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Performance Evaluation of Single PEM Fuel Cell (PEMFC) with Novel Bio-Degradable Polymer Membrane Based on Agar -Agar

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Abstract In this present work, we report a solid bio-polymer membrane based on agar/NH_4NO_3 plasticized with glycerol by solution casting technique. The effect of glycerol on the structural and electrochemical properties of agar NH_4NO_3 polymer complex was explored. X-ray diffraction (XRD) revealed the significant structural changes from semi-crystalline phase to amorphous phase with the addition of plasticizer. The maximum room temperature ionic conductivity of 1.44×10^{-3} S cm^{-1} was achieved upon inclusion of 40 wt% of glycerol to 40 agar /60 NH_4NO_3 composition. Highest conducting solid bio-polymer membrane was tested in a single PEM fuel cell at room temperature. The performance evaluation showed peak power density of 84.3 $mWcm^{-2}$.

Keywords Biopolymer electrolyte, Agar, Glycerol, Ionic conductivity, PEM fuel cell.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical devices which converts chemical energy of a fuel to electrical energy. Recently, they have received much attention because of their high power density, efficiency and zero-environmental pollution. However, PEMFC commercialization is strictly related to the possibility of a significant reduction of the cost of all the device components. And also the usually employed polymer electrolyte membrane Nafion®, is a synthetic membrane made out of perfluorosulphonic acid (PFSA) which is toxic to humans involving manufacturing process and also causes environmental problems during disposal (Singh et al. 2016). The development of new polymer electrolytes that allow for replacing Nafion®, with other membranes of comparable performances but lower cost is a key issue. Therefore, bio based polymers have drawn keen interest from researchers because of their abundant nature, low cost, biocom-

patible, biodegradable, inert, safe and non-toxic (Prajapati et al. 2016).

Agar is a linear polymer based on disaccharide repeat unit of 3-linked β-D-galactopyranosyl and 4-linked 3,6-anhydro-α-L-galactopyranosyl (Guerrero et al. 2014) which is extracted from certain species of red seaweed. Agar has the advanage of high chain flexibility and having two types of cation coordinating oxygen sites in its structure, hydroxyl (-OH) and ether (-C-O-C-) oxygen atoms per repeating unit. This structure is capable of trapping large amount of ionic species, facilitating ion migration to support in the development of PEM fuel cell application (Nunes et al. 2017). NH_4NO_3 is chosen as doping salt in this work. It is an ionic salt in proton conducting electrolyte system as it provides proton (H^+) for conduction process.

In our previous work, agar/NH_4NO_3, SBPE has attained an ionic conductivity of 6.57×10^{-4} S cm^{-1} for fuel cell application (Boopathi et al. 2017). To enhance the ionic conductivity further, introduction of plasticizers as a guest species to SBPE system is more reliable. In this present study, we report the effect of glycerol incorporation on the environment friendly SBPE (agar/NH_4NO_3) system. The structural and electrochemical properties for SBPE were characterized.

Materials and Methods

Experimental technique

Solid biopolymer electrolyte preparation

The plasticized polymer electrolyte samples have been prepared using solution casting technique. From our previous work (Boopathi et al. 2017), the polymer complex of 40 mol% of agar and 60 mol% of NH_4NO_3 was found to have maximum ionic conductivity at room temperature. Thus, in this present work different weight percent (wt %) of glycerol was added to the polymer complex to study the plasticization effect on the host matrix. The agar powder (Colloids Impex) was dissolved in distilled water at 85°C by continuously stirring until a homogeneous solution was obtained. With this solution, NH_4NO_3 salt (Merck) was added and stirred for another 1 h for complete solubilization of salts. After that, different wt% of glycerol (Sigma Aldrich) was added and stirred until complete dissolution. The prepared solutions were casted on to glass petri dish and dried at 45°C in hot air oven. After drying, transparent and free standing flexible films were obtained. The sample compositions and its designation were given in the Table 1.

Characterization techniques

X-ray diffraction (XRD)

XRD analysis were carried out using Rigaku Ultima IV Multipurpose X-ray diffraction system with the Cu-ka radiation range of diffraction angle 2θ from 10 ° to 85° at the rate of 2° min^{-1} to study the nature (crystalline or amorphous) of SBPEs.

Electrochemical impedance spectroscopy (EIS)

The impedance analysis for the SBPEs was carried out by using HIOKI 3532 LCR meterin the frequency ranging from 42 Hz to 1 MHz. The samples were sandwiched between two aluminium blocking electrodes with a contact area of 2.0 cm^2. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using EQ software. The conductivity (σ) of electrolyte was calculated based on equation (1).

$$\sigma = \frac{L}{A \times R_b} Scm^{-1} \quad (1)$$

Where, L is the thickness, R_b is the bulk resistance and A is the area of the SBPEs.

Table 1. Composition and electrolyte designation.

Agar : NH_4NO_3 : Glycerol (wt %)	Sample code
100 : 0 : 0	A0
40 : 60 : 0	SA1
40 : 60 : 10	PA1
40 : 60 : 20	PA2
40 : 60 : 30	PA3
40 : 60 : 40	PA4
40 : 60 : 50	PA5

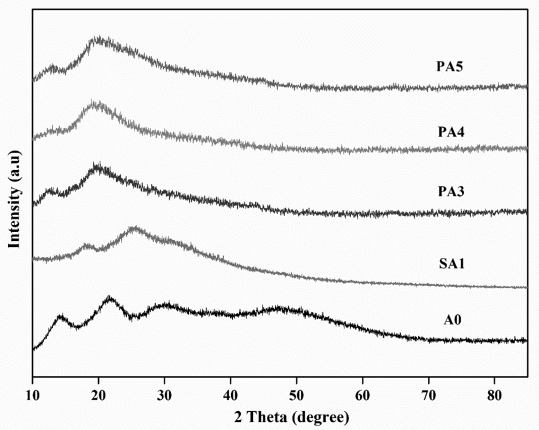

Fig. 1. XRD patterns for the selected SBPEs.

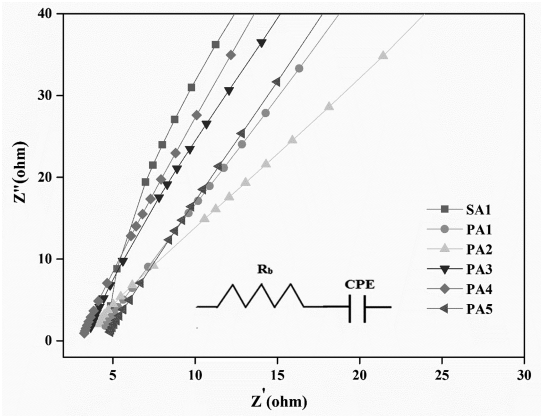

Fig.2a. Cole cole plot for unplasticized and plasticized SBPEs with equivalent circuit.

Single PEM fuel cell test

The performance of the single PEM fuel cell was evaluated using the highest conducting plasticized and unplasticized SBPE. The SBPE was sandwiched between the carbon cloth gas diffusion electrodes (GDE) supplied by cell with standard platinum loading of 0.25 mg/cm^2 (Anode) and 0.5 mg/cm^2 (Cathode). The membrane and GDE was enclosed between two graphite bipolar plates with double serpentine flow fields. The active channel area of the flow field was 25 cm^2. The channel width and depth were fixed at 1 mm. In order to avoid any gas leakage between graphite plate and GDE, silicone gasket of thickness 0.3 mm was used. Copper plate was used as current collector which was placed on both sides of the graphite plates. The whole setup was held together by means of acrylic end plates tightened with the help of bolts.

Results and Discussion

X-ray diffraction (XRD)

XRD is a prominent tool to analyse the nature of SBPEs which may have amorphous and crystalline regions. The XRD diffractograms of pure agar (A0) and different compositions of unplasticized polymer complex have been reported in our previous work. The broad peaks for A0 was observed at 2θ = 13.92^o, 21.5^o, 29.85^o, 31.7^o and 47.4^o. The unplasticized polymer complex SA1 was found to be more amorphous than A0 with three broad peaks at 13.92^o, 20.16^o and 26.7^o. Fig.1 depicts the XRD patterns for glycerol plasticized polymer complexes. It can be seen that the peaks become broader and shifts to a lower 2θ value as an effect of glycerol addition. The broadness of the peaks increased further upon addition of 40 wt% of glycerol (PA4) leaving only one broad hump at 2θ = 19.65^o. The amorphous materials are allied to boost the ionic mobility as it divulges more number of vacant oxygen for H^+ ion interaction and increases the ion transportation through the polymer side chains which subsequently increases the ionic conductivity value (Shukur et al. 2016). The reduction in peak intensity and absence of other peaks in any of the plasticized SBPEs confirms the complexation between agar, NH_4NO_3 and glycerol.

Electrochemical impedance spectroscopy

Cole cole plot

AC impedance analysis was carried out to understand the conduction mechanism in SBPEs with the inclusion of glycerol. The EQ software program developed by Boukamp has been used to find the bulk resistance (R_b) of the SBPEs. The ionic conductivity

Table 2. Ionic conductivity and activation energy values for the prepared SBPEs.

Sample code	Ionic conductivity (S cm^{-1}) at different temperature					Activation energy at room temperature (eV)	R'value
	303 K	313 K	323 K	333 K	343 K		
SA1	6.57×10^{-4}	6.68×10^{-4}	8.90×10^{-4}	9.06×10^{-4}	1.09×10^{-3}	0.12	0.98
PA1	8.11×10^{-4}	9.43×10^{-4}	1.08×10^{-3}	1.24×10^{-3}	1.38×10^{-3}	0.10	0.96
PA2	9.71×10^{-4}	1.14×10^{-3}	1.31×10^{-3}	1.56×10^{-3}	1.70×10^{-3}	0.08	0.95
PA3	1.26×10^{-3}	1.65×10^{-3}	1.81×10^{-3}	1.99×10^{-3}	2.14×10^{-3}	0.05	0.98
PA4	1.44×10^{-3}	1.81×10^{-3}	2.01×10^{-3}	2.23×10^{-3}	2.41×10^{-3}	0.04	0.98
PA5	7.44×10^{-4}	8.82×10^{4}	9.78×10^{-4}	1.07×10^{-3}	1.08×10^{-3}	0.11	0.99

(σ) of the SBPEs can be calculated using the Eq (1). The cole cole plot for the unplasticized system has been reported in our previous work and the ionic conductivity value obtained for the sample A0 and SA1 was 1.98×10^{-8} and 6.57×10^{-4} S cm^{-1} respectively. Fig. 2a shows the cole cole plot for the plasticized polymer electrolyte system at 303 K. The values of ionic conductivity were reported in Table 2. A high ionic conductivity value of 1.44×10^{-3} S cm^{-1} has been observed for PA4 electrolyte at room temperature which was comparable to other reported agar based SBPE system (Leones et al. 2012). The addition of glycerol promotes the dissociation of NH_4NO_3 in agar matrix by weakening the inter-ion columbic force between two different charged ions, forming (H^+ and NO_3^-). These transit provide an alternative pathway for the mobility of H^+ ions and participate in ion conduction when the neighbouring oxygen atom is in conduction with another H^+ ion (Kadir et al. 2018). However, with the addition of more than 40 wt% of glycerol decreases the conductivity values which may be due to the formation of ion pairs that could hinder the segmental motion of polymers chain, thus decreasing the ionic mobility. The reduction in ionic mobility leads to the drop in ionic conductivity of SBPE system.

The temperature dependence of ionic conductivity for the plasticized polymer electrolyte system is given in Fig.2b. The measurements were taken in the temperature range of 303 K to 343 K. The linear variation of this plot suggests an Arrhenius type thermal activated process. The value of conduction and activation energy as the function (10 to 50 wt%) of glycerol were listed in Table 2. From the results it could be observed that, the increase in ionic conductivity values with increase in temperature is due to decrease in activation energy (E_a) (Shukur et al. 2016). The rise in temperature enhances the mobility of biopolymer chain thereby increasing the fraction of free volume in the system. This provides free pathway for the mobile ions which increases the ionic mobility. It can also be noted that the glycerol plasticized system is in amorphous state, which would become more amorphous when the polymer electrolyte system is heated by opening up the plasticizer-rich phases for greater ionic transport. Apart from that, the vibration mode of macromolecules expands the polymer membrane by creating free space for conduction mechanism (Andrade et al. 2009). As a consequence, the transport of charge carriers can easily move into free volume and thus high degree of ionic conductivity.

Single PEM fuel cell test

The single PEM fuel cell test was carried out using

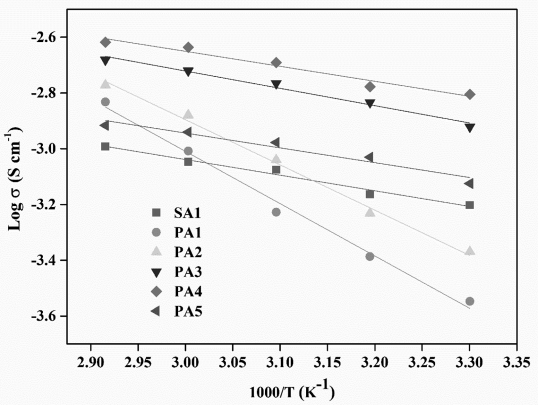

Fig. 2b. Temperature dependence of ionic conductivity of plasticized SBPEs.

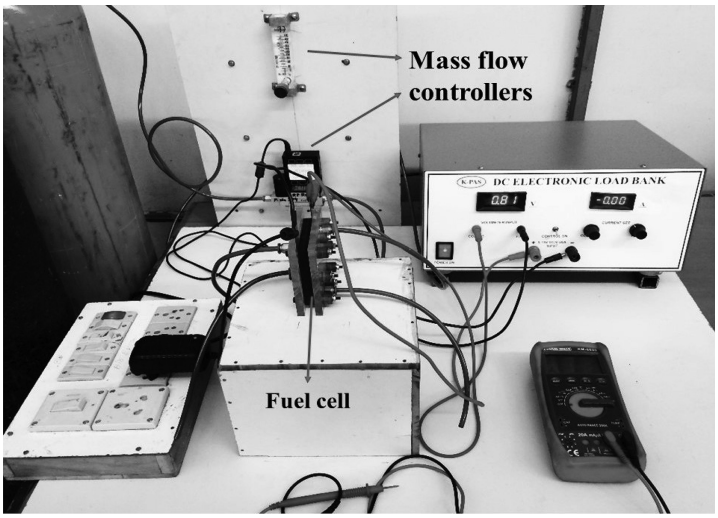

Fig. 3a. Single PEM fuel cell test setup.

H_2 (99.5% pure) and O_2 (99.5% pure) as the fuel and oxidant respectively. The single PEMFC test setup was shown in the Fig.3a. A DC electronic load bank (KPAS Instronics, Chennai, India) was used to test the performance of the single cell. The DC electronic load bank has the current drawing capacity in the range of 0.01 to 19.99A. The fuel flow rates were fixed at 200/100 ml min^{-1} of H_2/O_2 respectively. In order to understand the plasticization effect on device performance, highest ion conducting unplasticized (SA1) and plasticized sample (PA4) were used in the construction of the fuel cell.

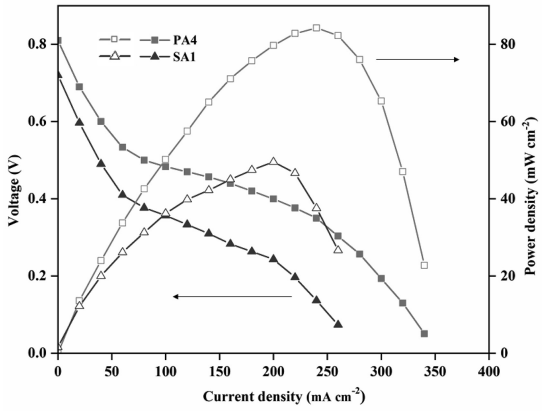

Fig. 3b. Polarization curves for the highest conducting Plasticized (PA4) and unplasticized (SA1) samples.

The performance of single PEMFC using the sample SA1 and PA4 were evaluated at room temperature and the polarization curves were shown in the Fig. 3b. It was evident from the figure that, the plasticized sample PA4 outperformed the unplasticized sample SA1. The lower OCV values of the sample SA1 and PA4 of 0.72 and 0.81 respectively, was due to the higher activation losses which suggests that performance of the catalyst was deprived (Santamaria et al. 2017). The higher performance of plasticized sample PA4 was primarily due to its higher ionic conductivity which affirms that there is a direct relationship between ionic conductivity and performance of fuel cells.

Conclusion

A green solid biopolymer electrolytes composed of agar/NH_4NO_3 plasticized with glycerol were developed by solution casting technique and their behavior were evaluated. The amorphousness of pure agar and optimized composition 40 agar/60 NH_4NO_3 were increased with the addition of plasticizer glycerol. The changes in FTIR spectra with the addition of glycerol

content confirm the complex nature of SBPE systems. The room temperature ionic conductivity of SBPEs increases with increasing glycerol concentration and attains a high value of 1.44×10^{-3} S cm^{-1} for PA4 electrolyte. The temperature dependant ionic conductivity obeyed the Arrhenius rule. Finally, the highest conducting plasticized membrane with cheaper cost and low enviromental impact has ability to replace conventional electrolytes used in commercial PEM fuel cell application.

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