SYNTHESIS AND CHARACTERIZATION OF MEMBRANE FOR DMFC

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by

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Dedicated to the Almighty God and my Parents

Certificate

This is to certify that the thesis entitled **"Synthesis and Characterization of Membrane for DMFC",** being submitted by Mr. Jay Pandey to the Indian Institute of Technology Delhi, New Delhi, for the award of the degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide research work carried out by him. Mr. Jay Pandey has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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Abstract

Energy is among the most basic necessities of human being. Due to the heavy consumption of existing energy resources and rapid depletion of fossil fuels (petroleum and natural gas), an extensive research is going on all over the world for alternative sources of energy. Mobile and portable electronic devices have emerged as an increasingly important fraction of energy consumption and addressing their power demand through new and renewable sources that can help in reducing demand on the large stationary power generation systems. Direct methanol fuel cell (DMFC), an electrochemical conversion device, has the potential to fulfill the energy demand of for mobile and portable devices as a clean and economical energy source having very high gravimetric energy density (1600 $Whkg^{-1}$) compared to traditional lithium ion batteries (200 $Whkg^{-1}$). However, DMFC is still far from wide commercialization mainly due to higher cost of DMFC materials like electrode catalysts, bipolar plates and membrane. Ion exchange membrane, a core component of DMFC, is usually a polymeric polyelectrolyte allowing selective transport of proton. Nafion series of membrane are most commonly used. The conventional DMFC membranes suffers from high methanol crossover ($>10^7$ cm^2s^{-1}), poor performance at elevated temperature (above 80^oC) and lower humidity (< 60% RH) which reduces the cell efficiency considerably. In addition, they are very costly (particularly Nafion series). Thereby search of an environmentally benign, cost effective, mechanically and thermally stable membrane for potential applications in DMFC has been an area of great interest in last few decades.

In my present work three different inorganic-organic ion-exchange membranes (Si-PWA/PVDF, ZrP/PVDF and Si-PWA/PVA) were synthesized, characterized and their performance in DMFC was analyzed. For this first two different inorganic ion-exchangers (silica

immobilized phosphotungstic acid (Si-PWA) and zirconium phosphate (ZrP)) were synthesized via sol-gel and in-situ techniques respectively and characterized separately. The initial two membranes (PWA/PVDF and ZrP/PVDF) were synthesized by impregnating Si-PWA and ZrP particles in porous poly (vinylidene fluoride) (PVDF) film and the third (Si-PWA/PVA) was synthesized by blending the Si-PWA particles into the poly (vinyl alcohol) (PVA) matrix. Properties of the three membranes were compared to the state of the art Nafion-117 membrane. The physico-chemical (XRD, FT-IR, SEM/TEM and TGA/DSC) and electrochemical properties (transport number, IEC, proton conductivity and methanol crossover) of the synthesized membranes were measured and compared with the state of the art Nafion-117 membrane. Si-PWA/PVDF membrane was thermally stable up to 350^{o}C higher than other two synthesized membranes and Nafion-117. Si-PWA/PVA membrane's tensile strength (93 MPa) was the highest. The Si-PWA/PVA composite membrane has good electrochemical properties (IEC: 0.90 meqg^{-1}, Na^{+} transport no.: 0.92) compared to other two membranes and was comparable to Nafion-117. Methanol crossover for all the synthesized membrane (1.6×10^{-7} cm^2s^{-1}) was much lower than Nafion-117 (12.8×10^{-7} cm^2s^{-1}). Areal resistances of the Si-PWA/PVDF (1.39 Ω–cm^2) and Si-PWA/PVA (1.42 Ω–cm^2) were comparable to Nafion-117 (1.34 Ω–cm^2). At 35^{o}C, DMFC with synthesized membranes gave higher OCV than Nafion-117 due to lower methanol crossover. For the Si-PWA /PVDF and Si-PWA/PVA membranes the peak power density was comparable to Nafion-117.

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