Development of Polyvinyl Alcohol based Alkaline Membrane Electrolyte for Direct Sodium Borohydride Fuel Cell

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by

NEERAJ KUMAR YADAV

DEPARTMENT OF CHEMICAL ENGINEERING & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI-221005

Roll No: 18041502 **2024**

CHAPTER 6

CONCLUSIONS

In the present thesis, a comprehensive study on the synthesis of alkaline pristine PVA-TEOS and physically crosslinked membrane electrolytes was performed for the application in direct sodium borohydride fuel cell (DSBFC). The various characterization techniques such as water uptake and NaOH uptake, ion exchange capacity (IEC), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), sacanning electron microscopy (SEM), mechanical strength and electrochemical impedance spectroscopy (EIS) of the synthesized membrane electrolyte were thoroughly studied and then tested in DSBFC under various operating condition. The half-cell study of the prepared electrode using cyclic voltammetry (CV) and chronoamperometry were also performed substantiate the result of single cell. The detailed conclusions and findings are given in the following sections.

6.1 Pristine PVA-TEOS membrane electrolyte performance

The silica doped PVA composite membrane was successfully prepared using TEOS as a precursor by the sol-gel method without adopting any crosslinking of the PVA-TEOS matrix. The synthesized PVA-TEOS membrane was further doped with NaOH for the use in the alkaline direct borohydride fuel cell. As a result of the inclusion of silica in the polymer matrix, water uptake and NaOH uptake were improved significantly. The field emission scanning electron microscope (FE-SEM) analysis of the synthesized membrane electrolyte confirmed the uniform distribution of silica in the membrane electrolyte and it also showed that high NaOH doping concentration of 6 M causes NaOH deposition on the membrane surface, resulting in the decrease of ionic conductivity. The FTIR analysis of the synthesized pristine PVA-TEOS membrane electrolyte showed the successful implementation of the TEOS into PVA matrix which was confirmed by the presence of Si-O-Si and Si-O-C bond in the membrane matrix. The XRD analysis of the synthesized membrane electrolyte showed the amorphous nature of the PVA-TEOS membrane electrolyte increases on the addition of TEOS upto 10 wt. % which helped to improve the ionic conductivity of the membrane electrolyte. The ionic conductivity of the membrane electrolyte was measured by EIS analysis using two-probe through plane arrangement. The highest ionic conductivity of the PVA-TEOS-(4M) membrane was found in order of $9.09 \pm 0.5 \times 10^{-3}$ S/cm at the temperature of 25 ^{o}C. The ionic conductivity of the membrane electrolyte increases with increase in temperature and the highest ionic conductivity of $9.98 \pm 0.5 \times 10^{-3}$ S/cm was found at the temperature of 55 ^{o}C. The mechanical strength test showed that the addition of TEOS in the PVA membrane matrix increases the tensile strength and decreases the elongation. For the performance evaluation of synthesized PVA-TEOS membrane electrolyte, very low loading of Pt (40 wt. %)/C_{HSA} was used as an anode and cathode electrocatalyst. The optimum loading of 1 mg/cm^2 and 2 mg/cm^2 were found for the anode and cathode, respectively. When the pristine PVA-TEOS-(4M) membrane electrolyte tested in a single DSBFC, membrane resulting in the highest cell performance, producing a maximum power density of 54.91 mW/cm^2 at the room temperature of 25 ^{o}C at optimum loading of anode and cathode electrocatalyst. Based on the above conclusions, the key results are:

- The highest ionic conductivity of the PVA-TEOS-(4M) membrane was found in order of $9.09 \pm 0.5 \times 10^{-3}$ S/cm and $9.98 \pm 0.5 \times 10^{-3}$ S/cm at temperature of 25 ^{o}C and 55 ^{o}C, respectively.

- The addition of TEOS in the PVA membrane matrix increases the tensile strength and decreases the elongation.
- The optimum loading of 1 mg/cm^2 and 2 mg/cm^2 were found for the anode and cathode electrocatalyst (Pt (40 wt. %)/C$_{HS}$), respectively.
- The highest cell performance in terms of power density, producing a maximum power density of 54.91 mW/cm^2 at the room temperature of 25 ^{o}C at optimum loading of anode and cathode electrocatalyst.
- The maximum power density of DSBFC enhanced significantly i.e., 45.46 % when cell temperature was increased from 25 ^{o}C to 55 ^{o}C.

6.2 Physically crosslinked PVA-TEOS membrane electrolyte performance

The properties of the PVA-TEOS membrane electrolyte were further improved by physical crosslinking using freeze-thaw method. The physically crosslinked PVA-TEOS based membrane electrolyte i.e., PT$_{\mathrm{Wwt.\%}}$-nCy-(X) was successfully synthesized for the application in direct sodium borohydride fuel cell (DSBFC). The synthesized membrane electrolytes were characterized by water and NaOH uptake, FTIR, XRD, SEM and EIS analysis. The effect of the freeze-thaw cycle, TEOS loading, and NaOH doping concentration were considered as the major controlling parameters in synthesizing PVA-TEOS membrane electrolytes. The water and NaOH uptake of the physically crosslinked membrane electrolyte decreases with increase in the freeze-thaw cycle. The water uptake decreases as the NaOH doping concentration increases whereas NaOH uptake increases as the NaOH doping concentration increases up to 6 M and beyond 6 M, the NaOH uptake starts decreasing. The FTIR analysis showed the various functional groups present the physically crosslinked membrane electrolyte. The FTIR analysis also showed that the increase in the freeze-thaw cycle leads to stronger bond formation between PVA and TEOS. The XRD analysis of the physically crosslinked membrane electrolyte showed that the amorphous nature of the membrane electrolyte increases when the freeze-thaw cycle increases, which is favorable for better ionic conductivity. The present study shows that the ionic conductivity of the membrane electrolyte depends on delicate balance between water uptake and NaOH uptake in the membrane matrix. The membrane electrolyte $PT_{5wt.\%}$-7Cy-(4M) with 7 freeze-thaw cycle and 5 wt. % TEOS loading shows the highest ionic conductivity of $9.26 \pm 0.03 \times 10^{-3}$ Scm^{-1} as the XRD analysis shows the amorphous nature is high for 7 freeze-thaw membranes. The water uptake (65.80 wt. %) and NaOH (22.38 wt. %) uptake was in the intermediate range for this membrane. The amount of TEOS also affects the ionic conductivity of the membrane electrolyte. The membrane electrolyte $PT_{10wt.\%}$-7Cy-(4M) with 10 wt. % TEOS loading exhibited highest ionic conductivity of $9.67 \pm 0.04 \times 10^{-3}$ Scm^{-1}. The surface morphology of the different freeze-thaw cycle membrane electrolytes was also studied. It is seen from the SEM analysis that the surface of the membrane electrolyte becomes more compact as the freeze-thaw cycle increases due to more crosslinking. The mechanical strength test of the synthesized physically crosslinked membrane electrolyte with different freeze-thaw cycles and with varying TEOS loading was performed and it was found that the tensile strength of the membrane electrolyte increases with increase in freeze-thaw cycle upto 7 cycle. The maximum power density of 66.96 mW/cm^2 was obtained using the best membrane electrolyte $PT_{10wt.\%}$-7Cy-(4M) in DSBFC at room temperature of 30 ^{o}C. The maximum power density got enhanced to 27.22 % when the cell temperature was increased from 30 ^{o}C to 60 ^{o}C. Thus, the physically crosslinked $PT_{10wt.\%}$-7Cy-(4M) membrane was found to be very promising which have potential to be used in DSBFC system and it could replace Nafion® membrane in near future.

The performance of the sodium hypochlorite (NaOCl) in NaOH solution as oxidant was also tested in DSBFC using best synthesized membrane electrolyte i.e., $PT_{10wt.\%}$-7Cy-(4M). The commercial Pt (40 wt.%/C_{HSA}) was used as both anode and anode electrocatalyst. The alkaline sodium hypochlorite proved to be excellent oxidant for DSBFC. The electrochemical study in half cell was done by cyclic voltammetry and chronoamperometry. The CV study well demonstrate the reduction behaviour of NaOCl in NaOH solution. On the basis of CV study, the effect of various parameters on the electrochemical reduction of NaOCl in NaOH was investigated. The optimum oxidant concentration of NaOCl was found to be 2 M at cathode side and 1 M $NaBH_4$ at the anode side. The maximum power density of 58.80 mW/cm^2 at 112 mA/cm^2 current density was obtained at the cell temperature of 30 ^oC at the optimum oxidant concentation of at cathode and fuel ($NaBH_4$) concentration at anode. Whereas, the maximum power density of 69.44 mW/cm^2 at 160 mA/cm^2 current density was obtained at the cell temperature of 60 ^oC and same optimum oxidant and fuel ($NaBH_4$) concentration. Based on the above conclusions, the key results are:

- The membrane electrolyte $PT_{5wt.\%}$-7Cy-(4M) with 7 freeze-thaw cycle and 5 wt. % TEOS loading shows the highest ionic conductivity of $9.26\pm0.03 \times 10^{-3}$ S/cm.
- The water uptake (65.80 wt. %) and NaOH (22.38 wt. %) uptake was in the intermediate range for $PT_{5wt.\%}$-7Cy-(4M) membrane.
- The membrane electrolyte $PT_{10wt.\%}$-7Cy-(4M) with 10 wt. % TEOS loading exhibited highest ionic conductivity of $9.67\pm0.04 \times 10^{-3}$ S/cm.
- The maximum power density of 66.96 mW/cm^2 and 85.19 mW/cm^2 were obtained using the best membrane electrolyte $PT_{10wt.\%}$-7Cy-(4M) in DSBFC at cell temperature of 30 ^oC and 60 ^oC, respectively.

- The performance of the sodium hypochlorite (NaOCl) in NaOH solution as oxidant was successfully tested in DSBFC using best synthesized membrane electrolyte i.e., $PT_{10wt.\%}$-7Cy-(4M).

6.3 Optimization of process parameter of physically crosslinked membrane electrolyte using RSM

In the present work, the BBD model of the RSM was used to optimize the process parameters of membrane electrolyte synthesis to obtain the highest cell performance in terms of power density (Y). The freeze-thaw cycle (A), NaOH doping concentration (B) and TEOS loading (C) of the PVA-TEOS membrane electrolyte used as effective variables/parametrs in the DSBFC. It was found that the selected independent variables, i.e., A, B and C, have a significant influence on the performance of the DSBFC in terms of power density (Y). The ANOVA analysis of the selected BBD model shows that the model is significant and it was also found from the F-value of the ANOVA analysis that the NaOH doping concentration (B) has higher effect on the response value (Y) followed by TEOS loading and freeze-thaw cycle. In the present study, a successful second-order quadratic model was developed by RSM for the determination of the power density of the DSBFC by optimizing the parameters involved in the preparation of the PVA-TEOS membrane electrolyte. The optimum values of the freeze-thaw cycle (A), NaOH doping concentration (B) and TEOS loading (C) were 6.86 (≈ 7), 4.25 M and 10.09 wt. %, respectively were predicted by the RSM model. The maximum power density predicted by the RSM model at the optimum independent variable was found to be 67.31 mW/cm^2. The experimentally determined power density at the predicted optimum conditions was 69.29 mW/cm^2, which was very close to the predicted power density (67.31 mW/cm^2) with an acceptable error of 1.51 %. The excellent adequacy of the developed mathematical model in determining the power density of the DSBFC can be confirmed by the consistency of experimental values with the predicted ones.

6.4 Future Scope

In the present work, the low cost NaOH doped pristine PVA-TEOS membrane electrolyte is successfully synthesized for the direct sodium borohydride fuel cell (DSBFC). The physical crosslinking using the freeze-thaw method proved to be excellent for the PVA-TEOS membrane electrolyte, which significantly improved the mechanical strength, ionic conductivity and hence, power density of DSBFC. The DSBFC setup used for the experiment is also fabricated in the laboratory, IIT (BHU). The membrane electrolyte was synthesized and tested on the laboratory scale. To test the performance of the membrane electrolyte for high electrical power generation, a stack of DSBFC is necessary for practical application. To generate the power on large scale, the study and optimization of the scale up fuel cell system using synthesized membrane electrolyte in the DSBFC is required. The electrocatalyst used was commercial Pt/C, thus, to develop fully low cost DSBFC setup, the non-noble metal can also be utilized and studied using the synthesized membrane electrolyte in DSBFC. The detailed study of permeability of $NaBH_4$ fuel through physically crosslinked PVA-TEOS membrane electrolyte may be done which can be beneficial to further analyze the DSBFC performance. The laboratory synthesized physically crosslinked PVA-TEOS membrane electrolyte shows the excellent characteristics, however, its characteristics can further be improved by addition of other polymer blend or other composite material into PVA-TEOS matrix. In addition, stability test of the developed DSBFC is necessarily done for longer duration of time to study the durability of synthesized membrane electrolyte in DSBFC.