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Block copolymers as anion exchange membrane in fuel cells

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Abstract. Anion exchange membranes play a crucial part as the primary component of alkaline fuel cells, yet their optimization remains an ongoing endeavor. While research and development efforts have made strides in advancing anion exchange membranes, a pressing need exists to further refine their mechanical properties, ionic conductivity, and chemical stability, especially in comparison to proton exchange membranes. Block copolymers have emerged as promising candidates among the array of materials explored for enhancing anion exchange membranes due to their inherent advantages. These copolymers offer unparalleled flexibility in adjustment and boast superior mechanical properties, making them highly adaptable for modifying anion exchange membranes to meet desired specifications. In order to demonstrate the benefits of block copolymer, this paper primarily summarizes and examines the techniques for varying the material content, investigating composition to identify the block copolymer anion exchanging membrane with exceptional performance characteristics, and contrasting it with the random copolymer, polymer blend, and homopolymer exchange membrane. The results unequivocally demonstrate the efficacy of block copolymers in improving the material structure of exchange membranes by fine-tuning the polymer content. Notably, block copolymers outperform other copolymers in significantly enhancing the performance metrics of anion exchange membranes. In summary, studying block copolymers is a practical way to significantly enhance the performance and functionality of anionic exchange membranes, which will help the alkaline fuel cell industry move toward greater sustainability.

Keywords: Block Copolymer, Anion Exchange Membrane, Alkaline Fuel Cells, Ion Exchange Content, Ionic Conductivity

1. Introduction

Currently, the world is rapidly transitioning towards the era of clean energy, with the search for more efficient clean energy sources becoming a major trend in the economic development of nations worldwide. Fuel cells, which are known for their almost entirely emission-free and extremely effective energy conversion capabilities, have garnered a lot of interest because of their benefits. Particularly, as a representative of fuel cells, polymer electrolyte fuel cells have been widely used in automotive, aerospace, household appliances, and other fields due to their high-power density, small size, and low operating temperature [1].

Proton exchange membranes are widely utilized in the domain of fuel cells and are known for their great performance and durability; nevertheless, the expensive cost of the metal electrode catalyst is a downside. Advances in anion exchanging membrane research in recent years have the potential to produce better fuel cells that are alkaline with cheap costs and great efficiency. However, anion exchange membranes still face challenges in chemical stability and performance compared to proton exchange membranes. Consequently, efforts are underway to explore more advantageous materials, with block copolymers emerging as promising candidates compared to other polymers. The preparation techniques for anion exchange membranes with superior qualities using block copolymers are examined in this paper, along with the benefits and drawbacks of block copolymers in comparison to other copolymers. By chemically polymerizing block copolymers and investigating the impact of different polymer compositions on performance, the goal is to produce anion exchange membranes with improved synthetic features.

2. Block copolymer design for fuel cell anion-exchange membranes

2.1. Characteristics and benefits of block copolymers

A block anion exchange membrane has an evident hydrophilic/hydrophobic phase separation structure, which exhibits higher conductivity of hydroxide ions and better alkaline resistance [2]. An essential factor that is determined by the characteristics of the anion-exchanging membrane is ionic conductivity, which is a crucial quantity in the domain of alkaline fuel cells. In this intricate interplay, the polymer structure assumes a paramount role, exerting profound influence over the membrane's architectural morphology and defining attributes. Enter block copolymers – sophisticated entities comprising two or more polymer segments endowed with distinct properties, heralding the convergence of diverse polymer virtues.

In the intricate craft of anion exchange membrane engineering, block copolymers emerge as transformative entities. Their intrinsic capacity to engineer meticulously controlled multi-block architectures lays the groundwork for the establishment of a finely orchestrated interplay between hydrophilic and hydrophobic domains. This orchestrated phase separation not only engenders an environment conducive to ion migration but also facilitates the construction of intricately interconnected pathways optimized for efficient ionic transport. Indeed, a plethora of recent experimental endeavors serve as a testament to the remarkable ionic conductivity showcased by block copolymers.

Furthermore, the inherent versatility inherent in block copolymers unveils a realm of boundless possibilities. Variations in the composition of polymer components or the strategic incorporation of hydrophilic/hydrophobic side chains present avenues for fine-tuning membrane morphology and performance with surgical precision. Whether enhancing conductivity or modulating resistance, the adaptability of block copolymers unveils a panorama of limitless prospects.

Block copolymers are fundamentally the epitome of controllability and multifunctionality, which makes them crucial elements in the meticulous design and fabrication of anion-exchanging membranes meant for use in alkaline fuel cells.

2.2. Design principles and methods

Li and his co-workers produced polybutadiene-b-poly(4-methylstyrene) (PB-b-P4MS) precursors with four different block compositions and 92−95% 1,4-content in the polybutadiene block by living anionic polymerization in a nonpolar solvent [3]. Following this, the process involved the hydrogenation of four distinct polymer types to generate polyethylene segments. P4MS was brominated, and then it was quaternized with trimethylamine to create anionic exchange membranes. The primary distinction among these four membranes lies in the differing relative proportions of their P4MS precursors. It was demonstrated that variations in the relative quantities had an effect on the block copolymers' ion conductivity and absorption of water by examining the ion exchange content. The ion exchange content is positively correlated with the ion conductivity. Studies using scanning electron microscopy have clarified that every membrane includes features that are phase separated. However, with the reduction of relative P4MS precursor content, the degree of functionalization gradually increases, leading to a more organized structure. Moreover, it was noted that these membranes demonstrate commendable mechanical properties and flexibility [3]. The future research direction is to pay attention to the control of mechanical properties under wet conditions.

Buggy et al. hydrogenate an ABA triblock copolymer polychloromethylstyrene-b-polycyclooctene-b-polychloromethylstyrene (PCMS-bPCOE-b-PCMS) to form a new triblock copolymer. A polydisperse midblock was synthesized with narrowly dispersed outer blocks to favor nanoscale phase separation and promote an interconnected morphology [4]. Following quaternization with trimethylamine, anion exchange membranes were synthesized at different temperature settings. Intriguingly, at 80°C, these membranes displayed exceptional ion conductivity alongside moderate water absorption rates. Furthermore, post-hydration, notable improvements were observed in the mechanical resilience of the membranes. These observations highlight the versatile capabilities of triblock copolymers in optimizing both ion conductivity and water absorption, leveraging their scaffold structure to enhance mechanical stability [4]. However, more research is needed to support the chemical stability, especially in extremely alkaline settings.

Lin et al. also prepared anion exchange membranes from triblock copolymers, which showed certain chemical stability. Triblock copolymers bearing alkyl-tethered cycloaliphatic quaternary ammonium-head-groups are prepared via nucleophilic substitution, Friedel-Crafts acylation, ketone reduction, and Menshutkin reaction [5]. The incompatibility between hydrophobic and hydrophilic groups drives the self-assembly process of this block copolymer. As a result, it manifests a structured organization characterized by phase separation and intricately connected ionic domains. Consequently, this organized structure enables the creation of highly efficient ion transport pathways within the material. By facilitating ion flow, these routes give the copolymer exceptional qualities like a high ion exchange content and outstanding conductivity characteristics. The well-established ionic domains contribute to the copolymer's ability to efficiently conduct ions, enhancing its overall performance in various applications. Moreover, even after prolonged exposure to continuous alkaline immersion, the copolymer exhibits minimal changes in conductivity, showcasing its robust alkaline stability. This remarkable stability can be attributed to the influence of the cyclic alkyl structure present in its cationic groups. Furthermore, the copolymer demonstrates commendable thermal stability and mechanical properties, further enhancing its suitability for diverse applications requiring resilience and durability.

There is also an experimental simulation of the preparation of anion-exchange membranes using triblock copolymers. Its main research direction lies in the effect of hydrophobic or hydrophilic spacer addition on the cationic side chain, as well as on the overall structure. Polymers with aromatic (polyphenylene oxide, PPO) or aliphatic (polystyrene-ethylene-butylene-styrene, SEBS) backbones were created by Lee. Unmodified block copolymers alone are capable of establishing efficient ion transport pathways. The incorporation of hydrophobic spacers facilitates additional nano-phase separation, enabling the copolymers to maintain comparable ion conductivity even at lower ion exchange capacities. Conversely, the introduction of hydrophilic spacers hinders ion migration by impeding spatial transport pathways within the side chains. Nonetheless, subsequent structural modifications incorporating multiple side chains have effectively overcome this hindrance, resulting in sustained high ion conductivity. The simulation results therefore suggest that the hydrophilic spacers may improve the AEM morphology and the transport of anions at higher hydration levels compared to the currently synthesized membranes using alkyl spacers [6].

Tanaka et al. synthesized two oligomers, a hydrophilic block copolycondensation of

fluorene-containing and linear hydrophobic oligomers by block copolymerization and other methods to make anion conductive aromatic multiblock copolymers, poly(arylene ether)s containing quaternized ammonio-substituted fluorene groups [7]. This membrane boasts superior electrical conductivity compared to current comparable anion membranes. Visual evidence indicates distinct hydrophilic and hydrophobic phase separation, showcasing remarkably high ionic conductivity at maximum ion exchange capacity. It also exhibits chemical stability and strong mechanical qualities, which improve its overall performance and robustness in a variety of applications. Applying a multiblock copolymer structure improves the overall performance of the battery by striking a good balance between attributes like as chemical stability and ionic conductivity.

Lai and co-workers synthesized a series of phenolphthalein-based poly(arylene ether sulfone nitrile) multiblock copolymers containing 1−methylimidazole groups to prepare anion exchange membranes for alkaline fuel cells [8]. Selective and densely packed ionic groups are introduced onto phenolphthalein units to serve as hydrophilic segments, forming distinct ionic clusters. To enhance dimensional stability, strongly polar cyano groups are incorporated into the hydrophobic segments. The membrane exhibits a unique phase separation morphology that capitalizes on the advantages of the incredibly polar cyano assemblages on the hydrophobic sections and the large aromatic composition of the phenolphthalein units on the hydrophilic portions to aid in the creation of ion transport pathways. In addition, the membrane's low swelling rate guarantees outstanding stability in terms of mechanics, heat, and acidity in addition to enabling high water absorption and hydroxide ion conductivity. The amalgamation of these attributes highlights its potential for an extensive array of uses.

Rao et al. prepared an ethyl imidazolium-functionalized poly(arylene ether sulfone) block copolymer as a novel anion exchange membrane [9]. The hydrophobic and hydrophilic ionic components of the block copolymers have a different phase separation morphology in the membranes made from these. Their extensive benefits also include high hydroxide ion conductivity, excellent mechanical, chemical, and dimensional stability, and imidazole functionality's ability to provide thermal and chemical stability. Furthermore, membranes prepared through homogeneous functionalization demonstrate superior defined morphologies, thus better preserving their structural integrity. This combination of attributes enhances their potential for diverse applications.

3. Comparison with other polymer types

3.1. Block Copolymer versus Random Copolymer

The ion conductivity was always reported to be several factors (or even orders of magnitude) higher in block copolymers compared to their analogous random copolymers due to the microphase separated morphologies in block copolymers and their ability to localize ion concentration and movement in an ordered structure [10]. Experiments on several sets of block copolymers and their matching random copolymers have shown that phase-separated morphologies and well-defined ion channels are more readily generated when the block copolymers have continuity and amphiphilic features. However, random copolymers do not form microphase separation. Block copolymers consistently show greater ion conductivity than random copolymers across a variety of experimental settings, including varying temperature ranges and similar ion exchange capacity criteria.

3.2. Block Copolymer versus Polymer Blend

To ascertain their shared characteristics, block copolymers were contrasted with random copolymers and the analogue mix of the two polymers. The conductivities were an order of magnitude higher for the block copolymer compared with the blend over the temperature range studied at various film thicknesses [10]. These variations in morphology-block copolymers show microscale phase separation, whereas polymer blends show nanoscale phase separation-can be ascribed to these differences. In addition, conductivity is influenced by the film's thickness, and changes in film thickness may have a greater impact on microscale morphology than on nanoscale characteristics.

3.3. Block Copolymer versus Homopolymer

Under identical experimental circumstances, block copolymers exhibit stronger ion conductivity than analogous homopolymers at higher ion exchange capacities, but at lower ion exchange capacities, the former may exhibit poorer conductivity than the latter. Subsequent studies have indicated that the microphase separation of block copolymers contributes to an enhancement in conductivity, a feature absent in homopolymers, which do not demonstrate microphase separation. Overall, these results of experiments suggest that the ion-rich microdomains accelerate water-assisted ion transport in the block copolymer compared to the homopolymer [10].

3.4. Advantages and limitations of block copolymers and their future research directions

Drawing from previous experiments and conceptual designs, block copolymers demonstrate a remarkable capacity for microphase separation, allowing for precise control over the morphology and structure of nanomaterials. By reducing steric resistance and facilitating the creation of extremely effective ion transport channels, this inherent benefit eventually improves ion conductivity. However, challenges persist, particularly concerning their chemical stability in highly alkaline environments. The performance of various block copolymers can vary significantly, necessitating extensive real-world testing to validate and optimize their efficacy. Although anion exchange membranes have shown considerable progress, they are still not performing up to the level of proton exchange membranes that are now on the market. Achieving equilibrium between stability, conductivity, and mechanical qualities of block copolymers need to be the primary focus of future research endeavors. If cutting-edge scientific and technological methods like self-aggregation, cross-linking, surface modification, and coating techniques are researched, there is also a great deal of potential for the advancement of membranes for anion exchange with increased conductiveness, stability of chemicals, and mechanical durability. These advancements are pivotal for advancing alkaline fuel cell technology and fostering the widespread adoption of sustainable energy solutions. Through the resolution of current constraints and the use of novel methodologies, scientists can expedite the advancement of superior anion exchange membranes, consequently catapulting alkaline fuel cells into a feasible substitute energy source for the times ahead.

4. Conclusion

When anion exchange membranes were first developed, they had issues with poor chemical stability, low OH conductivity, and poor electrochemical performance because of their delayed development. However, in the past decade, significant advancements have been made. Fuel cell performance, dimensional stability, and alkali resistance have been improved to differing degrees owing to the use of cationic functional units and various kinds of polymer main chains. Fuel cells with anion exchange membranes are developing at a steady pace due to their inherent benefits, and they are now closely competing with fuel cells made with proton exchange membranes in terms of density of power and operational stability as research continues. Future study on how to increase anion exchange membrane conductivity while preserving exceptional stability both chemically and physically is still one of the most fruitful avenues of investigation. Therefore, it is necessary to develop block copolymers with better alkali resistance and expansion resistance. In addition, it is necessary to design them carefully in morphology and structure, and conduct a lot of experiments to test their performance for subsequent optimization and upgrading. Anion exchange membrane design can benefit from additional concepts and techniques when combined with contemporary high-tech technologies. In the future, block copolymer anion exchange membranes are expected to outperform membranes that exchange protons in the alkaline fuel cell application system.

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