

論文内容要約

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授与学位 博士(工学)
学位授与年月日 平成27年4月8日
学位授与の根拠法規 学位規則第4条第2項
最終学歴 平成22年1月
Ph. D.
Department of Materials Science and Engineering
Gebze Institute of Technology, Kocaeli, TURKEY
学位論文題目 Enhancement of Anhydrous Proton Conductivity of Nafion by
Blending with Azole-Based or Phosphonic Acid-Based
Structures as Proton Transport Facilitators
(アゾール系もしくはホスホン酸系構造をプロトン輸送促進剤
として添加したナフィオンの無水性プロトン伝導率の向上)
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要 約

The most outstanding candidate to take the place of internal combustion engines is polymer electrolyte membrane fuel cells (PEMFCs) as they are more efficient and emit low pollutants. The heart of a polymer electrolyte membrane (PEM) fuel cell is a proton conducting membrane, which is commonly fluoropolymers. Perfluorosulfonic acid membranes which have high thermal and chemical stability provide high proton conductivity only when they are hydrated. The reason is the mobility of the protons along the water swelled phase which can be feasible up to dew point of water. High-temperature (100-200 °C) PEMFC systems has been interest of researchers because of their outstanding benefits like catalytic activity, low cost, elimination of CO poisoning, and ease of device cooling and water management. For these fuel cell systems, it's crucial to have PEMs exhibiting high proton conductivities at relatively high temperatures. So, a strong need for the new polyelectrolyte systems of high conductivity at the temperature ranging from 100 °C to 200 °C has arisen. First, Nafion/Azole composite membranes were prepared and characterized. 1H-1,2,4-Triazole (Tri), 3-amino-1,2,4-triazole (ATri) and 5-aminotetrazole (ATet) are promising heterocycles whose melting points are 120 °C, 156 °C and 203 °C, respectively. Tri, ATri and ATet are crystalline solid at room temperature and different from imidazole they contain three or more nitrogen atoms in the ring. Previously, proton transfer reactions in 1,2,3-Triazole have been investigated by computational methods and deduced that Tri forms clusters that favors intermolecular proton transfer reactions. Although the proton conductivity of pure 1H-1,2,4-triazole was reported to be near 1×10^{-4} S/cm at 115 °C and 1.2×10^{-3} S/cm at the melting point, the mechanical property is inadequate for fuel cell application. The use of Tri, ATri and ATet as blend components in an acidic polyelectrolyte can be useful for the development of high temperature resistant free-standing films. Since polymer electrolyte membranes consisting of acidic polymer host and heterocycle

may allow long range proton transport via structure diffusion. Nafion-based proton conducting anhydrous composite membranes were prepared via two different approaches. In the first, commercial Nafion115 and Nafion112 were swelled in the concentrated solution of azoles such as 1H-1,2,4-triazole (Tri), 3-amino-1,2,4-triazole (ATri) and 5-aminotetrazole (ATet) as heterocyclic protogenic solvents. In the second, the proton conducting films were cast from the Nafion/Azole solutions. The partial protonation of azoles in the anhydrous membranes were studied by Fourier transform infrared (FT-IR) spectroscopy. Thermal properties were investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA results showed that Nafion/ATri and Nafion/ATet electrolytes are thermally stable at least up to 200 °C. Methanol permeability measurements showed that the composite membranes have lower methanol permeability compared to Nafion112. Nafion115/ATri system has better conductivity at 180 °C, exceeding 10^{-3} S/cm compared to other Nafion/heterocycle systems under anhydrous conditions.

Second, Nafion/ poly(1-vinyl-1,2,4-triazole blend membranes were prepared and characterized. Although the use of heterocyclic systems as composite components in an acidic polyelectrolyte was useful for the development of high temperature resistant films, the solvent leaching out could be problem for prolonged fuel cell application. Alternatively, Nafion/polymer blends have been reported claiming to reduce methanol permeability and reduce the solvent exclusion. The use of poly(1-vinyl-1,2,4-triazole, PVTri, as a blend component with Nafion would be interesting since PVTri bears triazole as repeating and showed high proton conductivity when it is doped with phosphoric acid. In addition, PVTri is thermally as well as electrochemically stable polymer and it can be used for high temperature applications. The polymer blends consisting of acidic and heterocyclic polymers which may allow long range proton transport via structure diffusion. The homopolymer poly(1-vinyl-1,2,4-triazole), PVTri, was synthesized by free radical polymerization of 1-vinyl-1,2,4-triazole. The membranes were prepared successfully solution casting which led to controlled impregnation of the PVTri into Nafion. The materials showed high chemical and thermal stability, i.e., Nafion-P(VTri)_n systems decompose well above 300 °C. Calorimetric studies illustrated that the blended systems have no first order or glass transition up to 200 °C. SEM results demonstrated that Nafion-P(VTri)_n membranes are homogeneous irrespective to composition. From the FT-IR studies, it was found that protons are dissociated from the acidic groups and protonated azole units of the polymer, leading to hydrogen bonding network formation. Compared to Nafion 112, the blend membrane Nafion-P(VTri)₁ has lower water uptake that proves the polymer complex formation. The swelling character of the membranes increased with the fraction of PVTri in Nafion. Methanol permeability experiments demonstrated that the anhydrous blend membranes have lower methanol permeability compared to pristine Nafion112. Electrochemical stability of PVTri was confirmed by cyclic voltammetry. In the anhydrous state, Nafion-P(VTri)₁ system has the highest proton conductivity of 5.3×10^{-4} Scm⁻¹ at 220 °C. After humidification the conductivity of the samples increased about three orders of magnitude at the corresponding temperatures. These results demonstrated that the insertion of PVTri into hydrophilic channels of Nafion resulted in the production of electrochemically, thermally and mechanically stable membranes that can be suggested for application as polymer electrolyte membrane for direct methanol fuel cells.

Third, Nafion/poly(vinyl phosphonic acid) blend membranes were prepared and characterized. Membranes based on phosphonic acid are quite promising due to their thermal stability and oxidation resistivity. The use of poly(vinyl phosphonic acid), PVPA, as a blend component with Nafion would be interesting since PVPA bears

phosphonic acid as repeating and showed high proton conductivity. In addition, PVPA is thermally as well as electrochemically stable polymer and it can be used for high temperature applications. In recent study, commercial Nafion membrane was modified by irradiating in the presence of concentrated vinyl phosphonic acid. In our study, Poly(vinylphosphonic acid), PVPA, was synthesized by free radical polymerization of vinylphosphonic acid. Then Nafion/Polymer blend membranes were prepared by means of film casting from the Nafion-PVPA solutions at several molar ratios of PVPA repeat unit to -SO₃H. Homogeneous Nafion-PVPA films were produced. Nafion-PVPA interactions were studied by fourier transform infrared (FT-IR) spectroscopy. Thermal properties were investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA results illustrated that all these Nafion-PVPA electrolytes are thermally stable at least up to 400 °C. The membrane properties were further characterized for their morphology by scanning electron microscopy (SEM). The proton conductivity of Nafion-P(VPA)₃ blend membrane was measured to be 1.1×10^{-5} S/cm in an anhydrous state at 130 °C. The conductivity of blends increased at least three orders of magnitude up on hydration, i.e., exceeding 10^{-2} S/cm with RH=50% at ambient temperature.

Fourth, the poisoning effect of triazole-like molecules were determined by calculating the binding energies on various catalyst surfaces. Fuel cell electrocatalysts might be poisoned by triazole and imidazole-like molecules due to the leaching out of azole units from the membrane matrix. Triazole and imidazole derivatives are extensively used as dopant molecules to synthesize anhydrous proton conducting composite membranes for fuel cell applications. Although they showed promising conductivities, their leaching out problem is a question mark for deactivation of electrocatalyst during prolonged fuel cell operation. In this study Density Functional Theory is used to investigate poisoning degree of series of electrocatalysts by 1,2,4-Triazole, 1,2,3-Triazole and Imidazole. Carbon monoxide which is both experimentally and theoretically known to be poisoning for electrocatalysts is used as reference. Both triazole and imidazole molecules showed similar binding energies that were nearly half of CO. The results showed that triazole-like molecules is not appropriate for fuel cell applications due to their high binding energies towards electrocatalysts; such as Pt, Pd, Ru, Ni, etc.

Finally, the morphologies of Nafion-based blend membranes were investigated. That the understanding of the process of micro-phase separation in various ionomers is important leads researchers to employ different modeling methods. It is surmised that molecular features and processing conditions result in mesoscale alterations of different length scales in morphology. The present section is a complementary to our previous experimental study on proton conducting PFSA-based polymer blends. In our earlier sections, Nafion-PVPA and Nafion-PVTri blend membranes with significant anhydrous proton conductivity were fabricated. There are also various studies on PFSA-based proton conducting blend membranes as alternative to costly fluorinated membranes. Although, mesoscale morphologies of hydrated PFSA-based membranes were investigated both experimentally and computationally, there is limited study to investigate the mesoscale phase behavior of blend membranes for polymer electrolyte fuel cells.

These results demonstrated that the insertion of basic or acidic units into hydrophilic channels of Nafion resulted in the production of thermally and chemically stable membranes that can be suggested for application in high temperature low humidity working PEM fuel cells.