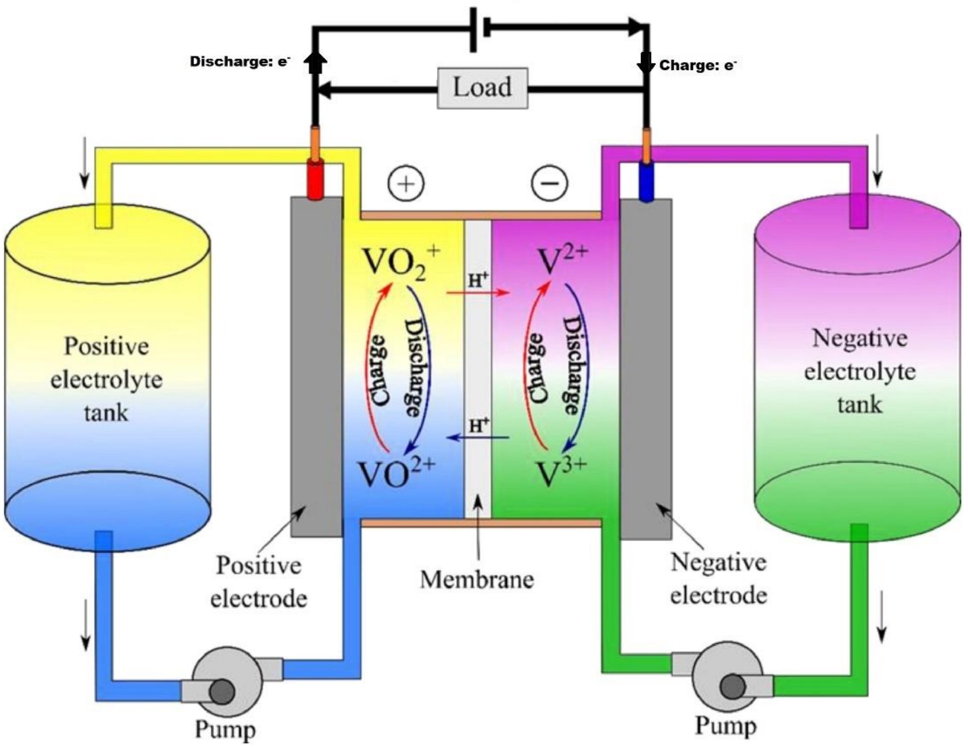

Figure 1.1 The illustration single-cell VRFB system.

The membrane is the most important part of VRFB, as in the redox flow battery, an ion-exchange membrane that separates the four oxidation states created by redox couples (Sharma *et al.* 2018). During charging, V^{2+} was converted to V^{3+} on the negative electrode. The other way around, V^{5+} accepts an electron and is converted to V^{4+} at the positive electrode. This charge/discharge required a suitable membrane to act as a separator and convert the oxidized and reduced ions from both electrolytes. During this conversion of ions process, the crossover of ions to pass through from the other side of electrolytes must be selectively low. The crossover of ions during the cycle charge/discharge process will affect the efficiencies of the battery system.

An ideal membrane should satisfy all the following properties to be high energy efficiency and long shelf life: high proton conductivity; low permeability of vanadium ions; low water uptake; good chemical and mechanical stability; and most importantly, low cost. It is crucial to optimize the cell system to find a suitable membrane to balance operation environments, electrolyte composition, and performance (Shi *et al.* 2019).

There are various methods to prepare ion exchange membrane, including radiation-induced graft polymerization, casting, sol-gel, and layer-by-layer self-assembly methods. In this work, the radiation-induced graft polymerization method is used because it offers simplicity and a better way to alter the physical and chemical properties of the membranes.

In recent work, the radiation-induced graph polymerization (RIGP) method was often used to develop new or upgrade materials. Its simplicity and effective ways to modify the surface without initiator or catalysts make it more environmentally and economically as no chemical residues are exposed to nature (Kumar *et al.* 2021; Tahir *et al.* 2021; Thinkohkaew *et al.* 2021).

1.2 Problem Statement

Electrical energy storage (EES) has great acuities for renewable energy. The EES demands have increased due to their self-generated and allow power to be decoupled from its supply (Chen *et al.* 2009; Lai *et al.* 2017). Vanadium redox flow batteries (VRFBs) is one of the demanded EES for large-scale electricity storage capacity available. Researchers have dominated discussions of the membrane as the main component in vanadium redox flow battery (VRFB) as large-scale energy storage for many years. Unfortunately, no membranes can replace the most commonly used membrane, Nafion. The PTFE backbone with the acidic sulfonic groups makes Nafion the most suitable candidate as an ion exchange membrane for vanadium redox flow batteries. It offers high conductivity, is chemically and mechanically stable, and has high proton conductivity.

However, Nafion is expensive and suffers from vanadium ion’s crossover, producing low coulombic efficiencies (Chuy *et al.* 2000). Its ion’s crossover results in severe capacity decay and voltage declination in an open circuit, thus leading to self-discharge. The higher water uptake of Nafion leads to severe water transfer problems during charge-discharge of the cell (Hickner *et al.* 2004). The continuous use of a high ion crossover membrane will result in feeble energy storage systems. Distinct research modifications of the membrane include Nafion, have been proposed to reduce this problem. Modified ETFE-grafted-2-hydroxyethyl methacrylate-glycidyl methacrylate membrane has suffered the crossover of vanadium, leading to a decrease in charge-discharge cycle time higher power densities than Nafion (Li *et al.* 2017).

In this study, the following approach is continued to prepare cation exchange membrane (CEM) for VRFB: polymer-based radiation grafted with two side functional group monomers collaborated in ETFE backbone also known as functionally-hybridized material is investigated. This approach was already implemented to synthesise CEMs for fuel cells (Flint and Slade 1997), but the ETFE will be modified through this study's one-step graft polymerization process. An ideal membrane should satisfy all the following properties: high energy efficiency and long shelf life; high proton conductivity; low permeability of vanadium ions; low water uptake; good chemical and mechanical stability; and, most importantly, low cost. Herein, pre-irradiate graft polymerizations ETFE with poly (styrene sulfonic acid) (SSS) and N, N-vinyl formamide (NVF) monomers were used as one-step graft polymerization. SSS possesses a sulfonic acid group at every repeating unit. Hence it increases the hydrophilic domain sizes of the resulting CEM (Peng *et al.* 2017), and an amine group from NVF will suppress the crossover of vanadium ion (VO^{2+}).

1.3 Research Objectives

The objective of this study is to modify the ethylene tetrafluoroethylene (ETFE) cation exchange membrane (CEM) for use in VRFBs with high proton conductivity and low vanadium ion crossover.

The specific objectives of this proposed study are outlined as follow:

(a) To determine the optimum parameter of ETFE membrane via radiation-induced graph polymerization (RIGP
(b) To study the physio-chemical properties, thermal stability, ionic conductivity and permeability of modified ETFE membranes with different degrees of grafting.
(c) To evaluate the performance of modified ETFE membranes in various VRFB-relevant conditions.

1.4 Research Scope

The scope of work can be outlined as follows:

i. Preparation of cation exchange membrane by RIGP through one-step grafting of NVF-SSS onto polyethene-tetrafluoroethylene (ETFE) film under different grafting parameters, including:
    - Type of solvents; dimethyl sulfoxide (DMSO), dimethylformamide (DMF), isopropanol and distilled water as a diluent.
    - The concentration of monomers; 5-25%.
    - Reaction temperature; varied in 20- 70 ºC

  - Reaction time; 1-5 hours.

ii. The grafted ETFE-NVF-SSS membrane were pre-treatment steps to convert the Na^+ with H^+
  - 3% H_2O_2 for an hour at 100 ºC followed by immersed in distilled water under the same temperature and reaction time.
  - 2.0 M H_2SO_4 for 1 hour at 100 ºC followed by immersed in distilled water under same temperature and reaction time.

iii. The new modified ETFE membranes physical and chemical properties compared to the original ETFE film. The characterization included:
  - Fourier-transform infrared spectroscopy (FTIR) to investigate the chemical composition.
  - Thermogravimetric (TGA) analysis to study thermal stability.
  - Field emission scanning electron microscope (FESEM-EDX) for cross-section mapping analysis of the grafted monomers distribution on the prepared PEM and elemental analysis on the surface of the cross-section.
  - X-ray diffraction (XRD) to investigate the crystallinity of the modified ETFE membranes.

iv. The characteristics of modified ETFE membrane before being as cation exchange membranes was determined through:
  - Ion exchange capacity (IEC), water uptake (WU) and proton conductivity (PC) will be conducted to evaluate the membrane properties.
  - Permeability test to determine the crossover rate of vanadium (VO^{2+}) ion.

v. The performances of the prepared CEM regarding the commercial membrane, Nafion 117, were analysed under the same condition.
  - For vanadium single-cell analysis, Neware BTS 4000 series will be used as a battery analyser to analyse the charge-discharge potential, discharge curve, coulombic efficiency (CE), Voltage efficiency (VE) and energy efficiency (EE).

1.5 Significance of Study

To substitute conventional energy that causes environmental disaster due to high carbon emissions, sustainable and clean power is preferable to reduce this issue. VRFB is one of the most versatile sustainable large-scale energy storage systems due to using the same electrolyte on both sides and being free from the explosion battery system. The findings of this study will redound to the benefit of society considering that the cost-effective modified ETFE membrane for vanadium redox flow battery has great potential to be used in upscaling the battery for the large energy storage system. The technique of introducing more than one functional group membrane through radiation-induced graft polymerization will widen the grafting technology with low cost and simplicity. Future research can have an idea that SSS monomers were grafted onto hydrophobic materials with the aid of co-monomers and have vast potential on other applications.

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LIST OF PUBLICATION

1. Hamzah, H. M., Ting, T.M., Abouzari-Loft, E., Ali, R.R., Sa’arani, S.S. (2021). The influence of the interdigitated flow field size on pressure loss and efficiencies in vanadium redox flow battery. *Journal of advance research in fluid mechanics and thermal sciences (2289-7879).* (Indexed by SCOPUS).