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Title : STUDIES ON PROTON EXCHANGE MEMBRANES-BASED SPEEKCHITOSAN
CROSSLINKED VIA ULTRAVIOLET CURING METHOD

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The use of proton exchange membrane (PEM) is very significant component in PEMFC and DMFC. It functions to separate anode and cathode, prevents fuel gas crossover, and transports protons from anode to the cathode through it. Nafion is widely used as a PEM material in commercial PEMFC due to high proton conductivity, good mechanical, chemical stability and excellent thermal stability. However, seeking for new materials as an alternative to Nafion is needed due to its expensive, low proton conductivity when temperature operation above 100 oC and high fuel permeability. As an alternative, sulfonated poly(ether ether ketone) (SPEEK) based membrane is a potential candidate due to low cost, exhibit good chemical and thermal stabilities. However, SPEEK with high degree of sulfonation (DS) exhibits gradually deterioration of the mechanical properties, excessive water uptakes at elevated temperatures and methanol permeability that leads to the reduction in cell voltage performance. The use of hybrid membrane is one opportunity to overcome the SPEEK drawbacks. SPEEK and Chitosan can be crosslinked through sulfonic (-SO₃H) and amine (-NH₂) functional groups. Introduction of Chitosan into SPEEK membrane can modify SPEEK properties particularly by improving its swelling ability. Several series of cross-linked membranes of SPEEK with a chitosan were prepared by solution cast technique. SPEEK and Chitosan was dissolved in DMSO and acetic acid, respectively. They were then mixed together and stirred until homogenous solution obtained. The solution was then exposed and treated under ultra violet (UV) light for curing process. Only six samples were prepared with different composition. The composition are pure SPEEK, 90 % SPEEK with 10 % Chitosan, 80 % SPEEK with 20 % Chitosan, 70 % SPEEK

with 30 % Chitosan, 60 % SPEEK with 40 % Chitosan and 50 % SPEEK with 50 % Chitosan. The membranes were then characterized by evaluating physical properties, physicochemical properties, thermal properties and electrical properties. Physical properties were analyzed through the results of DS, Fourier transform infrared (FTIR), X-Ray diffractogram (XRD) and surface morphology. The best composition of SPEEK with 74.2 % DS was successfully prepared. The FTIR study revealed considerable interaction between the sulfonic acid functions of SPEEK and amino groups of chitosan. No defects were observed on cross-section surface morphology. Physicochemical properties were analyzed through the results of water uptake, degree of swelling and ion exchange capacity (IEC). The results show that water uptake decreases with increasing of chitosan content from 52 % to 29 %. While, IEC decreases from 0.188 to 0.018 mequi. Thermal properties were studied using the results of TGA and DSC. Results showed that there is not much effect can be seen on both TGA and DSC trend. Characterizations of proton conductivity and transference number were conducted to further study electrical properties of the membranes. It is found that activation energy increases from 10.6 to 90.9 kJ/mol, while proton conductivity of the membranes decreases from 8.51×10^{-3} to 2.85×10^{-7} Scm⁻¹. Ionic transference numbers are found to be in the range of 0.81 to 0.94, indicating the conductor species in the electrolyte membrane system is predominantly ionic. The results from characterizations showed that the optimum sample which is 10 % Chitosan with 90 % SPEEK might be as a good potential candidate to modify the SPEEK properties.