EXTENDED ABSTRACT

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

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Extended Abstract

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Introduction

The primary factors driving to think on various alternative energy resources which provide the majority of the current energy demand are the limited reserves of fossil fuel like coal, petroleum oil and natural gas. The consumption of these fossil fuel directly and their derived fuels are causing severe environmental damage. The growing concern of environmental issues worldwide have led the scientists to use innovative, renewable, sustainable, and environmentally benign energy sources to harness low cost pollution free energy for better future. At present, the most promising alternative to fossil fuel is the fuel cell technology which produces clean and green energy via electrochemical reactions at the fuel cell electrodes using hydrogen and hydrogen rich other molecules e.g., lower aliphatic alcohols, $NaBH_4$ acetic acid, formic acid, glycerol etc. The fuel cells are being considered as an appealing alternative to traditional fossil fuels due to their minimal emissions of pollutants in some cases, high energy density, low operating temperature, simplicity in operation, easy in handling and ease of storing liquid fuel. Among the various types of fuel cells, alkaline fuel cell (AFC) has drawn much attention recently due to its simplicity, low cost and higher energy efficiency. Moreover, the faster kinetics of the oxygen reduction reaction process in an alkaline medium permits the use of non-precious metal electrocatalysts, which is one of the major benefits of the AFC. Recently, borohydride based alkaline direct borohydride fuel cell (DBFC) has become very popular due its various advantages over other fuel cells like high open circuit voltage (OCV) (e.g., 1.64 V for $NaBH_4$ fuel), high performance at low temperature, no storage issue like H_2 gas and easy to operate. It should be noted that the borohydride like $NaBH_4$ or KBH_4 are unstable in neutral and acidic medium. Whereas, generally the borohydride based fuel cells/DBFCs are typically operated in alkaline medium and thus, no such problem of borohydride instability takes place due to its hydrolysis. The most common fuel used in DBFC is $NaBH_4$ which is non-toxic, nonflammable, has no CO poisoning of anode electrocatalyst and byproduct $NaBO_2$ of anode reaction is harmless.

The synthesis of low-cost alkaline membrane electrolyte is very essential to achieve high power density from direct borohydride fuel cell (DBFC) at room temperature to moderate temperature. The poly(vinyl alcohol) (PVA) is very common and useful hydrophilic polymer that has received a lot of attention as a solid electrolyte material due to its non-toxicity, good film forming capability and relatively low production cost. The PVA is having mechanically weak structure and it easily absorbs water due to its highly hydrophilic nature which is not desirable properties for the electrolyte in any fuel cell application. Thus, the common trick is the adding of appropriate agent to the PVA membrane which could improve the water retention capacity of PVA membrane and also gives a robust structure of membrane electrolyte. Generally, the addition of inorganic substances with PVA has attracted much attention recently. This is owing to the potential benefits of these inorganic substances over conventional materials. The excellent qualities of the PVA material resulting from the synergism of the organic inorganic distinctive properties. Tetraethylorthosilicate (TEOS) is an excellent low cost and easily available precursor of silica. The incorporation of TEOS in the PVA matrix is generally done by sol-gel method and the final PVA-TEOS composite provides Si-O-Si backbone into the polymer matrix which improves the mechanical strength, thermal stability and also improves water retention capacity. The PVA-TEOS composite membrane can further be modified by crosslinking method which improves the basic properties of the membrane such as water absorption capacity, degree of swelling and its thermal, chemical and mechanical stability for longer life in fuel cell application even at higher temperature.

Towards the fulfilment of these requirements the research work has the following objectives:

1. Synthesis and characterization of NaOH doped pristine PVA-TEOS membrane electrolyte for the application in DSBFC.
2. Synthesis and characterization of NaOH doped physically cross-linked PVA-TEOS membrane electrolyte for the application in DSBFC.
3. Detailed study of sodium hypochlorite as oxidant in direct sodium borohydride fuel cell.
4. Optimization of process parameter of physically cross-linked NaOH doped PVA-TEOS membrane electrolyte vis Response Surface Methodology (RSM).
5. To study the stability test of PVA-TEOS based alkaline direct sodium borohydride fuel cell (DSBFC).

Experimental

In this study, the PVA membrane electrolyte was prepared by adding TEOS mixture in the PVA solution. The dried membrane was dipped in NaOH solution for 24 h to make it anionic conducting membrane. The polyvinyl alcohol (PVA) was used as membrane material obtained from Molychem, India. Tetra ethyleorthosilcate (TEOS) was purchased from Sigma-Aldrich, St. Louis, MO, USA. The PVA-TEOS membrane electrolyte was further improved by physical crosslinking using freeze-thaw method. The resulting membranes are characterized by X-ray diffraction (XRD), Fourier transform infrared **(**FT-IR), electrochemical impedance spectroscopy (EIS), ion exchange capacity (IEC), water uptake, and NaOH uptake. The fuel used was $NaBH_4$ mixed in NaOH solution. The oxidant used was oxygen and sodium hypochlorite in separate experiment. The $NaBH_4$ (98 wt. %) powder was used as anode fuel purchased from SDFCL, fine chem limited, India. The NaOH was purchased from Thermo Fischer scientific, India. The oxidant oxygen was procured from Sigma Gas, India.

Results and Discussion

The formation of PVA-TEOS composite was confirmed by the FTIR analysis which significant peak of Si-O-C bond. The SEM analysis shows that there is uniform distribution of TEOS derived silica on the surface of PVA which indicate that there is good compatibility between PVA and TEOS. The addition of TEOS in PVA increase amorphous nature of membrane of the membrane. The water uptake and NaOH uptake of the PVA-TEOS membrane electrolyte was higher than the pristine PVA. The highest ionic conductivity of $9.09 \pm 0.5 \times 10^{-3}$ S/cm was obtained when PVA-TEOS is doped with 4 M NaOH. The highest power density of 79.87 mW/cm^2 at current density of 166.4 mA/cm^2 was obtained at moderate temperature of 55 ^oC for the same membrane electrolyte PVA-TEOS-(4M). The power density of DSBFC enhanced 45.46 % when cell temperature was increased from 25 ^oC to 55 ^oC. The pristine PVA-TEOS membrane electrolyte was further improved by physical crosslinking by freeze-thaw method. The degree of crosslinking depends on the number of freeze-thaw cycle. The freeze-thaw cycle of 7 was found to be optimum which exhibited highest ionic conductivity due increase in amorphous nature and delicate balance between water uptake and NaOH uptake. The electrochemical impedance spectroscopy methodology was used to find the ionic conductivity of synthesized membrane electrolyte with respect to different NaOH doping concentration, freeze thaw cycle, TEOS loading and temperature. The increase in TEOS loading up to 10 wt. % increase the water uptake, NaOH uptake and hence, ionic conductivity. The highest ionic conductivity of $9.67 \pm 0.04 \times 10^{-3}$ S cm^{-1} was obtained for the membrane freeze-thawed of cycle

7 having 10 wt. % of TEOS and dipped in 4 M NaOH solution. The synthesized physically crosslinked PVA-TEOS membrane was thoroughly studied in direct sodium borohydride fuel cell. The effect of different operating parameters such as cathode and anode electrocatalyst loading, NaOH doping concentration, fuel concentration and cell temperature was studie in direct sodium borohydride fuel cell. The maximum power density of 85.19 mW/cm^2 at a current density of 184 mA/cm^2 at the temperature of 60 ^{o}C was obtained. The sodium hypochlorite as oxidant was thoroughly studied by cyclic voltammetry and subsequently tested in direct sodium borohydride fuel cell. The process parameter of physically crosslinked membrane electrolyte was optimized using response surface methodology.

Conclusions

The silica doped PVA composite membrane was successfully prepared using TEOS as a precursor by sol-gel method without adopting any crosslinking of PVA-TEOS matrix. The synthesized PVA-TEOS membrane was further doped in NaOH for the use in alkaline direct borohydride fuel cell. As a result of the inclusion of silica in the polymer matrix, water and NaOH uptake were improved significantly. The highest ionic conductivity of the PVA-TEOS-(4M) membrane was found in order of 9.09± 0.5 × 10^{-3} at 25 ^{o}C. Very low loading of Pt (40 wt. %)/C$_{HSA}$ was used as anode and cathode electrocatalyst and optimum loading of 1 mg/cm^2 and 2 mg/cm^2 were found for anode and cathode, respectively. When tested in a single DSBFC, the lab synthesized PVA-TEOS-(4M) membrane resulting in highest cell performance, producing a maximum power density of 54.91 mW/cm^2 at the room temperature of 25 ^{o}C. 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. The PVA-TEOS membrane was further improved by physical crosslinking using freeze-thaw method. The effect of the freeze-thaw cycle on the PVA-TEOS membrane was studied from 0 cycle to 9 cycle. The amount of TEOS also effect the ionic conductivity of the membrane electrolyte and 10 wt. % TEOS loading was found to be optimum. The highest ionic conductivity of 9.67±0.04 × 10^{-3} Scm^{-1} was obtained for PT$_{10wt.\%}$-7Cy-(4M) membrane electrolyte. The maximum power density of 66.96 mW/cm^2 at current density of 144 mA/cm^2 was obtained using PT$_{10wt.\%}$-7Cy-(4M) (TEOS loading is 10 wt.%, freeze-thaw cycle is 7 and doped with 4 M NaOH) membrane electrolyte in DSBFC at cell temperature of 30 ^{o}C. The maximum power density got enhanced 27.22 % when the cell temperature was increased from 30 ^{o}C to 60 ^{o}C. The highest power density of 85.19 mW/cm^2 at current density of 184 mA/cm^2 was obtained at cell temperature of 60 ^{o}C.

List of Publication from research work:

Journals

[1] Yadav NK, Pramanik H. Quick synthesis of low-cost NaOH-doped pristine PVA-TEOS composite alkaline membrane electrolyte for power generation from direct sodium borohydride fuel cell at moderate temperature. Ionics. 2023 Oct;29(10):4159-79.

[2] Yadav NK, Pramanik H. Performance enhancement of NaOH doped physically crosslinked alkaline membrane electrolyte by addition of TEOS to PVA solution for direct sodium borohydride fuel cell application. International Journal of Hydrogen Energy. 2024 Jan 2;50:1373-94.

[3] Yadav, N.K., Pramanik, H. Comprehensive investigation on sodium hypochlorite as oxidant in half cell and direct sodium borohydride fuel cell (DSBFC) for low-cost electrical power generation. Ionics 2024. https://doi.org/10.1007/s11581-024-05565-7.

Conferences:

[1] Neeraj k. Yadav, Hiralal Pramanik. "Performance study of a PEM based fuel cell using hydrogen fuel via hydrolysis of $NaBH_4$". **ASREEM 2021**.

[2] Neeraj k. Yadav, Hiralal Pramanik. "Performance study of a DBFC using laboratory synthesized physically crosslink NaOH doped PVA membrane." **CHEMCON 2022**.