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Synthesis and properties of chitosan membranes modified by reactive cationic dyes as a novel alkaline exchange membrane for low temperature fuel cells

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ABSTRACT

Using 1-aminoanthraquinone, cyanuric chloride, dimethyl propylene diamine, diethyl sulfate as reactants, a reactive cationic dye (RCD) was synthesized. Then the dye prepared was used to modify the pristine chitosan (CTS) membrane to synthesize a novel alkaline exchange membrane for low temperature fuel cells. The performance of the prepared membranes were researched in details. FTIR and SEM were used for chemical and structural characterization of the membranes while thermo gravimetric analysis was adopted to study the membranes' thermal stability. The properties of the membranes such as OH⁻ conductivity (σ), water uptake (WU), ion exchange capacity (IEC) and mechanical property were also investigated systematically to evaluate their application performances. The results showed that the OH⁻ conductivity of the membrane (52 μm) can reach $4.59 \times 10^{-3} \text{ S cm}^{-1}$ and increase with the temperature increasing from 30 °C to 80 °C. After immersing the CTS/RCD membrane (52 μm) in the KOH solution (80 °C, 8 mol L⁻¹) for 300 h, the OH⁻ conductivity of the membrane didn't decrease, on the contrary, it increased to $1.057 \times 10^{-2} \text{ S cm}^{-1}$, which indicated that the membrane had the excellent stability to resist the strong alkaline lye.

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Introduction

Fuel cells are expected to become a prominent technology in a variety of power generation applications due to their high

efficiencies for energy conversion along with low pollution levels, noise and maintenance costs [1–3]. As a key component of fuel cell, the ionic exchange membrane has dual functions of ionic conduction and separation of the anode

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from the cathode. Currently, low-temperature fuel cells fall into two categories: proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs) [4]. The former can start quickly at room temperature, expresses excellent ionic conductivity, and has the advantage of light weight and small volume. However, the high cost of expensive proton exchange membranes such as Nafion[®] and platinum catalysts is still an economic barrier to the widespread application of PEMFCs [5,6]. The latter which operates at high pHs can offer faster fuel cell reaction kinetics than that of PEMFCs in the oxygen reduction reaction, so conventional metals (such as Ag, Co, Ni and Fe) have enough good catalytic activity to replace noble metal catalyst Pt, this can greatly reduce the manufacturing cost of fuel cells [7–11]. But the typical and traditional alkaline exchange membrane (AEM) which is composed of polymer backbone with OH⁻ exchange groups has an obvious defect that the diffusion coefficient of H⁺ is four times more than that of OH⁻, thus in order to achieve the conductive level of the proton exchange membrane (PEM) a fourfold increase in OH⁻ is needed. In other words AEMs need a higher ion exchange capacity (IEC) than that of acidic PEMs, but high IEC can result in excessive swelling and loss of mechanical properties [12]. Therefore new AEMs with low cost, good mechanical performance and the required electrochemical characteristics for low temperature fuel cells need to be urgently exploited and utilized.

Recently, great interests have been evoked on developing novel AEMs, and the quaternary ammonium AEM is increasingly becoming a very important research direction [13–18]. Using PVC materials, Hu et al. [13] prepared a new AEM named P1NOH of which the ionic conductivity reached 0.0145 S cm⁻¹ at 20 °C, however, its power density reached only 1.4 mW cm⁻² in a direct-methanol fuel cell at room temperature. Wang et al. [14] designed a PTFE-QDPSU membrane whose ionic conductivity and power density reached 5.1 × 10⁻² S cm⁻¹ at 55 °C and 146 mW cm⁻² at 50 °C, respectively. Although the membrane showed relatively high electricity generating performance, the stability of the quaternary ammonia groups tended to decrease in concentrated alkali solutions with elevated temperatures via either E₂ Hofmann elimination or SN₂ substitution reaction. Danks et al. [15] used radiation grafting technology to construct a novel AEM based on Polyvinylidene Fluoride (PVDF), vinylbenzyl chloride (VBC) and trimethylamine (TMA), but the mechanical properties of the membrane suffered a greater impact because of the deterioration of the main chain. Zhang et al. [16] used poly(vinyl alcohol) (PVA) and poly(diallyldimethylammonium chloride) (PDDA) to prepare a series of cross-linked membranes, which exhibited high OH⁻ conductivity up to 0.027 S cm⁻¹, but PDDA were kept in the membrane only by forming the semi-interpenetrating polymer networks and could be gradually lost during the period of use. Although novel AEMs for low temperature AEMFCs, especially quaternary ammonia types, emerge more and more, most of them have various drawbacks such as raw materials of high price, complex quaternization process, unfriendly manufacture process to environment. So existing AEMs still cannot satisfy the demands of AAEMFCs and the rational membrane design is still a big challenge [12,19–23].

In order to solve the problem of low conductivity, poor stability and mechanical properties of AEMs, a novel AEM based on chitosan (CTS) and reactive cationic dyes (RCD) were synthesized by dyeing means in our work. Natural high molecular substance CTS ((1–4)-2-amino-2-deoxy-D-glucan) possesses many excellent characteristics such as low cost, biodegradability and environmental friendly, excellent mechanical and film-forming property, good alkaline and thermal stability, high contents of reactive groups for cross-linking or grafting [24,25]. However, since CTS has not acid resistant and can be dissolved under acidic condition, thus CTS needs a complex process to be applied in PEMFCs [26,27]. This issue can be eased up because CTS has alkali resistant under alkaline conditions [28]. RCD is one kind of chemically-reactive dye which can react with some polymers via covalent bond. It always contains reactive and quaternary ammonium groups and is mainly used in the dyeing and printing of cellulose fibers. In this work, a novel RCD was synthesized to prepare CTS/RCD membrane via conventional dyeing processes. Compared with the blending technology [3,29,30], the dyeing method is a post-functionality means which can improve the components' compatibility effectively [31]. The home-made RCD can be firmly fixed on CTS matrix through the substitution reaction between the chlorotriazine groups of RCD and the –OH/–NH₂ groups of CTS at proper temperature. Dyes combined with CTS contain quaternary ammonium groups, so it can offer charge carriers to conduct hydroxide. However, since both the major components are hydrophilic, how to adjust the membrane's water up to balance the conductive performance and mechanical performance is a question worth thinking about. Glutaraldehyde (GA) can be adopted to solve this problem through chemical cross-linking method [32–36].

According to the above content, a series of cost-effective CTS/RCD membranes had been prepared using dyeing techniques. Then the chemical structure and morphological microstructure of the CTS/RCD membrane was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM). The membrane's thermal stability was studied by Thermo Gravimetric Analysis (TGA). The properties of the membrane such as OH⁻ conductivity (σ), water uptakes (WU), ion exchange capacity (IEC), mechanical properties and alkaline stability were also investigated systematically to evaluate their application performances.

Experimental

Synthesis of RCD

The whole reaction process is described as Fig. 1.

Firstly, as the reactive solvent, 300 mL of nitrobenzene (AR, Tianjin Damao Chemical Reagent Factory, China) was added into a 500 mL of three-necked flask. Then 11.2 g of 1-aminoanthraquinone (AR, Shanghai Jingchun Chemical Reagent Co., Ltd, China) and 12.9 g of cyanuric chloride (AR, Zhengzhou Alfa Chemical Reagent Factory, China) were added into the flask and mixed well by a MYP11-2A type magnetic stirrer (Shanghai Meipuhe Electronic Instruments Co., Ltd, China).

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