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Synthesis and Properties of Fluorene Based Anion Conducting Membranes for Fuel Cells

Doctor of Science (Material Science)

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Part 1: Research content

Background

Alkaline anion exchange membrane fuel cells (AEMFCs) are recognized as one of the most efficient power sources for portable electronics, stationary power generation, and transportation. AEMFCs offer higher reaction kinetics for oxygen reduction, lower fuel crossover, fuel flexibility, and independence on noble metal electrocatalyst than proton exchange membrane fuel cells (PEMFCs). The key component of AEMFCs is the anion exchange membranes (AEMs) that act as a separator between anode and cathode and migrate the ions. One of the key challenges is finding durable AEM that combines a long time alkaline stability and high ionic conductivity.

In recent years, many research groups have effort significantly to improve the AEMs; their focusing points involved molecular engineering of functional groups and polymer backbones. Different backbones including polyphenylene oxide, polyphenylene, polyarylene ether ketone, polyarylene ether sulfone, polyetherimide, polystyrene, and polyethylenes have been extensively studied. Among these, polymers containing arylene ether, arylene ketone, and arylene sulfone bonds in their backbones, activate hydroxide ion attack and chain scission. As a result, the chemical stability of the corresponding AEMs decreased.

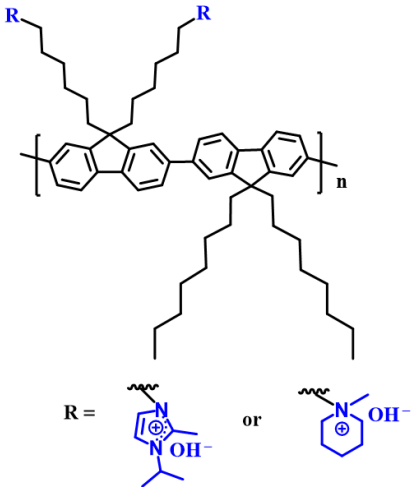

Fig. 1 Structure of the synthesized polymers.

On the other hand, the fluorenyl group containing polymers have attracted much attention due to high chemical stability in alkaline condition. It was reported that alkyl quaternary ammonium (QA) functionalized polyfluorene AEMs were stable in alkaline condition for a long time. There is no literature for imidazolium containing AEM with the same fluorene backbone. In this study, I have synthesized fluorene based polymer by using Pd catalyzed Suzuki cross-coupling reaction which is free from arylene ether, arylene ketone, and arylene sulfone bond and newly incorporated 1-isopropyl-2-methylimidazolium as a cationic group. I also investigated the effect of the N-methyl piperidinium cationic group on the same polyfluorene backbone (Fig. 1).

Objective

In this research, the design and synthesis of new polyfluorene AEMs containing 1-isopropyl-2-methylimidazolium and N-methyl piperidinium were demonstrated. The effect of two different

functional groups on the membrane properties including hydroxide conductivity, ion exchange capacity, water uptake and swelling behaviour, mechanical properties, thermal and chemical stability were systematically investigated. The chemical structure of synthesized monomers and polymers were confirmed by Nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and mass spectrometry. The AEMs were characterized using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy, thermogravimetric analyser, and impedance analyser.

Summary of Results

In **Chapter 2** of this dissertation, poly[(9,9-bis(6′-bromohexyl)-9H-fluorene)-co-(9,9-bis(6′-octyl) fluorene)] denoted as PFBr was synthesized from 2,7-dibromo-9,9-dioctyl fluorene and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6′-bromohexyl)fluorene by using Suzuki cross-coupling reaction. 1-Isopropyl-2-methylimidazolium was incorporated as a functional group. The membrane was casted from a 4 wt% dimethylformamide (DMF) solution of the polymer. The OH^- containing membranes (PF-IMI) were obtained by immersing the PF-IMIBr polymer in argon saturated 1M NaOH solution. Thermogravimetric analyser studies suggest that the synthesized polymer maintain high thermal stability up to 200 °C as shown in Fig. 2a, which is far beyond the desired temperature range for fuel cell applications. The water uptake and swelling behaviour studies unveiled that the dimensional stability of the resultant membranes was high and adsorbed a sufficient amount of water for ionic migration. The AEM exhibited an in-plane linear expansion ratio of 7% and OH^- conductivity of 46 mS cm^{-1} at 80 °C in liquid water, as shown in Fig. 2b & c.

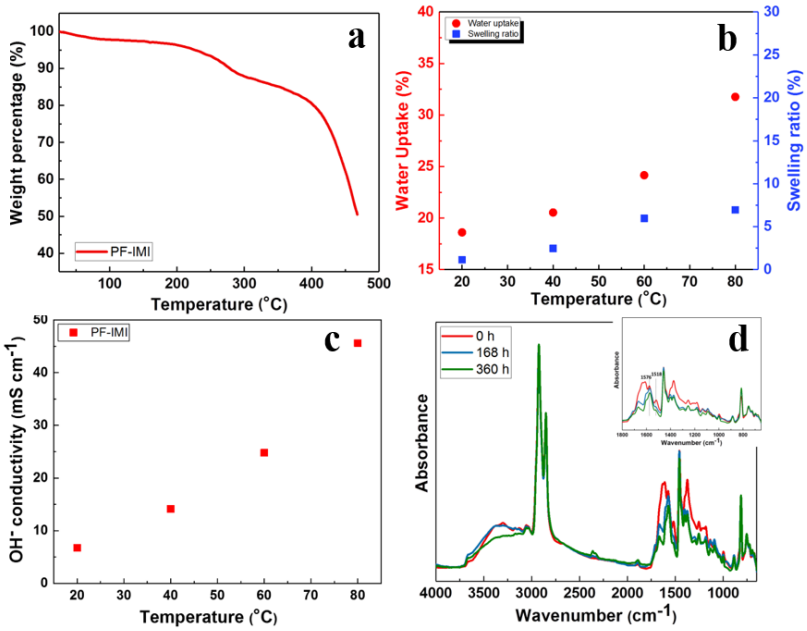

Fig. 2. a) TGA curve, b) water uptake & swelling ratio, c) hydroxide conductivity, d) alkaline stability at 80 °C of the PF-IMI membrane.

The alkaline stability of AEM in argon-saturated 1 M NaOH (aq.) solution was investigated by FT-IR spectra and demonstrated that imidazolium cationic groups were degraded upon exposure to 1 M NaOH solution at room temperature and 80 °C though the backbone was chemically stable (Fig. 2d).

In **Chapter 3,** N-methylpiperidinium was attached to the PFBr polymer and membrane properties of as-synthesized AEM were systematically investigated including water uptake, swelling ratio, ion exchange capacity, thermal stability, mechanical properties, hydroxide conductivity, and chemical stability. By introducing the piperidinium functional group, the properties of the membrane denoted

as PF-Pip were much improved. For example, the water uptake of PF-Pip increased to 81% and conductivity reached up to 58 mS cm^{-1} at 80 °C in liquid water as shown in Fig. 3a & b. The water uptake and ionic conductivity of the PF-Pip membrane were higher than that of imidazolium functionalized OH^- form (PF-IMI) membrane; this may happen, due to the higher free space or cavities of piperidinium containing AEM than that of imidazolium functionalized AEM. I have observed only 13% of the cationic loss by ^1H NMR spectra after storage in 1 M NaOH solution for 168 h at 80 °C.

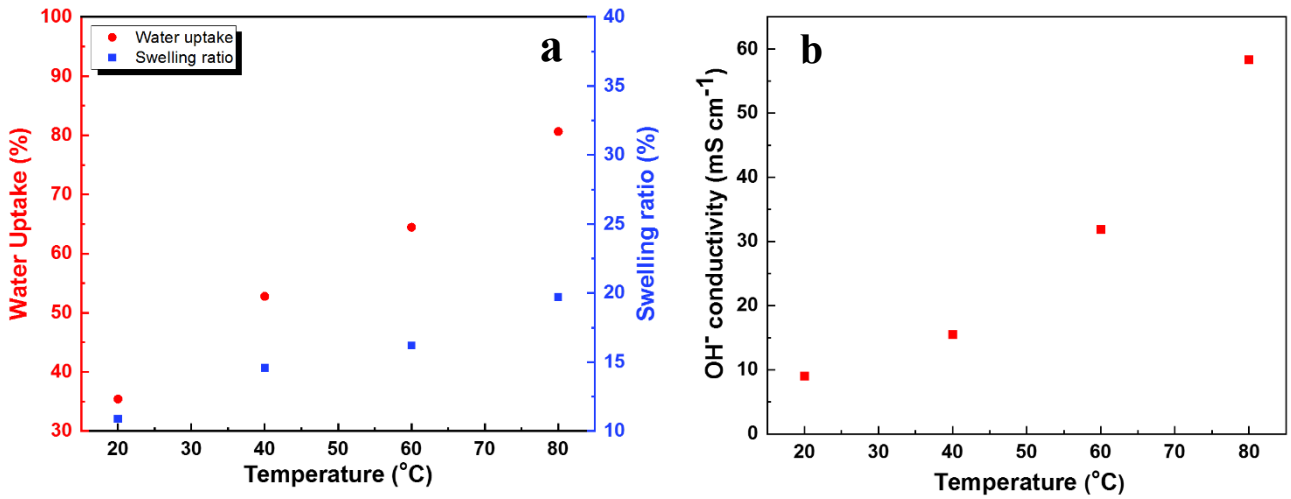

Fig. 3. a) Water uptake and swelling behaviour b) hydroxide conductivity of the PF-Pip membrane.

Chapter 4 highlighted the effect of functional groups e.g., imidazolium and piperidinium on the performances of the AEMs. In comparison to the imidazolium group containing AEM, the piperidinium functionalized AEM showed better membrane properties.

Part 2: Research Purpose

The design, synthesis, and findings of this thesis provide an opportunity of designing novel AEMs based on alkaline stable ether free polyfluorene polymer by using different functional groups that will enrich the diversity of the polymeric AEMs' structure. As some literature has revealed that imidazolium functional groups are chemically stable, but some other literature has suggested the less chemical stability of imidazolium groups. The investigated results of alkaline stability of imidazolium containing AEM can conclude this discrepancy state. Some researchers reported that alkyl tethered N-methyl piperidinium cationic groups were quite stable in alkaline condition. However, I have observed 13% cationic group was lost after 168 h of the alkaline test though it was alkyl substituted. So, from this study, I have outlined the challenge of chemical stability of imidazolium cationic groups on the polyfluorene backbone. Sufficient hydroxide conductivity and good chemical stability was observed in case of piperidinium containing membrane as only 13% cationic group was lost. The findings of this study will provide significant directions and insights

for choosing functional groups for the development of AEMs for practical applications. The results of this study can benefit a broad audience of fuel cells.

Part 3: Research Accomplishments

Publications

(i) **Umme Salma**, Dishen Zhang and Yuki Nagao "Imidazolium Functionalized Fluorene based Anion Exchange Membrane (AEM) for Fuel Cell Applications." *ChemistrySelect* **2020**, *5*, 1255-1263. (Peer-reviewed)

(ii) **Umme Salma** and Yuki Nagao "Alkaline stability of ether bond free fluorene based anion exchange polymer containing cycloaliphatic quaternary ammonium groups." (*Submitted*)

Conferences

(i) Umme Salma and Yuki Nagao "A polyfluorene polymer containing imidazolium cationic groups for anion exchange membrane fuel cells" 68th Polymer Symposium, September 25 -27, 2019, Fukui, Japan. Style of presentation: Poster.

(ii) Umme Salma, Dishen Zhang, Yuki Nagao "Hydroxide ion conducting fluorene based polymers for fuel cell applications" 2019 年度北陸地区講演会と研究発表会, 29 November 2019, Kanazawa, Japan. Style of presentation: Poster.

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