

4(5)-Vinylimidazolium Based Anion Exchange Membranes Prepared by Radiation-Induced Grafting for Hydrazine Hydrate Fuel Cell

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Introduction

Anion exchange membrane fuel cells (AEMFC) have recently received considerable attention due to their potential advantages of over proton exchange membrane fuel cells (PEMFC). The AEMFC works under alkaline condition, where the electrochemical reactions are more facile than in acidic medium, and non-precious metals such as nickel, cobalt and iron can replace platinum as the catalyst.^{1,2} The anion exchange membrane (AEM) is one of the key materials for AEMFC and several AEMs were prepared by radiation-induced grafting.^{3,4} Because of high temperature and highly basic fuel cell operating condition, it is desirable to develop alkaline durable AEMs. Previously, we prepared alkaline durable AEM1 by radiation-induced grafting of N-vinylimidazole into poly(ethylene-co-tetrafluoroethylene) (ETFE) film followed by N-alkylation reaction and alkalization for AEMFCs, especially in direct hydrazine fuel cells (Fig. 1).⁵ However the alkaline durability of this membrane was still not enough under the high temperature alkaline medium (ca. 1 M KOH, 60°C). In this work, we synthesized AEM based on a poly(4(5)-vinylimidazole (4VIm)) grafts by radiation-induced grafting to prevent Hoffman elimination reaction through β -hydrogen sites.

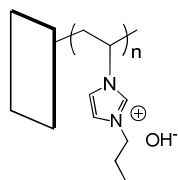
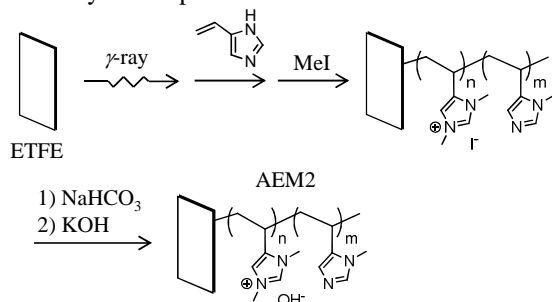


Fig. 1. Structure of AEM1.

Experimental

4VIm was prepared according to a literature procedure.⁶ Anhydrous urocanic acid was heated under vacuum (1 mmHg) at 220–240 °C to melt and decarboxylate the compound. After continuous heating, the product distilled as a colorless liquid that crystallized readily at 23 °C. The off-white powder sublimed at 80 °C under vacuum (0.5 mmHg) to further purify the 4VIm. White crystals (42% yield) were collected on the coldfinger and were dried under reduced pressure. The new AEM was synthesized by pre-irradiation grafting of 4VIm into ETFE films and subsequent N-alkylation by alkyl halide and alkalization (Scheme 1).

Scheme 1. Synthetic procedure of AEM2.



The ETFE films were pre-irradiated with a ⁶⁰Co γ -ray source (JAEA Takasaki, Gunma, Japan) at room temperature in argon atmosphere to a total dose of 50 kGy at a dose rate of 17 kGy h⁻¹. The pre-irradiated ETFE films were immediately immersed into the argon-purged monomer solution consisting of 50 wt% 4VIm in 1,4-dioxane to initiate the grafting reaction. After grafting, the imidazole pendant group was alkylated using methyl iodide. The resultant AEMs were immersed in 1 M NaHCO₃ solution 60°C for 24 h to convert into a HCO₃⁻ anion. And then immersed in 1 M KOH solution at room temperature for 16 h to convert into a OH⁻ anion. The ionic conductivity was measured by two-point probe AC impedance spectroscopy at 100% relative humidity. The ion exchange capacity (IEC) was measured using standard back titration methods.

Results and discussion

Radiation-induced graft polymerization successfully afforded 4VIm-grafted ETFE film, and gravimetrically determined degree of grafting was 60%. The alkylation reaction for AEM2 was not completed probably due to steric hindrance between adjacent imidazole units. The yield of imidazolium iodide salt was 66%. The ionic conductivities at 60°C of AEM2 was 85 mS/cm, and observed IEC value of 2.30 meq/g was close to the calculate value (2.38meq/g). This result indicated that the ion exchange reaction was completed without degradation reactions.

The alkaline stability of AEMs was estimated by monitoring the change in conductivity of AEMs in 1 M KOH at 60°C. As a result, the conductivity of AEM1 suddenly decreased within few hours, while the initial decrement of conductivity of AEM2 was clearly suppressed. The prevention of Hoffman elimination reaction enhances the alkaline durability of imidazolium-type AEM. Accordingly, AEM with alkylimidazolium cations without β -hydrogen is promising material for highly alkaline durable direct hydrazine fuel cells.

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