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論 文 要 旨
THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this dissertation, development of novel hydrocarbon-based polymers for alternative of perfluorinated polymer electrolyte membranes (PEMs) for fuel cell application is summarized into 9 chapters as follows:

In chapter 1, the general introduction about the background of this study is described. Polymer electrolyte membrane fuel cell (PEMFC) has certain potential advantages attracting increasing attention in the past decade. In the PEMFC system, the polymer electrolyte membrane (PEM) is a crucial component. Recent years, many different kinds of hydrocarbon-based membranes, *e.g.*, sulfonated polystyrene (SPS), sulfonated polyimide (SPI), sulfonated polyphenylene (SPP) and phonsphoric acid (PA)-doped polybenzimidazoles (PBI) have been prepared as alternatives to the sulfonated perfluoropolymers (PFSA)-based membranes. However, these sulfonated membranes still show lower proton conductivity at low relative humidity (RH) and lower oxidative stability compared to that of PFSA polymers. On the other hand, PA-doped PBIs have several drawbacks such as low solubility of PBIs and poor mechanical strength after absorbed PA. This dissertation focused on the development of the PEMs to solve problems described above.

In chapter 2, the first section, the ether containing PBI, poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI), was synthesized to improve the solubility of PBI. The OPBI with the doping level (defined as the molar ratio of the PA per PBI repeat unit) of 6.5 showed power density of 366 mW/cm^2 at 160 ^{o}C with H_2-O_2 under ambient pressure without any external humidification. In the second section, for further improve the fuel cell performance, sulfonated copolybenzimidazoles (SPBIs) have been prepared. The SPBI membranes exhibited relatively high PA doping level of 8-13, while still maintained high mechanical strength. They showed high output power density of 580 mW/cm^2 at 170 ^{o}C with H_2-O_2.

In chapter 3, a series of polystyrenes with phosphonic acids via 4, 6, and 8 methylene spacers have been synthesized by radical polymerization. These membranes with the ion exchange capacity (IEC) value of 3.0-3.8 also exhibited a very low water uptake, similar to that of Nafion 117 over the wide range of 30-80% RH. And the proton conductivity comparable or higher than those of the reported phosphonated polymers with much higher IEC values, such as the phosphonated poly(*N*-phenylacrylamide) (PDPAA, IEC: 6.72 mequiv/g) at low RH conditions.

In chapter 4, the cross-linked random copolystyrene derivatives based on a hydrophobic alkoxystyrene unit and a hydrophilic styrene unit containing a pendant alkyl sulfonic acid with the IEC of 2.57-3.03 mequiv/g were prepared by using 4,4'-methylene-bis[2,6-bis(hydroxyethyl)phenol] (MBHP) as the cross-linker in the presence of acid agent. The cross-linked membrane with the IEC value of 3.03 mequiv/g showed a high proton conductivity compared to that of Nafion 117 over the entire range of 50-95% RH. Furthermore, the cross-linked membranes had a high oxidative stability against Fenton's reagent regardless of their high IECs.

In chapter 5, for further improvement of the proton conductivity at low RH, especially at 30% RH, the cross-linked block copolystyrene derivatives, which have the similar structure with the random copolysytene (chapter 4), have been synthesized by the living anionic polymerization. The cross-linked membrane (IEC=2.89 mequiv/g) displayed high proton conductivity (0.01 S/cm) at a 30% RH and 80 ^{o}C, which was comparable to that of Nafion 117, and 2.5 times higher at 95% RH.

Furthermore, to improve the thermal and mechanical properties, the polymer aromatic main chain was chosen in place of polystyrene. The poly(*m*-phenylene)s and poly(phenylene ether)s with sulfonic acid via alkyl side chains were prepared in chapter 6 and 7, respectively. In chapter 6, the c-SPMPs produced transparent membranes with a relatively high mechanical property in the dry state. The rigid main chains and the cross-linking structure improve the thermal stability and suppressed the unacceptable water uptake and dimensional change of the c-SPMPs membranes even in the hydrated state. The c-SPMP8-2 membrane with IEC = 2.93 mequiv/g showed a higher proton conductivity than Nafion 117 over a wide range of 30-95% RH at 80 ^{o}C. Both of the membranes showed high mechanical properties and proton conductivity. To prepare more flexible membrane, which is required for fabricating MEA, the poly(phenylene ether)s (SPPE) with ether group on the main chain have been synthesized by Nickel-mediated homocoupling reaction in chapter 7. The SPPE shows high mechanical properties, good oxidative stability and high proton conductivity, *e.g.*, 0.0086 S/cm under 30% RH at 80 ^{o}C, which is higher than that of Nafion 117.

In chapter 8, to synthesize polymer by sample method and the study on clarifying the detailed structure-property relationship for the design of future PEMs, the poly(arylene ether ether nitrile)s with different length of alkylsulfonated side chains was synthesized. The introduction of longer alkylsulfonated side chains induced better well-organized nanodomains. The membrane containing longer alkylsulfonated side chain (SPAEEN-12) displayed higher proton conductivity than that of the shorter side chain membrane (SPAEEN-6) at 30% RH even its IEC value is lower than that of the latter membrane.

In chapter 9, the conclusion of this study and the prospection was also discussed.

備考： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 2 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 2 copies of 800 Words (English).