Dually Crosslinked Composite Membrane as Cation Conducting Solid Electrolyte for Electrochemical Energy Conversion and Storage System

by

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A thesis
presented to the University Of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2020

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Ion exchange membrane (IEM) is a key component of redox flow batteries (RFB) that heavily influences the electrochemical performances, energy efficiency and long term stability of the system. Ionic conductivity, ionic selectivity, chemical stability and cost effectiveness are four major parameters commonly adapt to evaluate and identify suitable candidate for applications in RFB. To achieve the optimal balance of these parameters, recent research and development try to be effective in tuning structural porosity, composition functionality, membrane selectivity, and ionic conductivity. Particularly, the sulfonated polyether ether ketone (SPEEK) based membrane was identified to process high ion selectivity and easy scale preparation, while PVA has been discovered as a decent transporting media for cation solid electrolyte.

Building on the discoveries of previous researches, this thesis aims to identify an optimal recipe and process to prepare the cation exchange membrane for applications in redox flow batteries. Matrix content and cross-linking agent are first systematically evaluated to lay a solid ground work for developing a membrane with good stability, easy forming as well as cost-effectiveness. Then, cross linking environment with different catalysts are investigated to optimize the process for crosslinking with PVA and building networks internal of the membrane to improve its stability. The condition of the physical cross-linking process are also compared to achieve ideal maturation of the membrane necessary to achieve sufficient chemical and physical stability. Additionally, the incorporation of GO was explored with the goal to utilize its special 2-dimensional nano structure for enhancing the stability and improving the ionic conductivity of the composite membrane.

As a result of the above series of experiments, PVA/PSSA/1 wt% GO are identified with the solution casting method. The 10 wt% poly (ethylene glycol) dimethyl ether (PEGDE) displays its advantage in setting-up networks internal of the membrane with the help of ethylenediamine as the reaction catalyst. The 2h, 100 ℃ physical cross-linking follows the chemical cross-linking step further improving the membrane stability and finally get the PVA/PSSA/1 wt% GO composite membrane demonstrates 33.3% of dimensional stability, 74.6 % of water up-take, and 0.91 S/cm of ionic conductivity, which is a good candidate for the redox flow battery.

Acknowledgements

I would like to take this opportunity to send my most sincere appreciation to Professor Zhongwei Chen, for giving me the chance to pursue a MASc degree at the University of Waterloo and also for all the support, guidance and advice through my research period. I would also like to sincerely thank Dr. Jing Zhang and Dr. Gaopeng Jiang for their generous guidance on my research project and safety management work.

I would like to I would like to extend my appreciation to the readers of my thesis.

Last but not least, I would like to thank my parents, family members and friends for their understanding and help.

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List of Abbreviations

Photovoltaic (PV)

Electrochemical energy conversion and storage (EECS)

Redox flow battery (RFB)

Ion exchange membrane (IEM)

Ion exchange resin (IER)

Cation exchange membranes (CEM)

Coulombic efficiency (CE)

Tetrafluoroethylene (Teflon)

Direct methanol fuel cell (DMFC)

Vanadium redox flow battery (VRFB)

Energy efficiency (EE)

Voltage efficiency (VE)

Sulfonated polyether ether ketone (SPEEK)

Open circuit voltage (OCV)

Poly (vinylidene difluoride) (PVDF)

Poly (tetrafluoroethylene) (PTFE)

Poly (ethylene-co-tetrafluoroethylene) (ETFE)

Styrene (St)

Dimethylaminoethyl methacrylate (DMAEMA)

Grafting yield (GY)

Ion exchange capacity (IEC)

Anion exchange membrane (AEM)

Sulfonated poly (tetramethydiphenyl ether ketone) (SDPEEK)

Dimethylaminoethyl methacrylate (DMAEMA)

Chloromethyl methyl ether (CME)

Poly (ether sulfone) (PES)

Polymer concentration (PC)

Solvent-responsive layer-by-layer (SR-LBL)

Polyelectrolyte (PE)

Graphene oxide (GO)

Poly (vinyl alcohol) (PVA)

Poly (4-styrenesulfonic acid) solution (PSSA)

Poly (ethylene glycol) dimethyl ether (PEGDE)

Epichlorohydrin (EPI)

Hydrochloric acid (HCL)

Electrochemical impedance spectroscopy (EIS)

Polymer electrolyte fuel cell (PEMFC)

Erlenmeyer flask (E-flask)

Room temperature (RT)

Chapter 1 Introduction

1.1 Motivations

Environment and energy are key factors restricting the development and progress of human society. The development and utilization of energy play a significant role in promoting the world economy and human development. However, according to BP Statistical Review of World Energy 2019, as shown in Fig. 1[1] , according to primary energy consumption of the world in 2019, oil, coal, natural gas, and other traditional fossil energy are still the main fuel in the world, accounting for more than 80% of the world's energy consumption. Although the proportion of corresponding new energy sources increases continuously, renewable energy still accounts for only a small portion of global energy consumption.[1] There is still a long way to go in the development of renewable energy since its development space is quite broad.

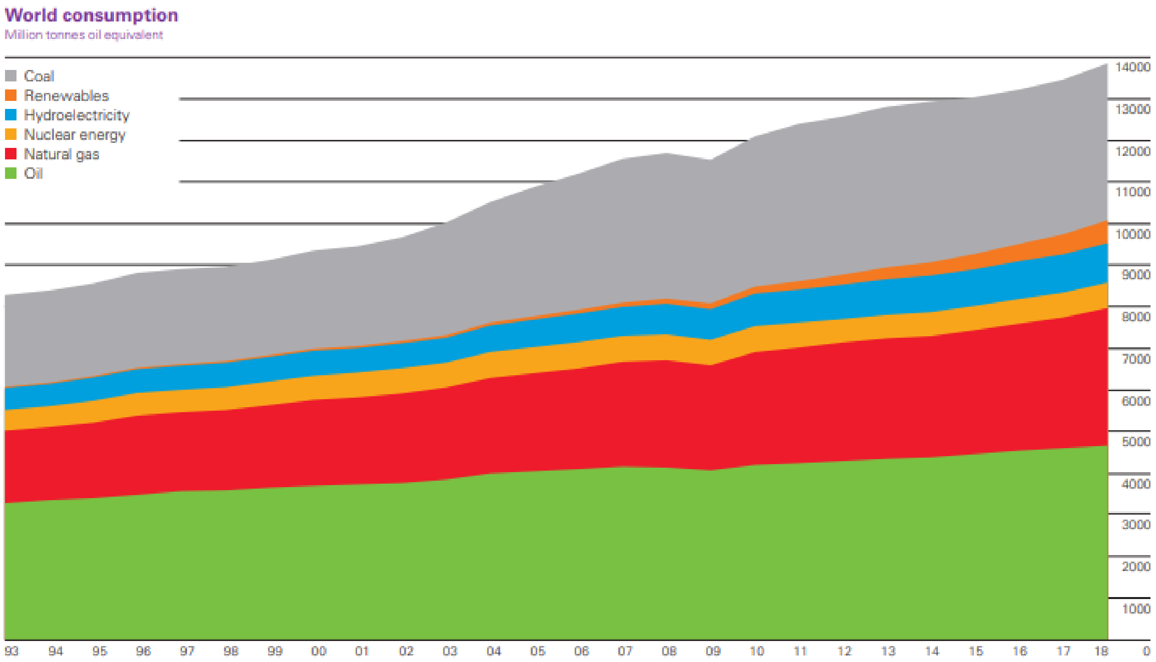

Fig. 1 World energy usage statistics 2019.[1]

Nowadays, petroleum, coal, and natural gas still account for the vast majority of the world's primary energy consumption in the social energy consumption structure, but renewable energy accounts for less than 3%. With the rapid development and close connection of globalization, the economies of various countries develop at a high speed, and people's living standards have been improved. At the same time, the increasing demand for energy makes the existing fossil energy (oil, coal) gradually in short supply. Petroleum and coal are our common fossil energy sources. These fossil energy sources are non-renewable energy sources, and existing reserves will be exhausted in the next 100 years. When these energy sources are extracted, they are seriously polluted and non-renewable.[2] Due to the limitation of the technical level, a series of problems often arise, like air pollution, which originates from the wide use of traditional fossil energy.[3] When fossil energy is used as raw material, a large number of gases that are not conducive to the environment will be released, such as $S0_2$, CO, NO_x, etc. The emission of these gases will not only cause global warming but also aggravate the destruction of the ecological environment, thereby affecting human survival and causing unpredictable consequences on the human body. These problems have also become hot topics of current concern.

To alleviate people's over-reliance on fossil energy, the shortage of fossil energy supply, and reduce the harm of pollution, the development and utilization of renewable alternative energy are a meaningful action.[4] During this process, continuous optimization of the energy structure, increasing the proportion of renewable energy in the energy supply, and eventually replacing fossil energy becoming the main source of energy supply are major issues for the economic development of all countries. These actions are of great significance in ensuring the sustainable development of the national economy.[5]

With the development of science and technology, new energy sources such as renewable energy have received widespread attention. Renewable energy has just been developed or utilized, including other forms of energy besides fossil energy, such as solar energy, wind energy, ocean energy, geothermal energy, nuclear fusion energy, and biomass energy. Compared with fossil energy, the biggest feature of new energy is that it has small pollution, large reserves, and can be regenerated in a short time. Therefore, further development and utilization of new energy will be an imperative means to solve the problems of environmental pollution and energy crisis, and will play a major role in promoting the development of the world economy. So new energy will display a powerful vitality in the energy consumption of the 21st century.[6-8]

However, solar energy, wind energy, tidal energy, and other renewable energy generation are restricted by sunshine time, season, and other factors, respectively. Thus they are discontinuous and intermittent.

To ensure the continuous supply of energy, renewable energy need to be combined with energy storage equipment to increase the stability and quality of e.g. photovoltaic (PV).[9] As a result, it is necessary to develop large-scale energy storage devices to solve these problems and improve energy efficiency.

So far, several kinds of energy storage technologies have been proposed and developed, which are can be divided into physical energy storage and chemical energy storage. Physical energy storage includes water storage and compressed air storage. The characteristics of these two types of energy storage systems are large scale, high energy conversion efficiency, long cycle life, and low operating cost.[10] However, an appropriate operation site is needed, which is limited by construction.[11] Chemical energy storage can also be named as electrochemical energy conversion and storage (EECS) system, which is complementary to physical energy storage, mainly includes various kinds of energy storage batteries in electrochemistry, such as lead-acid batteries, lithium-ion batteries, sodium-sulfur fused batteries, and supercapacitors.[12] Various energy storage technologies have their irreplaceable advantages and shortcomings that cannot be ignored. We need to use them according to the actual situation to maximize their social and economic value.[13] Especially, redox flow batteries (RFB) are more suitable for large-scale energy storage systems, which process the advantages of large capacity, low operating cost, long service life, and flexible design.[14]

The ion exchange membrane is one of the key components of the RFB, which is essential for the high performance of the RFB.[15] It is responsible for completing the ion transmission between the positive and negative electrodes and forming a closed loop. It also isolates the positive and negative electrolytes, preventing the electrolyte leakage between the two electrodes and reducing the loss of energy.[16, 17] At present, the Nafion series membranes produced by DuPont are the most widely used ion exchange membrane in RFBs.[18] Nafion shows high ion conductivity and good chemical stability, but poor ion selectivity and high price restricting the industrialization in RFB systems. Therefore, it is of great significance to reduce the cost of RFB membranes and explore a cheaper membrane material with better performances than the existing perfluorosulfonic acid membrane.[17]

1.2 Fundamentals of Redox flow batteries

Conventional accumulators wrap reactive substances in solid anode and cathode, which are easy to use but limit the battery's performances and storage capacity. The RFB stores soluble active substances of different valences as electrolytes in divided electrolyte reservoirs.[19] This method can not only increase the capacity of the RFB but also retain the stability of the RFB. The RFB uses a pump to circulate the electrolyte inside and outside of the battery. The anolyte and catholyte are separated by the membrane, sitting in the middle of the battery system, which prevents the mixing of the bipolar electrolytes, thus ensuring the performance of the battery.[20] It uses the reaction between two redox pairs to perform the reversible conversion of electrical and chemical energy.[21] The RFB realizes the energy storage and conversion of "electric energy-chemical energy-electric energy" through the change of the valence state in the reaction process of active substances.[22]

Fig. 2 Market size of redox flow batteries.[23, 24]

The concept of the RFB was first proposed in 1970. RFBs can be roughly divided into all-vanadium flow batteries, lithium-ion flow batteries, lead-acid flow batteries, and zinc-bromine flow batteries, etc. according to the different active substances in the electrolyte.[25] Flow battery has the following advantages: (1) flexible design, the capacity of the battery system is only determined by the concentration of electrolyte and the volume of the electrolyte storage tank, and the output power is determined by the number of battery stacks; (2) high safety, it can achieve deep charge and discharge without causing irreversible damage to the battery; (3) assembly materials are easy to be recycled and will not cause environmental pollution; (4) without the restriction of geographical conditions, the closed operation of the battery system is almost pollution-free.[26, 27]

Fig.3 [28] shows the conventional structure of the RFB system, the redox-active substances are supplied from external tanks and redox reactions occur immediately on the electrodes' surfaces when the liquid electrolyte is flowing into the battery. Electrolyte circulation is a unique feature of the RFB which is realized through pumps connected to the stack and continuous supply of catholyte and anolyte to the cell. Fig. 4 [29] illustrates how to assemble a redox flow battery stack layer by layer.[30] In the middle of the RFB system is the ion exchange membrane (IEM), which has a significant effect on battery performance.

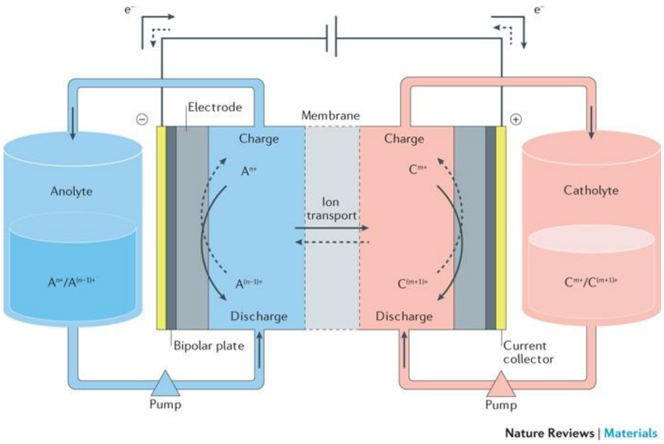

Fig. 3 Schematic of a typical RFB which has two divided compartments containing dissolved active materials separating by the membrane held between tow electrodes. Reported from reference 28, copyright 2008, with permission from American Chemical Society.

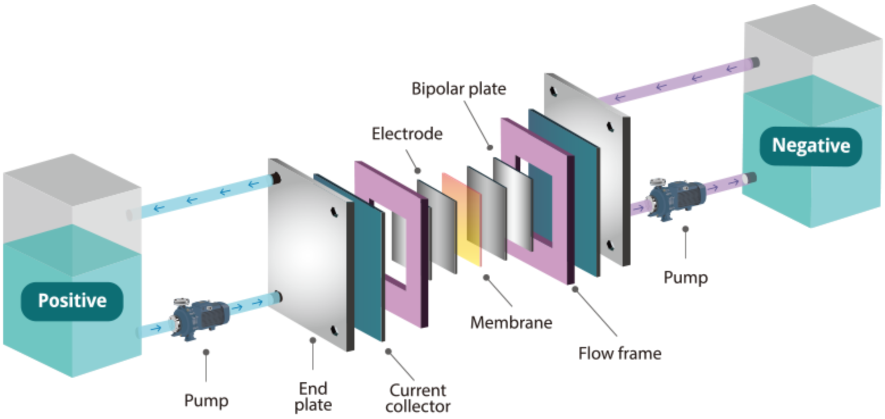

Fig. 4 Assembly of a single redox flow battery.[30] Copyright 2015, with permission from Journal of Materials Chemistry A.

1.3 Ion exchange membrane for the redox flow battery

According to the structure (Fig. 4) of the RFB stack, there are several components needed to set-up the RFB, including two separate tanks, pumps, current collectors, electrodes, bipolar plates, and the IEM which is in the middle of the system.[31] As a significant component of an RFB, an IEM performs to transfer charge-balancing ions to complete the internal current circuit and acts as a physical barrier to prevent cross mixing between the positive and negative electrolytes of the RFB. Therefore, the properties of an IEM play a critical role in the performance of RFBs.[19, 32-35] IEMs are also been regarded as one of the main obstacles in the commercialization of many RFBs.[36] Thus, researchers have put a great amount of effort to develop a suitable IEM for the RFB.

The IEM is a kind of polymer functional membrane with the property of ion-selective permeability. It is a membrane-like ion exchange resin (IER). However, the mechanical requirements of the IEMs are different from that of the IERs.[37] Since IERs don’t need to be dimensionally stable, as cation exchange resins are often brittle as well as anion exchange resins are soft.[38] Compared with IERs, IEMs exhibit backing material that gives membranes the necessary strength and dimensional stability.[39] The IEM does not only play the role of ion exchange but the role of ion-selective transmission, so it should be more accurately called the ion-selective transmission membrane. Besides, in the RFBs, IEMs need to have ionic conductivity.[40]

The IEMs are composed of cross-linked linear polymer chains, forming a three-dimensional network to maintain the stability of IEMs in the application in the RFBs.[36, 41] Chemical cross-linking can efficiently prevent the IEM from dissolving in water and then leading to a polyelectrolyte solution. IEMs own a certain amount of ion functional groups as well as oppositely charged ions to maintain the electrically neutral.[36, 39] The ion exchange procedure carries out when the counter ions are replaced by other ions with the same charge from the electrolyte. This process is reversible and stoichiometry, including the displacement of one ionic species by another on the exchanger.[42] According to the difference of bonding strength, the difficulty of ion replacement on the membrane is varied.[43] A majority of the practical IEMs are rather homogenous and composed of either hydrocarbon or fluorocarbon polymers, which host the ionic groups.[44]

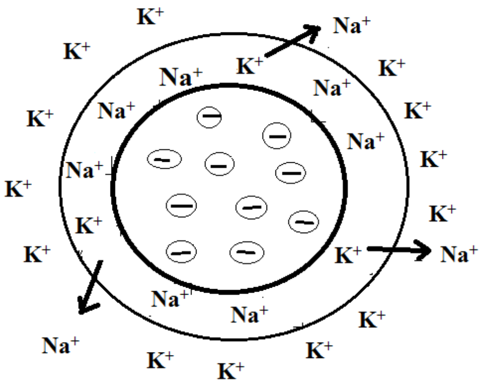

Fig. 5 Schematic representation of an ion exchange process.[41] Copyright 2003, with permission from Journal of Membrane Science.

1.3.1 The ideal properties of the ion exchange membrane

To satisfy the criteria of the RFB, the ideal properties of an IEM should process the following properties:

1) Good ionic conductivity

Since IEMs have to complete the current circuit by transferring charge-balancing ions from one side to another side of the RFBs. The high ionic conductivity is required to minimize the cell internal resistivity and the loss of the voltage efficiency.[45]

2) Good chemical stability

According to the situation that RFBs' membrane are often operated in acid, alkaline or oxidizing medium, which means excellent chemical stability of the IEM is required to ensure the battery's cycle life in the operation process.[46]

3) High ion selectivity:

The IEM, which is employed to separate the negative and positive half cells must be permeable to the ions (e.g. proton, sulfate ions) of the supporting electrolyte to balance the charges at both cell parts and complete the current circuit. What's more, it must prevent diffusion of some active species in the electrolyte which would result in self-discharge of the RFB, leading to low coulombic efficiency (CE).[9, 42]

4) Low cost

Currently, the commercial membranes commonly used in RFBs are the Nafion series membranes produced by DuPont. Although the Nafion membranes have better stability and higher ionic conductivity, they show poor ion selectivity, serious cross-contamination, and high prices, which cannot meet the needs of large-scale energy storage. As a result, researchers are now working on the development of IMEs with low-cost and excellent performances.[47]

1.3.2 Categories of the ion exchange membranes

Similar to the membrane development in the fuel cell, RFB membranes are carrying out in the same pattern. According to the natural matrix materials of the IEMs, the membranes for the RFBs can be roughly divided into four types, including perfluorinated membranes, partially fluorinated membranes, non-fluorinated membranes, and porous membranes.[48]

1.3.2.1 Perfluorinated membrane

Perfluorinated membranes, like Nafion, which is one of the most popular cation exchange membranes (CEM) being used in the RFBs to date. Tracking back to 1970s, a chemically stable CEM with quite good electrochemical property and chemical stability was first invested by Dupont as Nafion® [39], leading to large scale use of Nafion in the chlor-alkali production industry and energy storage or energy conversion system (e.g. fuel cell).[49] The chemical structure of Nafion is incorporating perfluoro vinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone, providing the membrane with specific morphology, and finally leads to its specific performance in RFBs.[9] Fig. 6 is the proposed chemical structure of the Nafion. Thanks to the hydrophobic Teflon backbone gives the Nafion good mechanical and chemical stability. And the acidic sulfonic groups combined on the supporting material, guaranteeing the hydrophilic zone and ion conductivity of Nafion.[50] Nafion is usually been used as an IEM in direct methanol fuel cell (DMFC) [51, 52] and in vanadium redox flow battery (VRFB) applications.[19] There are several kinds of Nafion membranes varying from the thickness, like Nafion 115 is 0.127 mm; Nafion 117 is 0.183 mm, and so on.[53, 54]

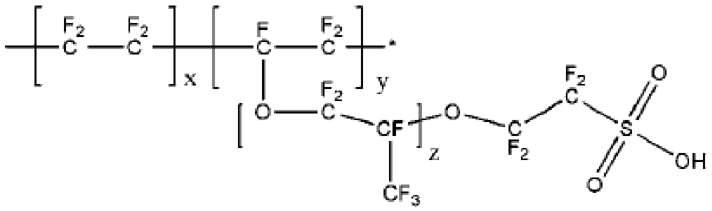

Fig. 6 Proposed structure of Nafion.[9] Copyright 2011, with permission from Energy & Environmental Science.

In RFBs, Nafion is currently one of the most promising IEMs in demand, indicating comparative good chemical stability and electrochemical property.[55] Different membrane thickness makes a difference in battery efficiency. For instance, in the same operation process, Nafion 115 exhibits an energy efficiency (EE) of 84% and a CE of 94% at the current density of 80 mA cm^{-2}. Nevertheless, Nafion 112, which is thinner than Nafion 115, shows a CE reaching 91%. According to the charge and discharge curves from Fig. 7, the discharge time of Nafion 112 is shorter than that of Nafion 115, because of the cross-over issue of vanadium ions. It can be found that the thickness of the Nafion matters when measuring the charge and discharge curves, the thinner it is, the more serious vanadium cross-over will happen.[9]

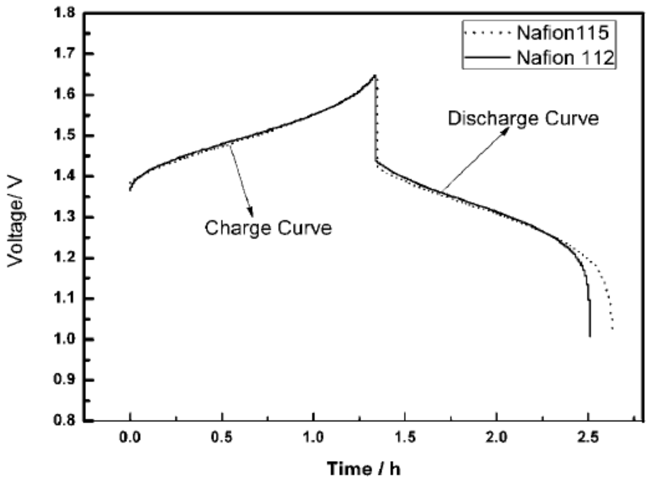

Fig. 7 Charge and discharge curves of Nafion 112 and Nafion 115.[9] Copyright 2011, with permission from Energy & Environmental Science.

Since Nafion (perfluorinated membranes) owns excellent electrochemical performances in RFBs. Considering the low ion selectivity and high cost of Nafion, researchers begin to modify it to improve its properties. In VRFBs, to solve the issue of vanadium ions crossover, scientists try to use some types of organic as well as inorganic nanoparticles to block the hydrophilic clusters in the Nafion to further improve the membrane performance.[56]

Yang's group successfully synthesize the Colloidal silicalite-Nafion composite membrane containing two-layer structure. They use the one-step suspension method by pouring a thin colloidal silicalite layer on a pure Nafion base layer. Fig. 8 is the illustration of Nafion/inorganic composite membrane. This two-layer-structured composite IEM process merits of high proton perm-selectivity of the zeolite, good mechanical stability, and low electrical resistivity of Nafion. These composite membranes are applied in VRFs to investigate their performances as well. Results demonstrate that the vanadium ions permeation lowered than the commercial Nafion since the actual membrane area for vanadium ions is reduced. Apart from that, the decrease of IEM thickness leads to the lower electrical resistivity of the synthesized samples. The composite IEM with 5 wt% silicalite shows higher CE, EE, and VE (voltage efficiency) than Nafion 117 in the same operating condition. The composite membrane has achieved an EE of 77% at 60 mA/cm^2 while Nafion 117 membrane obtains 65% efficiency. In the one-month cycling test of the composite membrane, the results indicate that it had excellent chemical and physical stability.[57, 58]

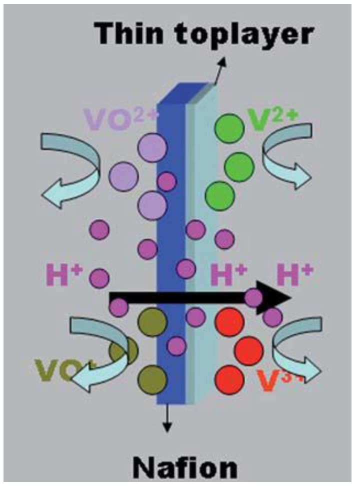

Fig. 8 The illustration of Nafion/inorganic composite membranes.[58] Copyright 2019, with permission from Applied Energy.

Researchers also prepare Nafion/organic hybrid composite membranes for the RFBs. Another multilayered composite membrane with a base layer of sulfonated polyether ether ketone (SPEEK) ionomer membrane and outer layer of recast Nafion membrane is fabricated using the chemical cross-linking method. To lower the cost, maintain adequate electrochemical conductivity, good mechanical, and thermal stability, this work chooses SPEEK as the non-fluorinated base layer of the composite membrane. In this experiment, the Nafion membrane which contains sulfonic acid groups is placed on the top layer, is aiming to prevent oxidation degradation of the SPEEK ionomer membrane resulting from VO^{2+}. Diamine was employed as the cross-linker to enhance the combination between the SPEEK layer and the top Nafion layer. Furthermore, according to testing results of membrane applied in VRFBs, the CE is higher than the cell assembled with Nafion, but VE is lower, due to the high resistivity. But in general, this is a promising way to find the balance between the budget and chemical performance of the membrane.[37]

Qiu and his coworkers derive Nafion/SiO_2 hybrid membrane from simple dealing Sol-gel method. They block Nafion with inorganic materials and applied the hybrid membrane in VRFs to explore its properties. In this design, they try to use polar clusters of the Nafion membrane which is filled with SiO_2 nanoparticles to inhibit the crossover of vanadium ions in the cell. The analysis indicates that the specific nanostructure of the composite membrane can efficiently lower permeation of vanadium ions, thus it presents a higher CE and EE than Nafion. At 20 mA cm^2, the EE of VRF with Nafion/SiO_2 hybrid membrane arrives at 80% compared with 74% of cells installed with Nafion. Furthermore, the open-circuit voltage (OCV) of the synthesized membrane (35h) is two times longer than that of Nafion, meaning that Nafion/SiO_2 reduces the self-discharged rate successfully. This is a promising way to further improve the performance of RFBs.[35]

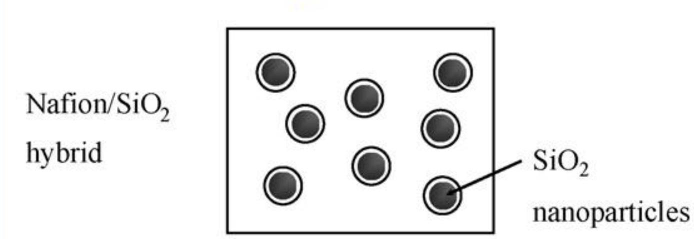

Fig. 9 Schematic illustration of Nafion/SiO_2 hybrid membrane.[35] Copyright 2007, with permission from Journal of Power Sources.

1.3.2.2 Partially fluorinated membranes

Although the commercial perfluorinated membrane, like Nafion and so on, show excellent chemical stability and ion conductivity. However, the high cost of these kinds of IEMs confines their further applications in large-scale energy systems in the future, especially industrialization.[59] Considering these facts, researchers try to investigate partially fluorinated membranes, including poly (vinylidene difluoride) (PVDF), poly (tetrafluoroethylene) (PTFE), poly (ethylene-co-tetrafluoroethylene) (ETFE), and so on, and find the balance between the cost and chemical properties of membranes of the RFB systems. The advantage of these type of membranes is excellent chemical stability due to the partially fluorinated unique membranes substrate.[60, 61]

Scientists prefer using radiation grafting techniques to prepare such kinds of membranes for electrochemical applications, like RFBs. Since the radiation grafting technique processes obvious merits than traditional methods. Because the composition and subsequent performances of the membrane can be easily controlled by the grafting conditions in the operation.[61]

PVDF is a good base membrane choice for perfluorinated membranes because of excellent chemical stability and low cost. It has been successfully grafted with styrene (St) and dimethylaminoethyl methacrylate (DMAEMA) via a handy radiation grafting approach. And after undergoing subsequent sulfonation and protonation processes, a novel PVDF-based membrane is synthesized. Results find that with the appropriate grafting yield (GY), the OCV of the test membrane maintains over 1.2V after 68h, which is much longer than Nafion 117 in the same condition. So it is significant to control the GY to manage the properties of the target membrane. Higher GY results in the growth in water up-take but higher conductivity and ion exchange capacity (IEC). Consequently, is it quite crucial to optimize the GY to further enhance the performances of the membrane.[61]

Qiu at al. report an ETFE-based membrane with lower permeation of vanadium ions using radiation methodology. As discussed before, water uptake as well as IEC of the grafted copolymer membrane increase with GY.[62] Particularly, the membrane achieves low vanadium ion permeation due to coulomb repulsion coming from cation groups of the membrane. In Comparison with the Nafion117 membrane, at 40% GY, the OCV of the VRB with the synthesized membrane performs better than that with Nafion117 membrane.

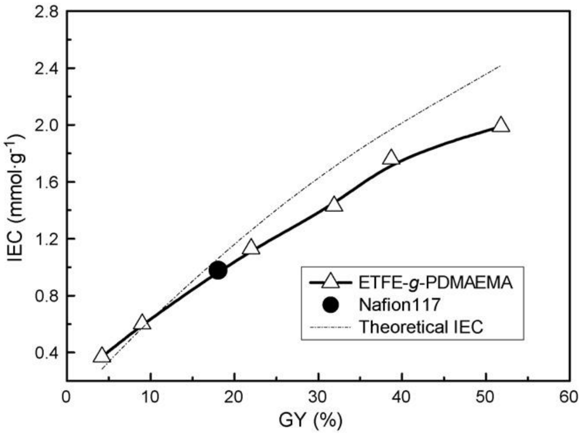

Fig. 10 Effect of GY on IEC of the AEM.[62] Copyright 2010, with permission from the Royal Society of Chemistry.

1.3.2.3 Non-fluorinated membranes

Nowadays, compared with fluorinated membranes and partially fluorinated membranes, non-fluorinated membranes win broad attention in RFB because of their low cost, excellent mechanical, chemical stability, and high ion selectivity.[45] Sulfonated poly (aryl ether ketone), sulfonated poly (vinyl chloride), sulfonated poly (aryl ether sulfone), sulfonated poly (imide), etc, are several families of polymers that are good candidates for non-fluorinated membranes.[63] Meanwhile, some of them can satisfy high-temperature operation requirements in RFBs. Traditionally, non-fluorinated polymers IEM can be divided into two kinds, including poly cation exchange membranes (CEM) and poly anion exchange membranes (AEM), which is decided by the type of ionic functional groups attached to the membrane backbone.[64]

1) Cation exchange membrane

CEM is negatively charged, with functional groups such as $–SO_3^−$, $–COO^−$,$–PO_3H^−$, so it is a membrane with selective permeability to cations, but are non-permeable to anions. This kind of membrane has fixed groups and dissociable ions.[65] For instance, the fixed group of sodium-type sulfonic acid type membrane is sulfonate and the dissociated ion is sodium ion. In applications, the dissociated positive ions are dissociated into the solution by the action of water molecules. Under the action of the electric field in the system, the positively charged ions can pass through the cation exchange membrane, while the anions are repelled by the same charge, thus realizing the membrane's selective transmission function.[66]

Back in 1980, CAMs were applied to RFBs, such as VFBs. In recent years, researchers have explored several kinds of materials to prepare the CEMs with improved properties. Li et al. describe a CEM using SPEEK with various degrees of sulfonation for VRB applications. Rigid biphenyl groups of the back supporter guarantee mechanical stability, meanwhile, the chains of sulfonated group realize the membrane high conductivity. In the same operating situation, the prepared CEM shows CE over 97% and low vanadium ions permeability, compared to that of Nafion 115. The OCV maintains over 1.3V about 140h, which means the SPEEK membrane successfully reduces the vanadium ions permeation.[67] They also use UV to crosslink sulfonated poly (diallyl-bis phenol ether ketone) (SDPEEK) membranes with different degrees of sulfonation. The result indicates that UV crosslinking effectively increases the ion selectivity and thus improves the CE and EE of the system. The SDPEEK with sulfonation degree at 80% (SDPEEK4-6) exhibited self-discharge time three times longer than that of Nafion 115, which is an alternative choice for the RFB.[68]

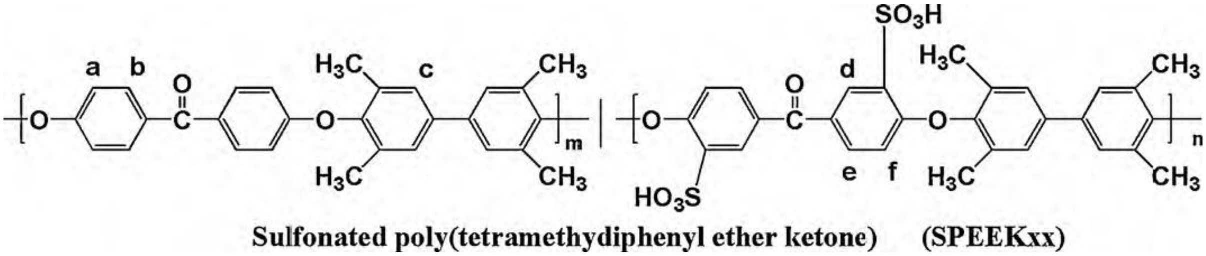

Fig. 11 Structure of polymerization of sulfonated poly (tetramethydiphenyl ether ketone).[67] Copyright 2012, with permission from Journal of Power Sources.

Hwang and his fellows prepare CEMs using vapor phase chlorosulfonation of polyethylene membranes. The homogeneous PE dense membrane is synthesized by this method and then it is cross-linked by accelerated electron radiation. According to the membrane life testing results, it is discovered that the cross-linked membrane doesn’t have any crack compared to the one without cross-linking after several months of cycling. Therefore, cross-linking improves the membrane durability in the acidic operation condition of the RFB, which would become a suitable separator for the flow battery.[69]

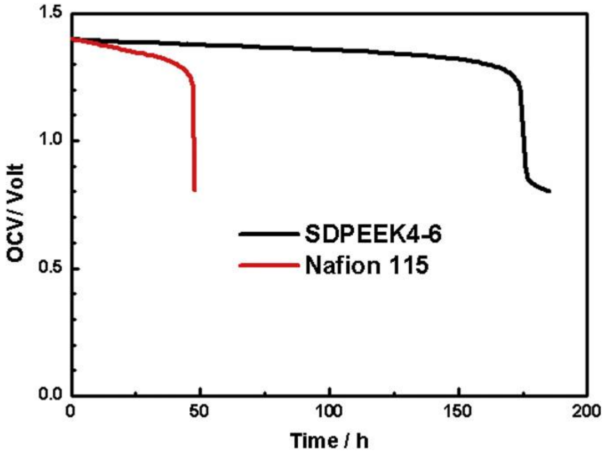

Fig. 12 Self-discharge curves of the VFB cell assembled with SD4-6 and Nafion 115 membranes.[68] Copyright 1996, with permission from Journal of Membrane Science.

2) Anion exchange membrane

AEM is a kind of polymer membrane containing alkaline active groups, which has selective permeability to anions. It is essentially an alkaline electrolyte.[70] The AEM consists of three parts: a polymer backbone with a fixed group (base membrane), a positively charged active group (cation), and an anion on the active group that can move freely. The anion AEM generally uses cations such as -NH_3^+, -NR_2H^+, or -PR_3^+ as active exchange groups, and generates OH- at the cathode as a carrier, and anions move to the anode through the AEMs.[71] Since AEMs play an important in reducing the cross-over of vanadium ions through the membrane due to Donnan exclusion effect, while it will lead to decreases the VE of the battery.[72]

Zhai et al. report an ETFE based-AEM, which grafted dimethylamino ethyl methacrylate (DMAEMA) onto ETFE based membrane by radiation technique. Furthermore, to patronize the prepared membrane, the ETFE-g-PDMAEMA membrane is immersed in equilibrated acid, after which PDMAEMA is grafted onto the ETFE membrane and gets the final product (Fig. 13). As expected, the AEM shows very low permeability of vanadium ions because of coulomb repulsion between the cation groups of the AEM and vanadium ions. After characterizing in the VRB, at GY 40%, the OCV of VRB with prepared AEM maintains over 1.4 V for roughly 30 h, much longer than that of Nafion 117 membrane, implying a good candidate for VFBs.[62]

Jian and his coworkers explore an AEM synthesized with poly (phthalazinone ether ketone). They chlromethylated poly (phthalazinone ether ketone) with chloromethyl methyl ether (CME) followed by using concentrated sulfuric acid as the solvent and finally quaternized the resulting membrane to get finial product (QAPEEK Fig. 14). It is found that the degree of chloromethylation reaction conditions on DCM of CMPPEK matters a lot. With the increase of DCM, the IEC and water content of the AEM go up. On account of the low vanadium ions permeability, the VRB with AEM displays higher CE (98.7%) compared to that with Nafion117 membrane (95.9%), meanwhile, the EE is lower that of Nafion (86%).[73]

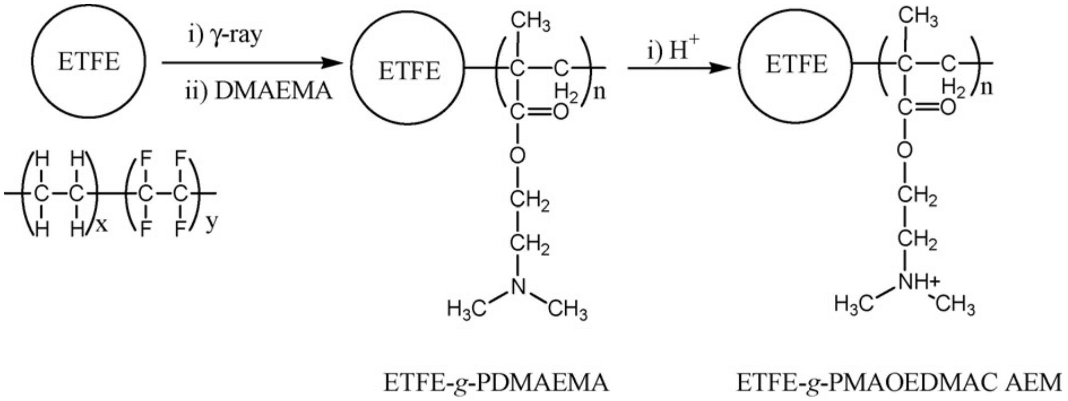

Fig. 13 The procedure to prepare the ETFE-*g*- PMAOEDMAC AEM.[62] Copyright 2010, with permission from the Royal Society of Chemistry.

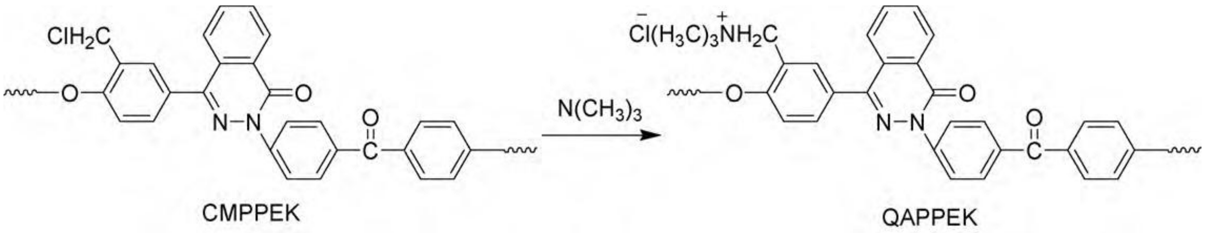

Fig. 14 Preparation of QAPPEK.[73] Copyright 2014, with permission from Chemical Communications.

1.3.2.4 Porous membrane

On account of further improving the chemical and mechanical stability of membranes to meet the practical requirements of the utilization. Humen begin to introduce porous membrane into RFB applications. Different from traditional IEMs, porous membranes can separate ions with different size mainly by pore size exclusion or Donnan exclusion effect.[74] For example, in VFBs, porous membranes are based on the concept of tuning vanadium ions selectivity via pore size exclusion.[75] Various categories of porous membranes are already prepared for RFB applications, which indicate comparable performance to the commercialized Nafion.[76]

According to many kinds of researches, porous ion-conducting membranes can be prepared via sorts of means, such as the phase inversion method[77], the hard template method [78], and so on. For the sake of satisfying the large-scale manufacturing of RFBs, the porous membrane with an appropriate pore size (the radius of ion transport channels) is critical, so the following criteria should be considered:

a) The size of the ion transport channel should smaller than vanadium ions (in nano-scale),to exclude them;

b) The density of ion channels should be high enough to promote proton transfer;

c) The ion transport channels should be connected to transfer protons.[79]

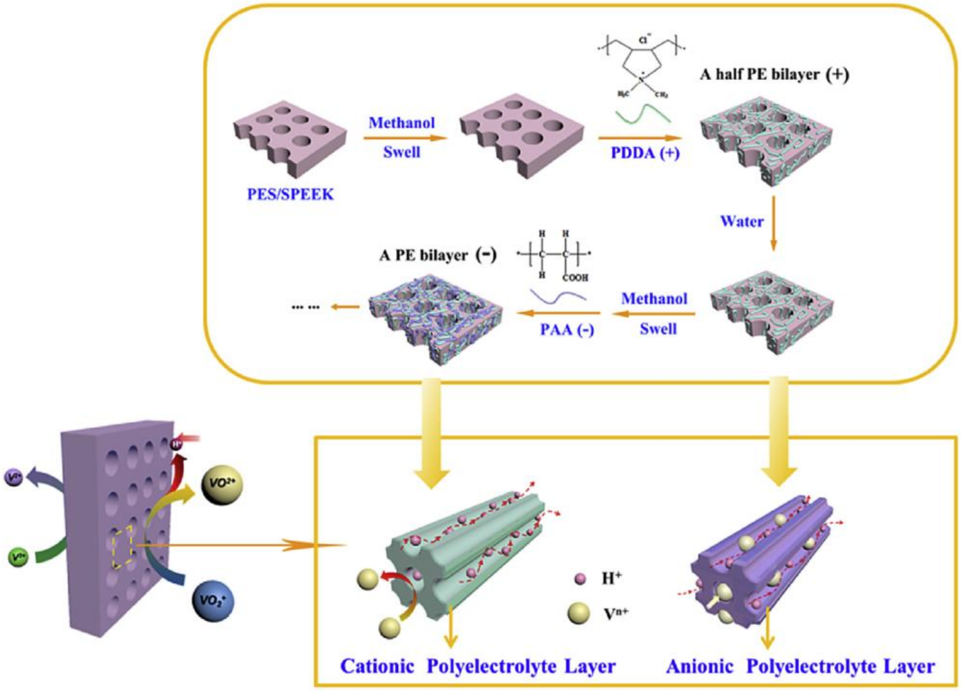

Fig. 15 The impact of prepared membranes with different surface charge [80]. Copyright 2014, with permission from RSC Advances.

Zhang et al. discuss a porous membrane with tunable morphology synthesized by poly (ether sulfone) (PES) via a phase inversion method. Through altering the concentration of polymer concentration (PC) and blending with SPEEK in the casting solution, the membrane morphology can be adjusted. It is found that the micro-voids gradually decrease with the increasing of the PC of mixture solution, meanwhile, the number of finger-like pores within the membrane goes up. There is a relationship between the membrane morphology and the performance. The join of the SPEEK can decrease the CE while help for the VE owing to the increased proton conductivity. After optimizing the morphology of the porous membrane, the VFB assembled with the optimized membrane indicates the CE of 92.8% and VE of 78.4%, which means it is facile to fabricate PES porous membranes.[81] Besides, they report a porous membrane employing solvent-responsive layer-by-layer (SR-LBL) method. This ion-conducting membrane’s surface and internal pore walls are assembled with a different charge, which is tuned by differently charged polyelectrolytes (PEs) on the pore walls and the surface of membranes. The charge on the surfaces and pore walls set up ion transfer channels contributing a lot for the proton conductivity in the VFB (Fig. 15). The results display that a VFB single-cell assembled with a positively charged porous membrane yields CE (98%), higher than the membrane with a negative charge. So it is useful to control the property of charges of the membrane to further improving the performances of the PEs membrane.[80]

Their team investigates PES/SPEEK porous membrane by a novel solvent template method with continuously controllable nano-scale ion transport channels. Thanks to this technique, one of the interacting polymer chains can twist with the other and finally forming a thoroughly interpenetrated solvent-polymer network, which leads to high porosity. Apart from that, the size of the ion transmission channel changes over with the components of the template solvent. The testing of VFB single-cell employed with the prepared ICMs shows CE over 99% and EE over 92%, with a current density of 40 mA/cm^2. Thus the solvent-template method is promising for fabricating high-performance ion-conducting membranes for the EECS.[79]

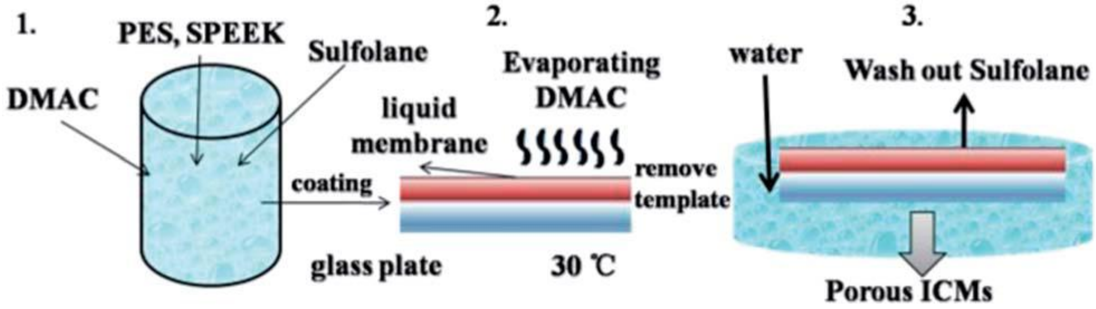

Fig. 16 The illustration of the solvent template method used in this article.[79] Copyright 2017, with permission from Journal of Power Sources.

1.4 Introduction of Crosslinking technique

Crosslinking is a significant method to improve the physical and chemical properties of polymer membranes. Properly cross-linked polymers have improved mechanical strength, heat (cold) resistivity, and chemical stability over linear polymers. Crosslinking is an effective method to improve the comprehensive properties of the ion-exchange membrane.[82] Studies have shown that cross-linking can successfully inhibit the swelling of non-fluorosulfonic acid membranes and improve the morphological stability of membranes after immersing in water. Crosslinking technique can be divided into chemical crosslinking and physical crosslinking.

1.4.1 Chemical crosslinking

Chemical cross-linking refers to the coupling of two or more molecules through the formation of covalent bonds between macromolecular chains under the action of light, heat, high-energy radiation, mechanical force, ultrasonic waves, and cross-linking agents to form a polymer with a network structure (Fig. 17).[83] Among them, the formation of covalent bonds mainly depends on the use of specific cross-linking reagents. Generally, the cross-linking reagent molecules contain active groups that can chemically react with proteins or other molecules, such as amino groups and mercapto groups.[84] Vulcanization of rubber, crosslinking of unsaturated resins, curing of epoxy resins, etc. are all examples of chemical crosslinking.[85]

Chemical cross-linking can improve polymer properties.[86] For example, the chemical cross-linking of polyethylene can improve its strength and heat resistivity, and the tanning process of leather is to use its protein molecules and formaldehyde to form a cross-linking bridge, and even lose its solubility. As one might expect, extensive cross-linking yields a product with more rigidity, hardness, and a higher melting point than the equivalent polymer without cross-linking.[83] Between cross-linked polymers, a great number of covalent bonds are formed, which could significantly enhance the hydrolytic and oxidative stability of the membrane.[87]

Chemical cross-linking, on the one hand, makes the membrane denser, significantly inhibits the swelling of the membrane, and at the same time restricts the migration of free radicals in the membrane, extending the life of the membrane; on the other hand, cross-linking can increase the entanglement between polymer chains, adjust the size of the ion channel and improves the selective permeability of the membrane. However, the covalent crosslinking leads to brittle or even broken membrane.[88]

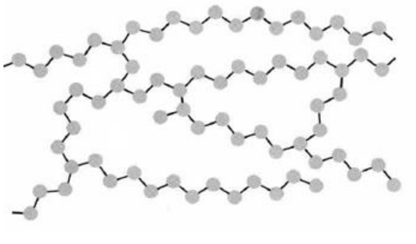

Fig. 17 A cross-linked polymer. (Only the carbon atoms in the chains and cross-links between chains occur at random are shown) [83].

1.4.2 Physical crosslinking

Physical cross-linking is through non-chemical bonds such as hydrogen bonding van der Waals force or entangled cross-linking. The cross-linking points of physical cross-linking are random and non-uniform. Since chemical cross-links are formed by covalent bonds, physical cross-links are derived from weak interactions. Different from chemical covalent cross-links, which are mechanically and thermally stable, physical cross-linking is easy to break.[83]

1.5 Research objective

The research aims to use dully cross-linked method to synthesize a CEM for the EECS, with expect to achieve low cost and high performance of the membrane. This thesis can be separate into two main objectives.

1. The first part of the thesis investigate the fundamentals of the CEM for EECS. And explore the membrane matrix polymer materials which are low cost and exhibit enough stability for synthesizing CEMs. To endow membrane with ionic conductivity, PSSA is incorporated into the PVA substrate. To improve the CEM chemical and mechanical stability, a suitable cross-linker with appropriate percentage for the membrane fabrication is developed. Various factors of the chemical cross-linking reaction are discussed. For the improvement of mechanical strength, physical cross-linking with optimized thermal treatment period and temperature are applied to the membrane after casting polymer solution drying in the room temperature. In the end, the cation conductivity and swelling of the CEM, the proportion of the functional polymer need to be further discussed.

2. The second part of this thesis further enhances the cationic conductivity and mechanical stability of the CEM. Graphene oxide (GO), a kind of filler, is synthesized and added into the polymer solution to interact with the polymer matrix to compose the composite CEM. Besides, the ratio of the GO also needs to be controlled properly to improve the mechanical stability as well as lower the water up-take of the synthetic membrane. The characterizations of properties of the membrane will be employed to investigate the performances of the CEM. Finally, every piece of the puzzle are linked together to form a complete description of the synthesized membrane.

1.6 Organization of the thesis

This thesis is composed of four chapters. **Chapter 1** describes the general background, fundamentals, the recent research progress of the membrane for the EECS, technologies for preparing membrane, and motivation of this work. In **Chapter 2,** kinds of materials as well as characterization measurement techniques employed throughout this thesis is introduced. **Chapter 3**, the CEM preparation procedure is recommended. **Chapter 4** focuses on various testing results, factors of the reaction are investigated. The relationship between the ratio of chemicals and the performance of the membrane is discussed in this chapter as well. In the end, in **Chapter 5**, a summary and suggestions for the future direction that work may take.

Chapter 2 Chemicals and characterization techniques

2.1 Materials

All materials listed in the Table 1 are used as received without further purification. This list presents chemicals and their suppliers.

Table 1 List of chemicals.

Chemicals	**Suppliers**
Poly(vinyl alcohol) (PVA)	Sigma Aldrich
Poly(4-styrenesulfonic acid) solution (PSSA)	Sigma Aldrich
Poly(ethylene glycol) dimethyl ether (PEGDE)	Sigma Aldrich
Epichlorohydrin (EPI)	Sigma Aldrich
Ethylenediamine	Sigma Aldrich
Glutaraldehyde	Sigma Aldrich
Hydrochloric acid (HCL)	Sigma Aldrich
Sulfuric acid	Sigma Aldrich
Phosphoric acid	Sigma Aldrich
Potassium permanganate	Sigma Aldrich
Hydrogen peroxide solution	Sigma Aldrich

2.2 Characterization techniques

This following part of the **Chapter 2** introduces several key performance measurement techniques related to the evaluation of membranes presented in this thesis. Furthermore, the morphological as well as physical properties are employed to generally characterize the nano-composite electrolyte membranes prepared in this task. The electrochemical techniques are also used to evaluate the performance of the CEM. For the detailed experimental processes, characterization, and evaluation of the materials is provided in the proceeding chapters.

2.2.1 Physicochemical characterization

(1) Water up-take of CEM

Water up-take is a measurement technique indicating the capability of a CEM to maintain the water within the electrolyte membrane.[89] CEM can conduct ions only in the medium of water solutions, which is similar to that of Nafion membrane. The researches show that the water content of the membrane make a big difference on the CEM's mechanical properties as well as transport properties. The decrease in hydration of the membrane reduces water up-take property, thus leading to a reduction of conductivity of the CEM, which might result in ohmic loss.[90]

To evaluate the water up-take of the CEM, the first step is to immerse the prepared sample into deionized water at room temperature for 24 hours to ensure the membrane saturation. After that, take out the saturated CEM immediately and quickly wipe the solution adhering to the membrane surface with a tissue paper before reweighting it. Then the membrane needs to be dried in a vacuum atmosphere at 80 ℃ for 24 hours. After taking out the dried membrane, it will be weighed again the same as before. The water up-take can be calculated according to the following equation:

$$\text{Water up-take (\%)} = (W_{\mathbf{wet}} - W_{\mathbf{dry}}) / W_{\mathbf{dry}} * 100\% \qquad (2\text{-}1)$$

Where Water up-take (%) is the weight percentage, $W_{\mathbf{wet}}$ and $W_{\mathbf{dry}}$ are the weight of wet membrane and the weight of dry membrane, respectively.[91]

(2) Dimensional change

The stability of the CEM applied in the EECS is also considered critical. It is the swelling behavior of the membrane, the swelling ratio is indicated as an area change rate of the membrane. Since the membrane will be applied in the solution system, if there is a big change in the dimensional of the membrane, there might be an influence on the further application. What’s more, the dimensional change of the membrane is likely to affect the durability of the system.

To calculate the dimensional change of the prepared membrane, firstly, the sample should be cut into a certain size before being immersed into the deionized water at room temperature for 24 hours. In the second step, take out the membrane from deionized water and measure its length and width. And then the sample will be dried in a vacuum atmosphere at 80 ℃ for 24 hours following by measuring the size of it again. Dimensional change is judged by the following equation:

$$\text{Dimensional change (\%)} = (L_1 * W_1 - W_2 * L_2) / W_2 * L_2 * 100\% \qquad (2\text{-}2)$$

Where L_1 and L_2 are the lengths of the wet sample and dry sample separately. W_1 and W_2 are the widths of wet sample and dry sample, respectively.

2.2.2 Electrochemical characterization

(1) Ionic Conductivity Measure

The accurate measurement of the ionic conductivity of synthetic membrane is via electrochemical impedance spectroscopy (EIS). It is well known that the precise measurement of ionic conductivity through the electrolyte membrane is of great significance for the further characterization of electrolyte materials. The conductivity property of the membrane can be investigated according to the measurement of resistivity of the humid conductive membrane against the running of alternating current, which is named as alternating current impedance method.[92] One of the alternating current impedance methods is four-electrode methods. During the test, this method will eliminate the interference of interfacial resistivity and polarization in the system.[89] Therefore, four-electrode alternating current impedance spectroscopy technique is employed for analyzing the conductivity of the sample. The prepared CEM needs to be hydrated overnight before determination and clamped between two Pt electrodes for the recording of the alternating current impedance spectroscopy. The ion conductivity is evaluated by the following equation:

Ionic Conductivity: $\sigma = L / R_m * A$ (2-3)

Where σ is the ionic conductivity (S cm^{-1}), L is the distance between two reference electrodes (cm), A is the cross-sectional area of the membrane (cm^2), R_m is the measured bulk resistivity of the sample (Ω).[92]

Chapter 3 Synthesize dually cross-linked composite membrane as cation conducting solid electrolyte

3.1 Introduction

As discussed in Chapter 1, as the heart of the EECS, the CEM is one of the most critical components of the system to contribute to the overall performances. Nowadays, the thriving field of CEM is becoming more and more popular and attracting ever growing attention than before. It is recognized that explore and investigate new kinds of solid polymer electrolytes is of great influence on the utilization of EECS.[93] Unfortunately, because of the high cost of the commercial membrane, which cannot satisfy all requirements of the EECS, scientists begin to develop polymer solid electrolyte membranes for future large-scale utilization. Since for the porous membrane, which is short of ionic selectivity, might result in the cross mixing of the cell. When it comes to the anion exchange membrane, it is hard for this kind of membrane to achieve high ionic conductivity because of the thermodynamic properties within the membrane.[67] Considering these facts, in the past few years, people devoted much effort to synthesize CEM to optimize the properties of it and to overcome the trade-off between the high ion conductivity and low ion selectivity. Researchers attempt to look for a promising method to circumvent the contradictory problems of high cost and stability in CEM preparation.[94]

Based on the existing studies of proton exchange membranes for polymer electrolyte fuel cells (PEMFC), it is well known that cross-linking of the polymer can endow it a lot of covalent bonds, which can contribute a lot to the hydrolytic and oxidative stability of the membrane.[95] Thus chemical cross-linking would be a good choice to improve the chemical properties of the membrane. What's more, with the help of the physical cross linking, there can be a great progress of the membrane stability. Generally, an ideal CEM applied to the EECS should not only promote productivity, but also cut down the operating cost. Recently, there is a tendency that CEM prepared with water-soluble polymer as a base material.[93]

Poly (vinyl alcohol) (PVA) is an attractive and cheap material for preparation electrolyte membrane, thanks to its good chemical and mechanical stability.[96] Moreover, PVA is a hydrophilic, semi-crystalline and good membrane-forming polymer. Containing a carbon chain backbone with –OH groups side chain, so PVA-based materials have already been applied to the biomedical area, like contact lenses and so on.[97] Since PVA is a poor cation conductor compared with commercial ones without any negatively charged ion negative organic functional groups such as -COOH or -SO_3H. As a consequence, people attempted to cross-link organic groups such as hydroxyl as well as sulfonate onto PVA to improve the cation conductivity and hydrophilicity.[98] In order to use the PVA-based membrane in the EECS, the negatively charged functional groups have to be blended into the PVA polymer host. Nevertheless, the PVA composite membranes' performance in the EECS does not exhibit the same behavior than commercial ones.[99] From this point of view, the polystyrene sulfonic acid) (PSSA) can give the PVA-based membrane reasonable cation conductivity, playing the role of a donor.[100] It is easy to prepare PSSA from the sulfonation of polystyrene (PS) at a low cost. And in the past investigations, it is regular for PSSA to be used to prepare ion exchange membranes for polyelectrolyte chemistry.[101] PSSA is a polymer contain rigid biphenyl groups and sulfonic acid (-SO_3H), which is a good option to incorporate with PVA to further enhance the cation conductivity of the synthesized membrane. It is known that PVA and PSSA can blend together and become compatible with each other, resulting in a miscible solution. Particularly, PVA and PSSA can form semi-interpenetrating polymer network with the help of a cross-linking agent undergoing chemical treatments.[102] In this way, the weak mechanical stability derived from swelling phenomena of the membrane will be control appropriately by the cross-linking strategy. According to Chapter 1, if chemical cross-linking in a company with physical cross-linking is carried out meanwhile, the stability of the membrane is enhanced.[103]

Studies indicate that a small amount of non-ionic filler helps to make a great contribution to the specific surface area along with interface reactions between filler and matrix.[99] Furthermore, as a non-ionic filler, the graphene oxide (GO) has also been used in various applications in electrochemistry, with the functionality originating from sp^2 and sp^3 carbon.[104] GO is an oxide of graphene. After being oxidized, its oxygen-containing functional groups increase, making its properties more active than graphene. Because GO contains many hydrophilic functional groups and a large specific surface area, it has long been regarded as a hydrophilic substance with excellent dispersibility in water. And there have been studies showing that GO can form nano-composites with PVA polymer matrix as a kind of nanofiller. In this direction, the utilization of PVA matrix blend with PSSA as well as GO for the CEM cross-linked with poly (ethylene glycol) dimethyl ether (PEGDE) are reported.[105]

3.2 Experimental methods

3.2.1 Synthesis of GO

The GO is synthesized using an improved method demonstrated by James tour *et al.*[106] To prepare the GO, the first step is to place the erlenmeyer flask (E-flask) (1L) in an ice bath with a stir bar, and then add H_2SO_4 (360mL) and H_3PO_4 (40mL) into the E-flask, with the same grad. Following by weighing "Graphite Powder, Natural, Microcrystal grade" (2g) and add into the flask, cycling the mixture for half an hour. After that, add $KMnO_4$ (18g) really slowly to the solution and give an additional 15min of stirring. During this period, add 1 g of $KMnO_4$ with at least 2 min intervals, keeping the temperature below 20 ℃. Raise the temperature of the mixture solution to 50 ℃ (with using oil bath). Check the temperature with a thermometer. Let it stir for 16 hours. After this, put the solution in the ice bath and let it cool down to 10 ℃ (or cooler). Prepare DDI (400mL, in the separatory funnel) and add DDI into the solution drop by drop (maintain the temperature to be below 10 ℃). After adding the DDI, let it stir for 15mins. Then add H_2O_2 (20mL) drop by drop into the solution. Once the reaction is done, place the GO solutions into centrifuge tubes and wash them with water until reach the PH of 6-7. Lastly, dry the resulting GO for further utilization.

3.2.2 Synthesis of CEM

Solution casting and solvent evaporation method are employed to synthesize the CEM and the preparation procedure is shown in Fig. 18 (e.g. PVA/10 wt% PSSA/PEGDE/1% GO membrane synthesis procedure).

In order to prepare the aim CEM, the hot play temperature is first set to 190 ℃, followed by dissolving 0.8 grams of PVA powder into 15 ml DDI water and stir for 20 min to dissolve. When the solution became clear and transparent, turn off the temperature and continue stirring until the solution cools down to the room temperature (RT~303K). Secondly, 0.08 g PSSA is added into the mixture solution slowly, keep stirring to dissolve for a period of 1.5h. After that, 1M ethylenediamine is added to the mixture and keep stirring for 1.5h. Third, slowly add 0.08 grams of crosslinking agent PEGDE into the beaker, keep stirring reaction 1.5h at RT. Afterwards, 80ml 1mg/ml GO solution synthesized before is added into the mixture and keep stirring for 1.5 h. Finally, stop stirring, the bubble-free polymer solution is casted onto a clean petri dish, and evaporate slowly at RT to form a membrane. After the membrane is dried, tearing it from the petri dish and placing in the oven under 100 ℃ for physical crosslinking for two hours. The heat treated membranes undergo acids exchange and are immersed in 1M aqueous HCL solution overnight at RT for further doping. After that, the sample is washed copiously with DDI water to remove any residual HCL on the membrane.

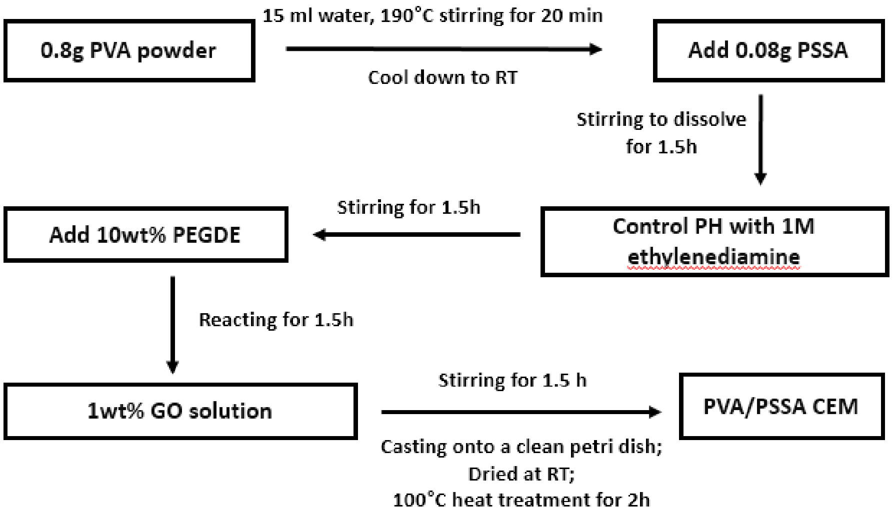

Fig. 18 Preparation protocol of dually cross-linked CEM (PVA/10 wt% PSSA/PEGDE/1% GO membrane).

A series of nanocomposite CEMs of PVA/PSSA/GO with different proportion of PSSA are prepared follow the procedure described before. A Nafion membrane is used as the reference membrane. It is pre-treated by immersing in three consecutives baths of 3% H_2O_2, 0,5M H_2SO_4 and DDI.

Chapter 4 Results and discussion

The physicochemical properties of as-prepared CEMs are first characterized by using water up-take, dimensional change. Furthermore, the electrochemical properties of the membranes are examined by EIS.

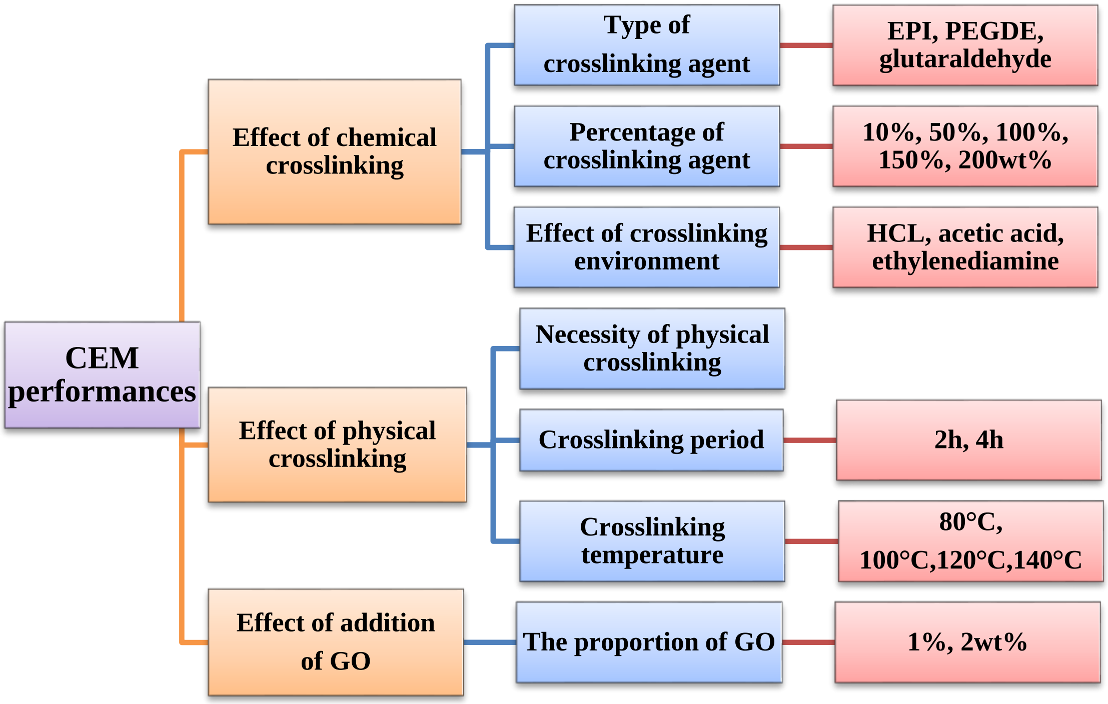

Fig. 19 The discussion of elements which have influences on the CEM performances.

4.1 Effect of the chemical cross-linking agent

It is well known that the type and the proportion of the chemical cross-linking agent play an important role in the formation and performance of the membrane since it can react with the polymer matrix to form networks internal of the membrane. In the beginning, in order to explore the suitable chemical cross-linking agent for the CEM to enhance its chemical stability and hydrophilicity, three types of cross-linking agents are used to synthesize membranes, epichlorohydrin (EPI), poly (ethylene glycol) dimethyl ether (PEGDE), and glutaraldehyde. Based on the reasons that all of them can react with -OH groups in the PVA chains and are widely used chemical cross-linkers.

A certain volume of glutaraldehyde is prepared to participate in the synthesis of CEM as a cross-linking agent, but the PVA and PSSA reaction solution turned into gel after the addition of a certain amount of the glutaraldehyde for a period. This phenomenon may be because the reaction liquid volume is small and glutaraldehyde is very easy to trigger the crosslinking reaction, which quantity is hard to control to form the membrane. So the other two crosslinking agents are used to synthesize membranes for further comparison.

Poly (vinyl alcohol) **Poly (ethylene glycol) dimethyl ether**

Fig. 20. Chemical structure of PVA and PEGDE

With two kinds of cross-linking agents, EPI and PEGDE (Fig. 20), a series of membranes with different PSSA content are prepared separately. The CEM chemical composition ratios are 0.8g PVA, 10, 30, 50, and 70wt % of PSSA, respectively. By comparing the physical and electrochemical properties of prepared membranes with different chemical cross-linking agents, it could discover which chemical cross-linker contributes more to fabricate a CEM (labeled as PVA/PSSA/EPI, PVA/PSSA/PEGDE, respectively). After drying the membrane in RT, the membranes are immersed into the DDI for further testing. Compared to the apparent morphology of these specimen, after physical cross-linking, the one synthesized with EPI shows poor toughness, uneven concentration distribution, and brittle than that using PEGDE (Fig. 21). On the basis of water up-take and dimensional stability testing results, from the diagram, it is discovered that PVA/PSSA/EPI membrane processes a strong ability to absorb water. For instance, the PVA/70 wt% PSSA/EPI membrane gets the water up-take of 361.7%, as well as dimensional change, reaches 215%, which are higher than those 277.2% (water up-take) and 126.7% (dimensional change) of PVA/70 wt% PSSA/PEGDE membrane (Fig. 22). Moreover, regardless of the type of cross-linking agent, the moisture content increases, and the dimensional stability decreases along with the increase of PSSA content in the membrane. For CEM synthesized with PEGDE, these physical properties change steadily and slowly. According to the conductivity of those kinds of CEM, after taking out from DDI, it is obvious that with the same membrane composition, the proton conductivity of PEGDE series CEMs are almost four times of EPI series CEMs, like 5.6*10^{-3} S/cm (PVA/70 wt% PSSA/PEGDE) compared to 1.4*10^{-3} S/cm of PVA/70 wt% PSSA/ EPI membrane (Fig. 23).

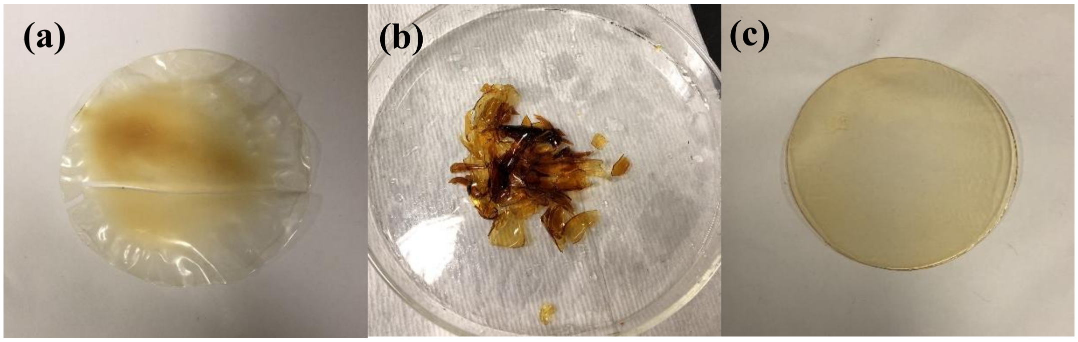

Fig. 21 Optical images of a) PVA/PSSA/EPI CEM is brittle (peeled from petri dish); b) PVA/PSSA/EPI CEM is took out from DDI after physical cross-linking; c) PVA/PSSA/PEGDE membrane

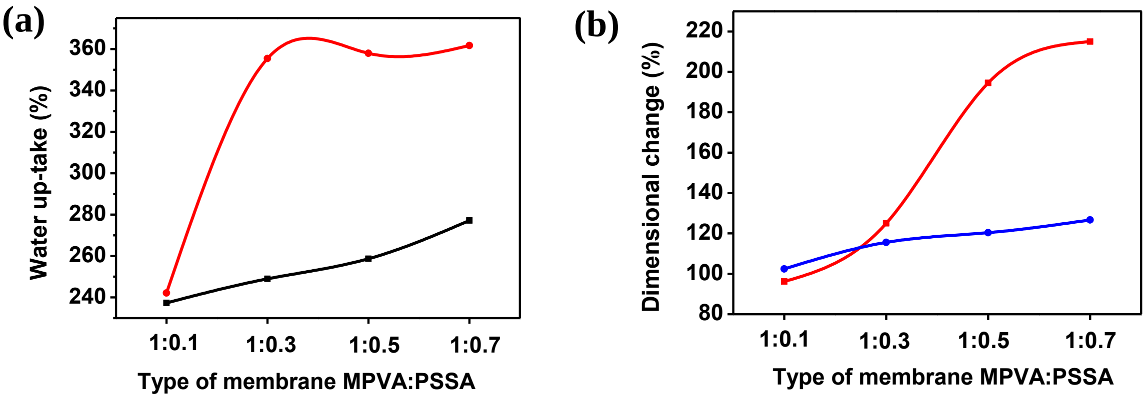

Fig. 22 Physical properties of CEMs with different PSSA ratio. (a) water up-take: black line- PVA/PSSA/PEGDE CEM; red line- PVA/PSSA/EPI CEM ; (b) dimensional change: blue line- PVA/PSSA/PEGDE CEM ; red line- PVA/PSSA/EPI CEM.

For instance, for membranes synthesized with PVA and 10 wt% PSSA, along with these two different types of cross-linking agents, the thickness of PVA/10 wt% PSSA /EPI membrane gets 110um and PVA/10 wt% PSSA /PEGDE membrane reaches 185um. After drying in the RT, these samples are immersed into DDI for ionic conductivity testing. Without the help of acids exchange with HCL, the resistivity of those membranes are around 71Kohm (PVA/10 wt% PSSA /PEGDE) and 350Kohm (PVA/10 wt% PSSA /EPI), respectively. From testing results, the membrane prepared with PEGDE demonstrates higher conductivity than the other with EPI, which is about two times higher than $5*10^{-4}$ S/cm (PVA/10 wt% PSSA /EPI membrane) (Fig. 24 & Table 2).

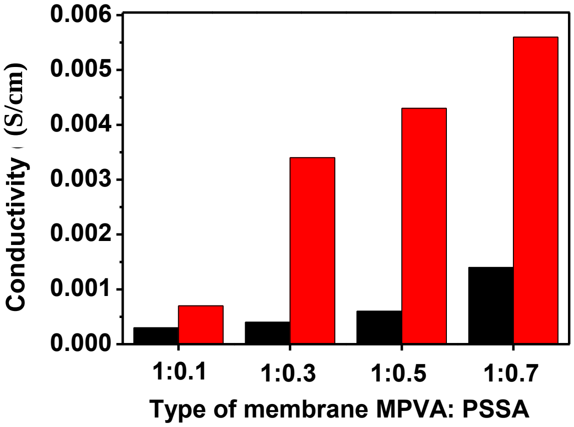

Fig. 23 Conductivity of CEM with different percentage of PSSA; PVA/PSSA/EPI CEM (black column); PVA/PSSA/PEGDE CEM (red column).

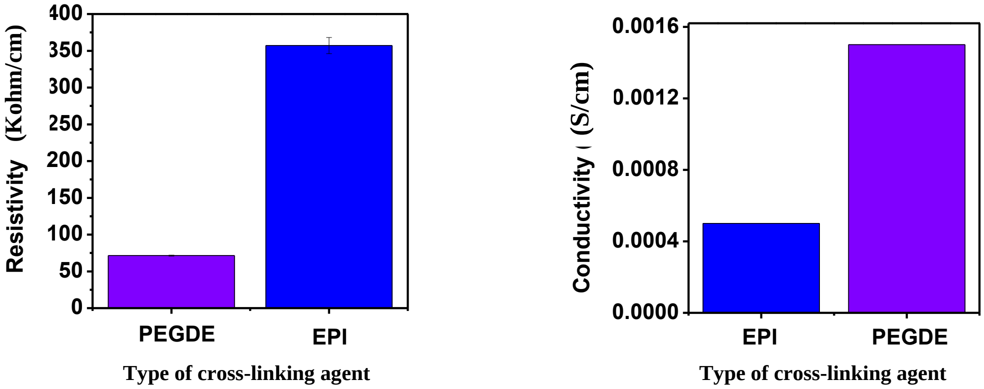

Fig. 24 Resistivity and conductivity of PVA/10 wt% PSSA /PEGDE (purple column) and PVA/10 wt% PSSA/EPI (blue column) membrane.

Table 2 Resistivity (Kohm/cm) and conductivity (S/cm) of PVA/10 wt% PSSA/PEGDE and PVA/10 wt% PSSA/EPI membrane (three parallel testing)

Experiment / Sample	Test 1	Test 2 (Resistivity (Kohm/cm))	Test 3	Conductivity (S/cm)
PVA/10 wt% PSSA /PEGDE	72.28	71.33	70.98	$1.5*10^{-3}$
PVA/10 wt% PSSA /EPI	367.3	358.7	345.3	$0.5*10^{-3}$

Therefore, PEGDE can be employed to be one part of the CEM compositions to build networks and further improve performances of the composite membrane. The merits of PEGDE originate from its particular structure, which processes a long flexible polyethylene glycol chain and two epoxy terminal groups, contributing to form polymer networks.[107] This advantage not only increases polymer rigidity but also makes the cross-linked PVA without losing the membrane flexibility. Researchers find that using PEGDE, which is non-toxic and non-expensive, can help to improve morphology as well as thermal properties of the CEM. What's more, chemical crosslinking with PEGDE is regard as a simple and valid way to lower the crystallization along with enhancing the mechanical strength of the membrane.

4.2 Effect of the PEGDE proportion

For the sake of improving the chemical cross-linking effects, the suitable percentage of the PEGDE also plays a critical role in the membrane formation process. Because different percentage of the PEGDE in the mixture affects the composite CEM in various profiles.

Different mass percentage (in terms of the weight of PVA) of PEGDE membranes are synthesized. The proportions of PEGDE are listed as 10%, 50%, 100%, 150%, and 200 wt%. After removing membranes in the RT from the petri dish, it is discovered that along with the increasing of the PEGDE ratio, the membranes are trend to shrink together and become thick. Furthermore, from the morphology, the distribution of the membrane concentration is uneven (Fig. 25), influencing properties of the membrane in the future utilization. Apart from that, the membrane possessing high proportion of PEGDE is easier to absorb water when putting into the solution, which means that this kind of membrane has poor quality of water up-take and dimensional stability (Table 3). Compared to the membrane with 50 wt% of PEGDE, the one possessing 10wt% cross-linking agent shows good mechanical strength and lower ability to swell, getting 277.2% of swelling and 126.7% of dimensional change. What's more, from the optical image it can be discovered that this membrane surface is smooth and the concentration distribution is even (Fig. 26), even the conductivity is higher than that of PVA/PSSA/10%wt PEGDE membrane (0.0045 S/cm). The PVA/PSSA/10wt% PEGDE CEM demonstrates good flexibility, and is able to be blended 180 degrees. Based on the pervious discussion, using 10 wt% of PEGDE in the membrane preparation process is suitable.

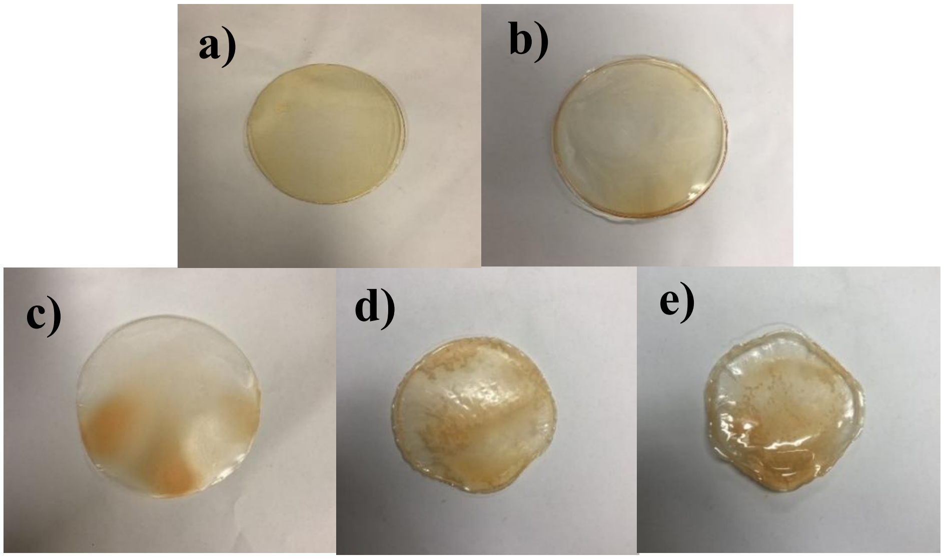

Fig. 25 The CEMs with the PEGDE ratio of a) 10%; b) 50 %; c) 100 %; d) 150 % and e) 200 wt%.

Table 3 Physical and conductivity properties (without HCL acid exchange) of PVA/PSSA/ 10%wt PEGDE and PVA/PSSA/ 50%wt PEGDE membrane.

Sample	Water up-take (%)	Dimensional change (%)	Ionic conductivity(S/cm)
PVA/PSSA/ 10%wt PEGDE	277.2	126.7	$5.6*10^{-3}$
PVA/PSSA/ 50%wt PEGDE	345.2	133.3	$4.5*10^{-3}$

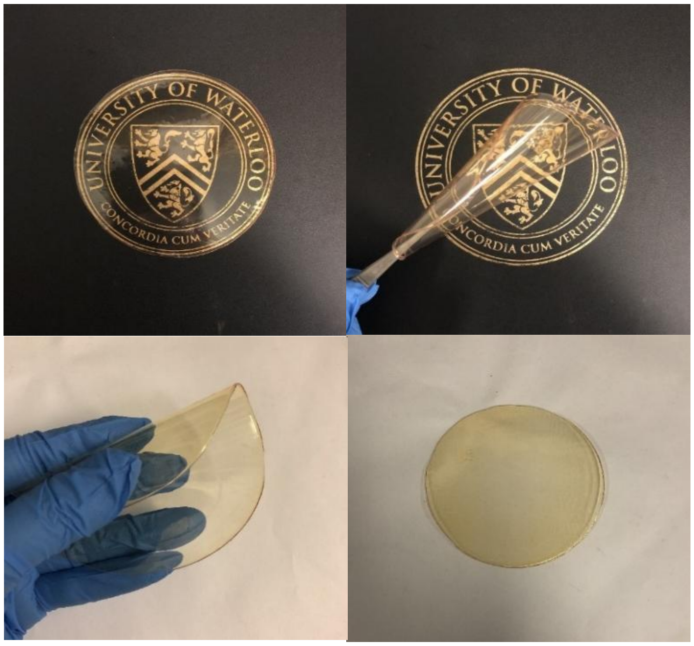

Fig. 26 The membrane with PVA/PSSA/ 10 wt% PEGDE.

4.3 Effect of chemical cross-linking environment

Besides the ratio and type of cross-linking agent, the chemical crosslinking environment also plays a critical role in the membrane fabrication procedure. An appropriate catalyst in the chemical cross-linking reaction can promote PEGDE to react with PVA, forming stable networks across the membrane.[108] With the purpose of identifying a suitable reaction environment, three categories of catalysts are employed to the membrane formation reactions, 1M HCL solution, 1M acetic acid solution, and 1M ethylenediamine solution, respectively, to control the PH of the mixture. As described before, follow the steps to prepare PVA/PSSA/10wt% PEGDE membranes with the help of different catalysts. After peeling off the membranes from the petri dish, membranes prepared with1M HCL or 1M acetic acid (Fig. 27) lead to the uneven concentration distribution and brittleness (Fig. 28), the specimen cannot be folded in half like the membrane fabricated with ethylenediamine. However, the one used ethylenediamine behaves much better than those two synthesized under acid environment, with the good morphology and flexibility (Fig. 28).

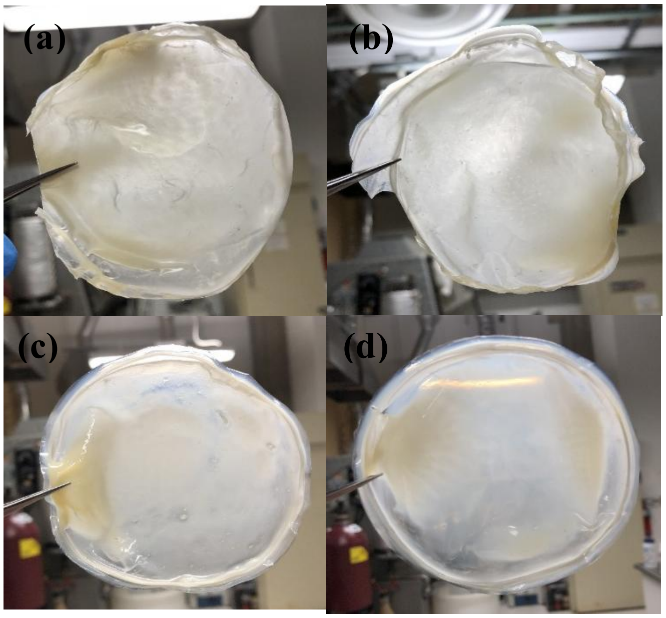

Fig. 27 The PVA/PSSA/ acetic acid membrane prepared with different percentage of PSSA; (a) 10 wt%; (b) 30wt%; (c) 50wt%; (d) 70wt%.

Different from membranes without ethylenediamine, becoming fragile and black after the thermal crosslinking, the membrane formed with ethylenediamine as catalyst demonstrates good mechanical strength as well as non-color change after physical cross-linking. This result indicated that in the presence of ethylenediamine, PEGDE opens the epoxy ring to react with PVA to form the networks internal of the CEM to enhance stability (Fig. 29). Furthermore, the provided ethylenediamine tends to react with PSSA in the solution, so that lower the fragile nature of the membrane is brought by the presence of PSSA. For enhancing the ionic conductivity of the prepared membrane, an increase in the proportion of PSSA is also a necessary choice, but it will lead to the problem of membrane fragility, due to the intrinsic properties of PSSA could not tolerate the following thermal crosslinking step. In this way, since the CEM is prepared with the help of ethylenediamine to improve the stability and strength, there may result in the loss of membrane conductivity, which means that the membrane should go through the acid exchange after all the synthetic process.

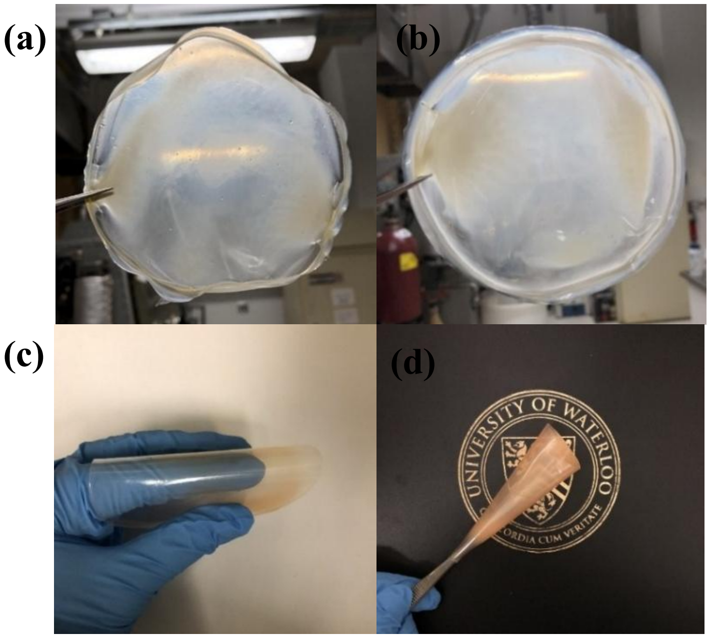

Fig. 28 Optical images of membrane prepared with (a) 1M HCL; (b) 1M acetic acid; (c) and (d) 1M ethylenediamine.

Besides, membranes synthesized with PEGDE absorbs less water than the ones using HCL and acetic acid, along with a smaller dimensional change of the sample, illustrating the formation of networks internal of the synthesized membrane effectively limited the swelling ability of it. The PVA/ ethylenediamine membrane shows the water up-take around 176.4%, smaller than that of PVA/HCL and PVA/ acetic acid membrane, which numbers reach nearly 260%. Reality large water absorption capacity may result in the CEM loss of ionic conductivity in further applications. Apart from that, the PVA/ ethylenediamine membrane displays the conductivity of $5.6*10^{-3}$ S/cm (without acid exchange), almost twice of the other two kinds of membrane mentioned before, owing to the good connections inside the membranes (Table 4). Moreover, from these images, it is obvious that after adjusting to the chemical crosslinking environment with the help of ethylenediamine, the CEMs do not turn into the black after going through the thermal treatment, which is good for the further testing and applications (Fig. 30).

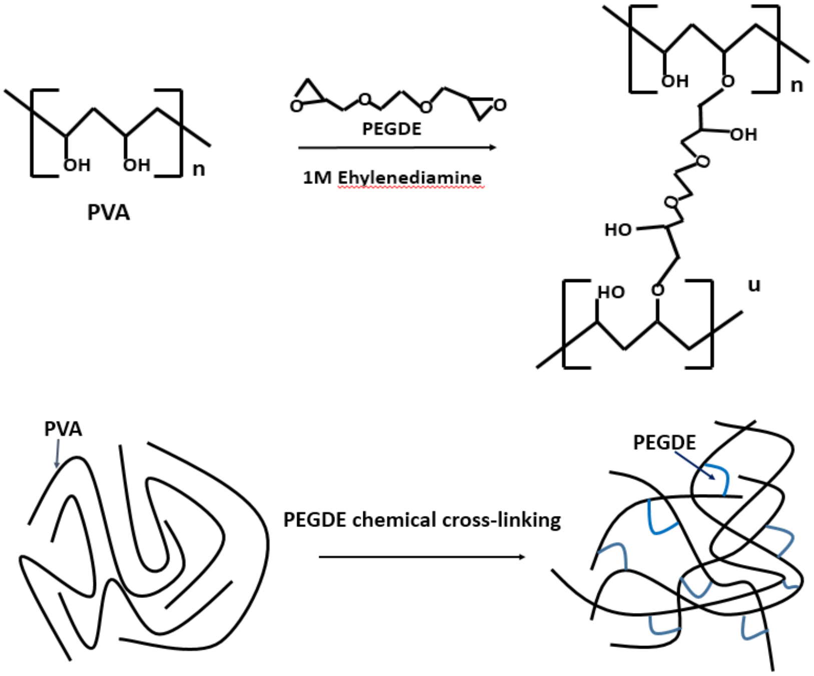

Fig. 29 Scheme for CEM prepared via crosslinking of PVA with PEGDE, showing the linkage positions (top one); schematic illustration of the formation of the cross-linked CEM from PVA and PEGDE (bottom one). PEGDE may react with the –OR or –OH groups on the other position of PVA and PSSA as well to build up linkages. This possibility was omitted in this diagram.

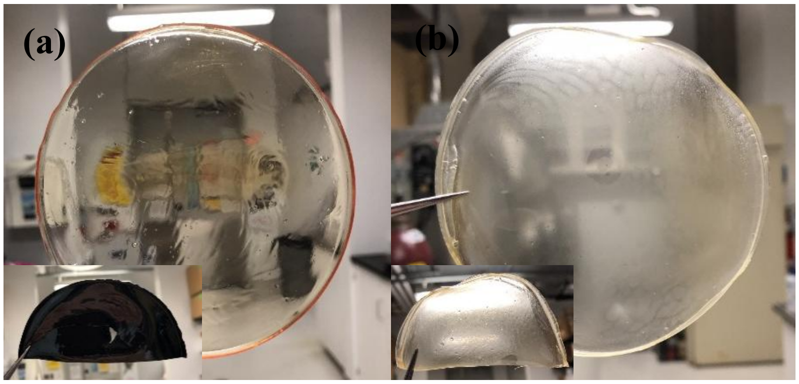

Fig. 30 CEMs in the RT and after physical crosslinking: (a) PVA/PSSA; (b) PVA/PSSA/ ethylenediamine.

Table 4 Summary of the membrane testing results with three types of catalysts

Categories	Water up-take (%)	Dimensional change (%)	Conductivity (S/cm)
PVA/PSSA/ PEGDE/ ethylenediamine	**176.4**	**86.6**	**$5.6*10^{-3}$**
PVA/PSSA/PEGDE/HCL	**258.7**	**120.4**	**$2.2*10^{-3}$**
PVA/PSSA/PEGDE/ acetic acid	**261.7**	**118.2**	**$1.9*10^{-3}$**

4.4 Necessity of physical cross-linking

Since the type of chemical crosslinking agent and its proportion have been decided. The membrane is fabricated followed by the designed process, chemical cross-linking followed by peeling from the petri dish, and taking for the physical property testing. However, after immersing the membrane into the DDI as well as taking it out from the solution, the sample sticks together, which is hard to separate apart (Fig. 31 (b)). According to this phenomenon, it comes to the conclusion that it is not enough for the membrane only to be chemically cross-linked. This membrane still possesses a certain viscosity and poor toughness. Thus apart from the covalent bonds among the polymer matrix, the membrane still needs another interaction to lower the viscosity as well as enhance the mechanical strength, to prevent the stickiness of the prepared membrane. Studies indicate that physical cross-linking is set through non-chemical bonds such as hydrogen bonding van der Waals force or entangled cross-linking, which is the second security of membrane stability.

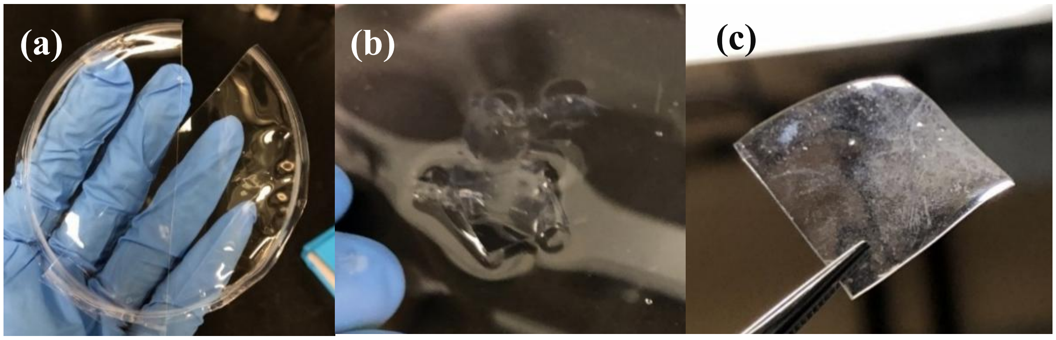

Fig. 31 PVA/PSSA membrane (a) after peeling off from the petri dish (just chemical crosslinking); (b) membrane (a) immersing in DDI; (c) the membrane after chemical crosslinking & physical crosslinking.

4.5 Effects of physical crosslinking temperature

Since covalent cross-linking built networks inside of the membrane, making the membrane denser and extending the service life of the membrane.[95] To further enhance the mechanical strength of the CEM, physical cross-linking is an effective method. Firstly, samples (PVA/PSSA/PEGDE/ ethylenediamine) are dealt under the temperature of 80 ℃, 100 ℃, 120 ℃ (Fig. 32), and 140 ℃ for 2h, respectively. Then followed by the physical property testing (Table 5), the membrane treated with 80 ℃ is found to stick together and expand its surface area in the DDI, just like the membrane performance in the DDI without physical cross-linking. Considering that, 80 ℃ physical cross-linking is unable to reinforce the membrane stability and lower water absorption. What's more, the membrane (dealt with 80 ℃) conductivity is lower than that of membrane treated under 100 ℃. For the conductivity of PVA/10wt% PSSA/ PEGDE kind of membrane, the former gets only about $3*10^{-4}$ S/cm, lower than the later one, which is about $1.5*10^{-3}$ S/cm (discussed in chapter 4.1) (Fig. 33). In 80 ℃, the degree of physical cross-linking is not enough, so the interactions among cross-linking networks are not stable and cannot contribute much to the membrane conductivity.

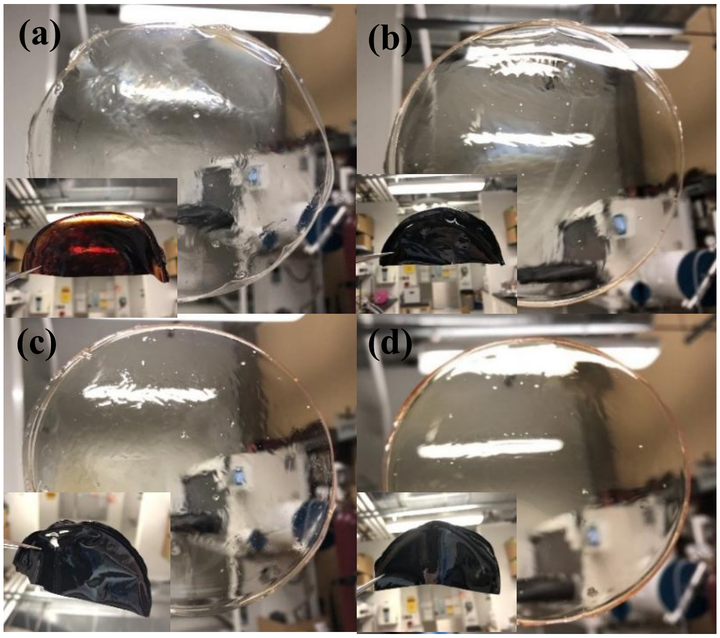

Fig. 32 PVA/PSSA/ PEGDE/ ethylenediamine membrane with different proportion of PSSA after peeled from petri dish and 120 ℃ physical crosslinking (the black ones) ; (a) 10wt%; (b) 30wt%; (c) 50wt%; (d) 70wt%.

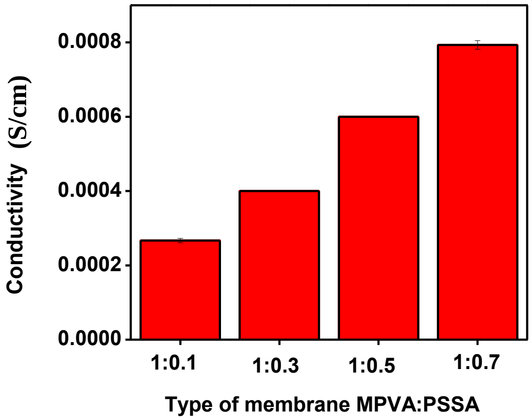

Fig. 33 The conductivity (without acid exchange) of PVA/PSSA/ PEGDE/ ethylenediamine membrane with different PSSA ratio under 80 ℃ for 2h physical crosslinking.

Compared with the membranes treated under 120 ℃, those undergoing 100 ℃ exhibits better mechanical strength, because the prior is easily crushed into pieces in the wet condition when being pressed during the measurement of the conductivity, although doing good in water up-take and dimensional stability. Moreover, membranes are more likely to turn into black under 120 ℃. This might due to the PSSA cannot suffer from high temperature and then leading to these phenomena. So 140 ℃ treated membranes are unable to be employed in the flow battery system in terms of its fragile nature. Through the above discussions, 100 ℃ is chosen as the physical crosslinking temperature for CEM, because the membrane is stretchable to a certain extent under wet conditions without behaving like a gel.

Table 5 Water up-take and dimensional change of membranes with different thermal cross-linking temperature

Temperature	Water up-take (%)	Dimensional change (%)
80 ℃	**202.4**	**136.2**
100 ℃	**176.4**	**87.6**
120 ℃	**140.7**	**82.2**
140 ℃	**85.6**	**78.2**

4.6 Effect of physical cross-linking period

The length of the physical cross-linking period can also influence the membrane performance. Thus PVA/PSSA/PEGDE membranes are treated with 100 ℃ for 2h and 4h separately. From testing results of physical properties, those dealing with 4h indicate a lower ability to absorb water and change their volume in the solution (Fig. 34). But the result differences between these two types of membranes are negligible, meaning that 4h had little influence on dimensional stability and swelling. Therefore, to reduce time and improve efficiency, 2h thermal cross-linking is adopted. Finally, the CEM will be treated for 2h under 100 ℃ after being peeled off from the petri dish for the physical crosslinking.

Since these factors, which have influences on the membrane fabrication, have been explored. A series of PVA/PSSA/PEGDE membranes with different PSSA proportion are fabricated, and find that the ionic conductivity goes up as the percentage of PSSA increased (Fig. 35). But it does not mean that the higher the PSSA content is, the better membrane quality will be, due to the high percentage of PSSA that might lead to the fragile nature of the membrane after physical crosslinking.

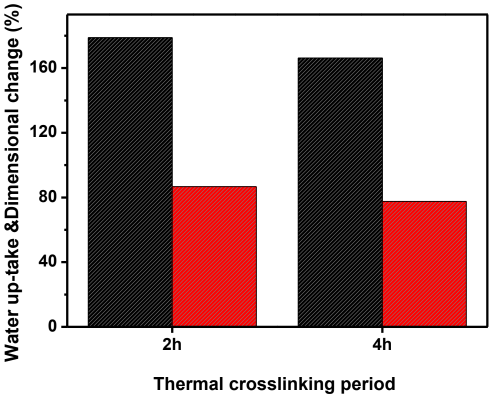

Fig. 34 Physical properties of PVA/PSSA/PEGDE membrane with 100 ℃ physical cross-linking for 2h and 4h; (black column: water up-take; red column: dimensional stability)

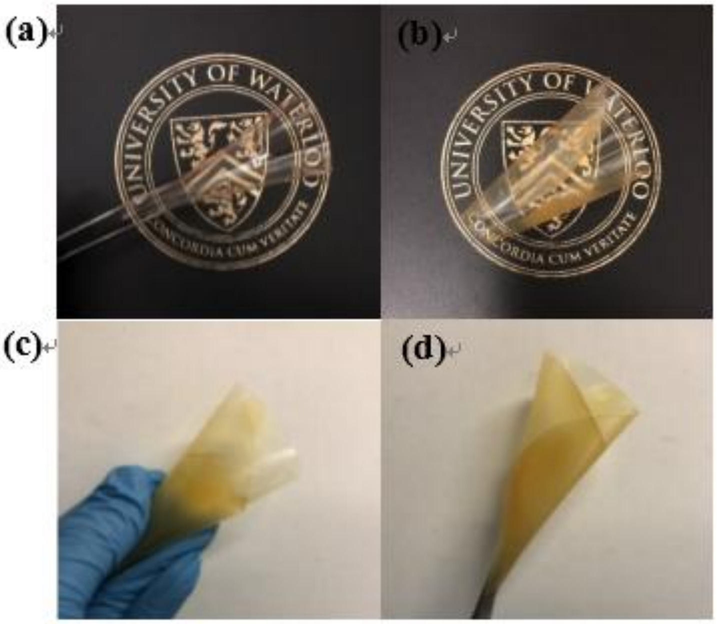

Fig. 35 PVA/PSSA/PEGDE membranes with different PSSA ratio; (a) 10wt%; (b) 30wt%; (c) 50wt%; (d) 70wt%.

4.7 Effect of addition of the GO

The CEM obtained from PVA, PSSA, and PEGDE as the chemical cross-linking agent are prepared to be used in EECS, such as RFB systems. So as to further improve the stability and control of the swelling property of the CEM, a small amount of non-ionic fillers, e.g. GO, with many surface oxygen-containing groups, are dispersed into the mixture solution to increase the specific surface area of the CEM, promoting the interfacial reactions with the PVA matrix, and then improve the membrane conductivity.[99] Since there are studies demonstrate that GO is a good non-ionic filler choice, if using low concentration, which has already been applied in many areas of electrochemistry [109]. What's more, it has been confirmed by studies that GO can form nano-composites with PVA polymer matrix as a kind of nano-filler.[99] At first, two kinds of PVA/70 wt % PSSA/PEGDE/GO membrane are synthesized (the GO weight ratio compared to PVA is 1% (Fig. 36) and 2%, respectively). According to the result, the GO dispersion of PVA/70 wt% PSSA/PEGDE/ 2wt % GO membrane is not as good as the one processing 1wt% GO, the former can be found the dark GO inclusions partially disperses throughout the polymer matrix. This phenomenon verifies that a high load of GO would tend to build bundled agglomerates among the PVA polymer matrix, then hindered performances of the membrane, leading to the fragile and uneven dispersion of CEMs, which might result in the change of the membrane conductivity and behavior. The conductivity of PVA/70 wt% PSSA/PEGDE/ 1 wt% GO membrane reaches 0.0911 S/cm in the RT, still has some gaps with the commercial Nafion 117 membrane, which is 0.13 S/cm (Fig. 37). The tested sample ionic conductivity is measured after washing with DDI water times until the conductivity did not change.

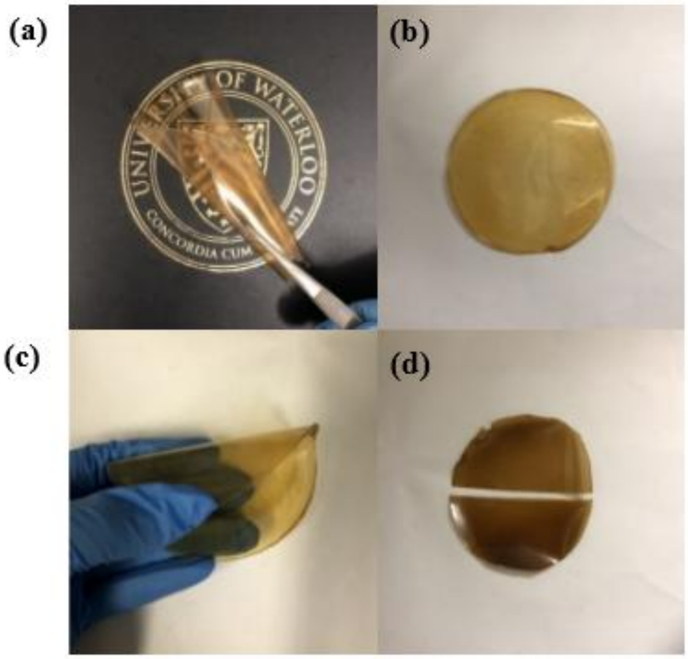

Fig. 36 Optical images of PVA/70 wt% PSSA/PEGDE/ 1 wt% GO; (a) (b) and (c) are the CEM after being removed from the petri dish;(d) is the CEM after thermal cross linking under 100 ℃ for 2h.

From Fig. 36, it is found that 1wt % GO has good dispersion in the CEM and the surface is uniform and smooth, which is good for further application and testing. That owns to the good compatibility of PVA, PSSA, and GO. What’s more, the GO membrane shows good flexibility, which can be rolled up or blended 180 degrees.

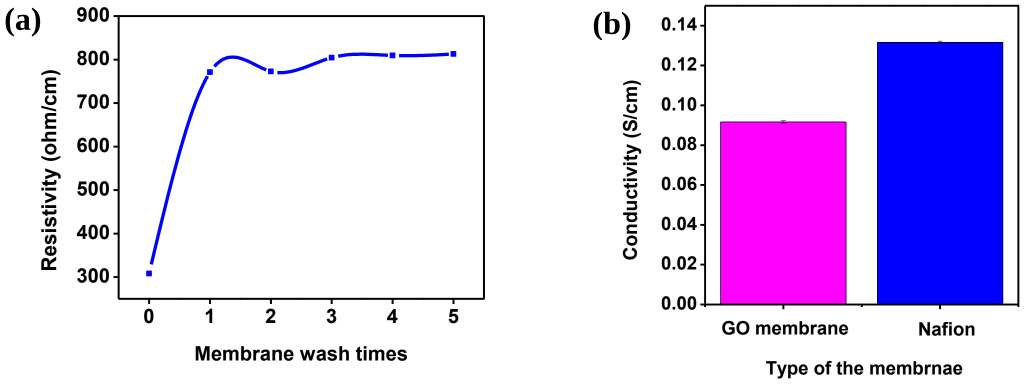

Fig. 37 (a) PVA/PSSA/1wt% GO CEM corresponding resistivity for 5 times of DDI washing; (b) conductivity of PVA/PSSA/1wt% GO CEM and Nafion membrane.

The physical property testing results of PVA/70 wt% PSSA/PEGDE/1 wt% GO membrane demonstrate that the addition of GO effectively lower the water absorption and swelling of the volume (Table 6). These performances due to the addition of GO reduces the moisture content and strengthens the thermal stability of the CEM. Since GO can interact with –OH and then reduced the hydrogen bonding with water molecules, and finally decreased swelling.[99] Unlike PVA/PSSA/PEGDE membranes, they possess high water uptake resulting from the hydrogen bounding between -SO_3H, -OH groups of PVA , PSSA, and water molecules.[110] Moreover, GO 2D nanosheets are also beneficial to improve CEM ionic conductivity, compared to membranes without GO. The tested overall ionic conductivity is consisted of in-plane and through-plane conductivity.[111] Since GO are two-dimensional (2D) nanosheets, which have tendency to self-assemble into a laminated membrane during the casting of the GO/PVA/PSSA composite membrane solution. Although GO interlayers accumulate layer by layer within the membrane, which might result in the conductivity decrease in the through-plane. Meanwhile, these 2D nanosheets can also bring many special ion transportation pathways throughout the polymer matrix as well as regulate the ion transport pathways to promote the in-plane ionic conductivity (Fig. 39). The increase of the overall conductivity might due to the conductivity increase brought by GO to in-plane is far greater than that brought by through-plane to decrease. Thus, after addition of 1 wt% GO, the composite membrane shows better electrochemical properties. As a result, there was a risen of the total number of ionic transports.

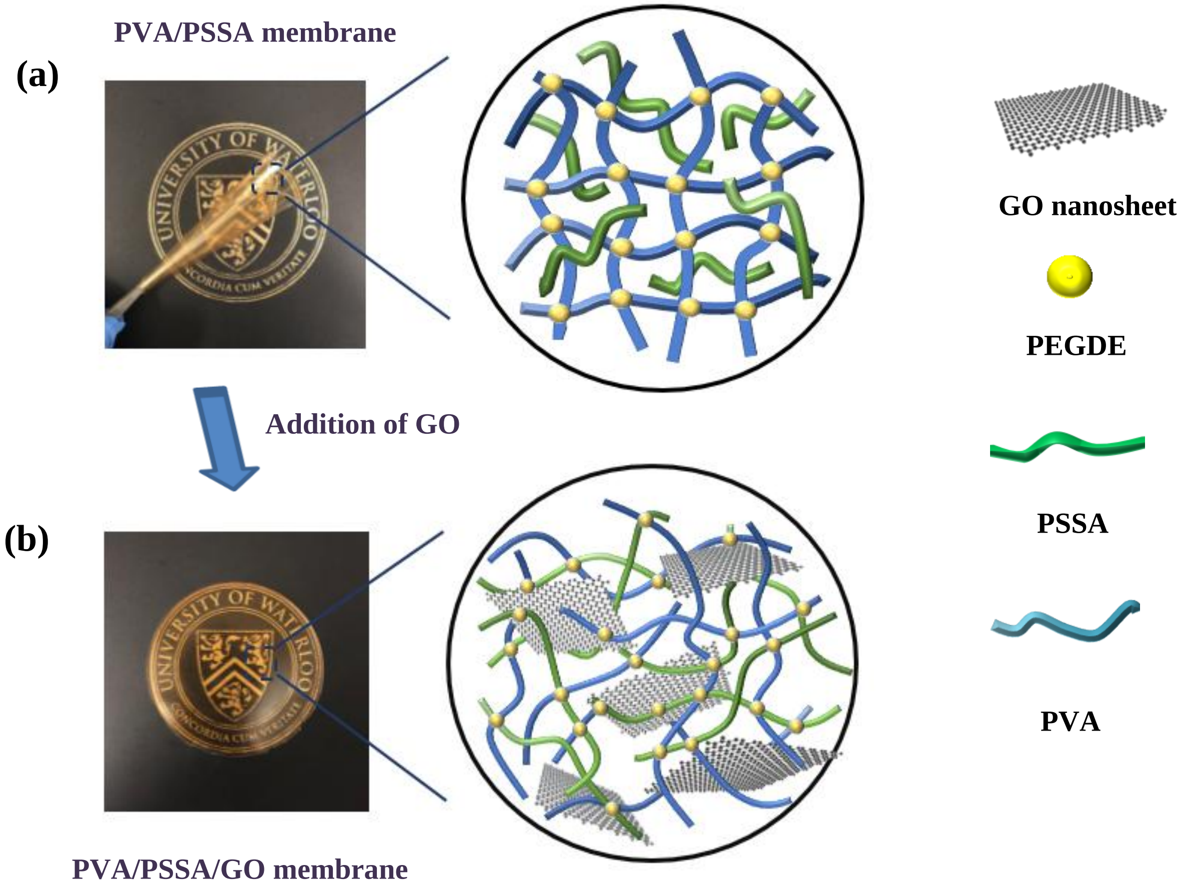

Fig. 38 Internal structure illustrations of (a) PVA/PSSA and (b) PVA/PSSA/GO membrane.

Table 6 Testing results of PVA/70 wt% PSSA/PEGDE/ 1 wt % GO membrane.

Sample	Water uptake (%)	Dimensional change (%)	Conductivity (S/cm)
PVA/70 wt% PSSA/PEGDE/ 1wt % GO	**74.6**	**33.3**	**0.091**
PVA/70 wt% PSSA/ PEGDE/ ethylenediamine	**176.4**	**86.6**	**0.034**

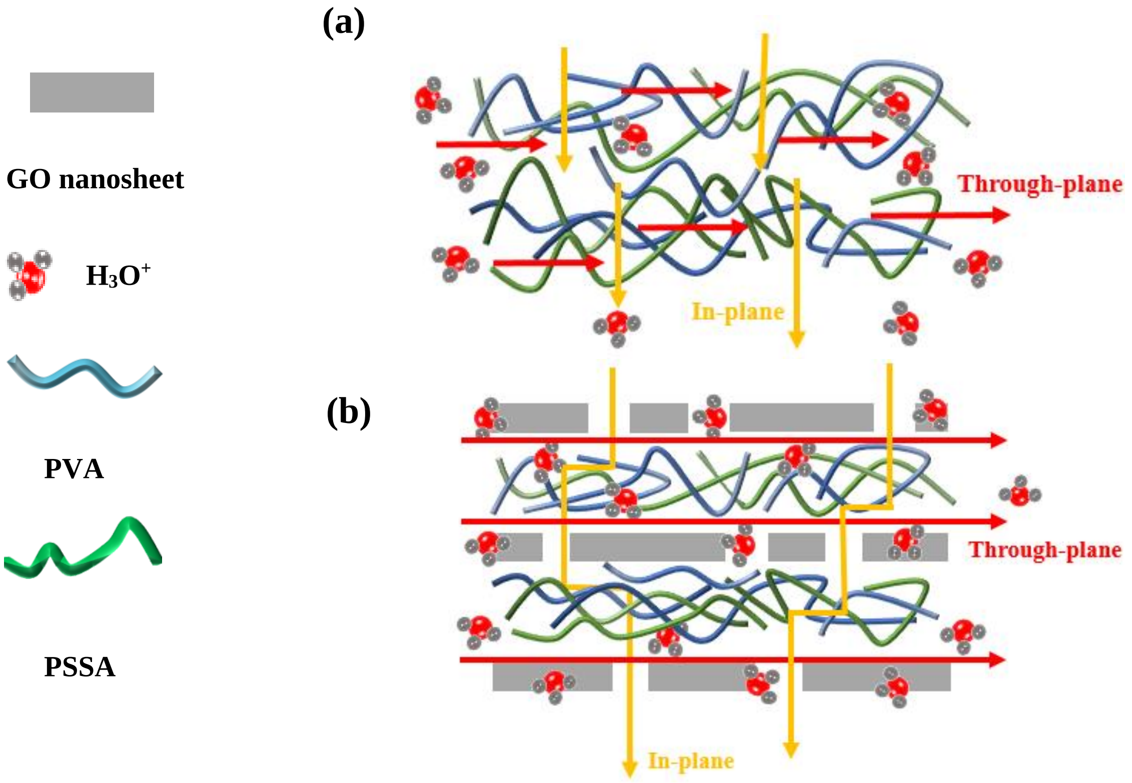

Fig. 39 Schematic illustration of proton transport through the (a) PVA/PSSA membrane and (b) PVA/PSSA/GO composite membrane.

Chapter 5 Conclusions and future work

In conclusion, since researchers are looking for renewable alternative energy systems to get enough large-scale energy supply. One of good candidates among those energy systems is FRB system, which demonstrates merits like low-cost, long service life as well as stable supply of large capacity. But to realize the large scale utilization of RFB system, one thing is to lower the cost of operation and components, especially IEM sitting in the middle of the whole setup. The commercial IEM, Nafion, is too expensive to apply in the large scale EECS, and poor ion selectivity also hints it application. One alternative route to overcome this defect is synthesis of composite CEM to replace Nafion. In this work, the aim is to correlate the cost eco-friendly polymers, i.e., PVA and PSSA, and non-organic filler, i.e., GO, with the help of PEGDE as the cross-linking agent to fabricate CEMs for EECSs.

To achieve this goal, the thesis uses dual cross-linking method to fabricate CEMs. And various factors of experiments influencing CEM properties have been discussed, including the type of cross-linking agents and its ratio, chemical cross-linking environment and physical cross linking temperature. The effects of different physical crosslinking period on the CEM morphology and performances are also investigated, and results illustrate 100 ℃ for 2h thermal treatment works best. What’s more, this work also try to disperse GO fillers into PVA polymer solution to enhance CEMs’ stability and get a growth in the ionic transport through the polymer matrix network. Besides, the proportion and functionality of GO is investigated. It is found that PVA/PSSA/1 wt% GO CEMs possess much better mechanical strength as well as electrochemical conductivity, which benefit from the addition of GO. This phenomenon owns to the special layered ion transportation channels as well as regulated the ion transport pathways brought by GO filler.

PVA/PSSA/1wt% GO CEMs show uniform GO dispersion, thus it leads to transparent and homogeneous CEMs. A series of physical and electrochemical characterizations of various PVA/PSSA/GO composite membranes are carried out and evaluated. In detail, the PVA/PSSA/1wt% GO membrane gets 74.6% of water up-take as well as 33.3% of dimensional stability. The ionic conductivity of PVA/PSSA/1wt% GO memebrane arrives at 0.091S/cm, a little bit lower than that of Nafion 117. In consequence, these results indicate dually cross-linked PVA/PSSA/GO CEM, along with cost effectiveness, might be a good solid electrolyte candidate for the RFB systems.

However, there are still many problems left about PVA/PSSA/GO CEMs. For one thing, other testing techniques of CEMs can be carried out to further explore performances of membranes, e.g., the morphology and internal structure detected by scanning electron microscope and transmission electron microscope. Moreover, the crossover of active species of CEMs which can demonstrate membrane ion selectivity also need to measure. At last, CEMs, as the solid electrolyte of RFBs, should be further optimized as well as exhibit better controllability of membrane performances and finally applied into to suitable electrochemical energy conversion and storage systems, e.g. RFBs.

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