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# Spectroscopic Characterization and Electrical study of Nano crystalline PEO based Conducting Polymer electrolyte system for low temperature Fuel cell applications

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**Abstract :** Solid conducting polymer electrolyte system, Nano crystalline polyethylene oxide (PEO) complexed with Sodium bicarbonate ($NaHCO_3$) salt was prepared by sol gel-technique. Several experimental techniques such as IR, composition dependence conductivity and temperature dependence conductivity in the temperature range of 303K - 368K and transport number measurements were employed to characterize this polymer electrolyte system. The conductivity of the ($PEO+NaHCO_3$) electrolyte was found to be about 3 times larger than that of pure PEO at room temperature. The transference data indicated that the charge transport in these polymer electrolyte systems is predominantly due to $Na^+$ ions. Using this nano crystalline polymer electrolyte system a three PEM fuel cell stack have been fabricated and their open circuit voltage and I-V characteristics are studied for various gas concentrations. The open circuit voltage was found to be 1.10 volts. A number of other cell parameters associated with the cell were evaluated and are reported in this paper.

**Key words:** Complex, conducting polymer electrolyte, ionic conductivity, transport number, Polymer electrolyte membrane (PEM) Fuel cell, Current-Voltage characteristics.

## INTRODUCTION:

The two primary concerns of scientists today are energy and environmental with the rapid depletion of fossil fuels. There is an urgent need to look for clean alternate source of energy. Fuel cells satisfy both these criteria. It's high time that we realize the need for cutting edge technologies which satisfy both the conditions i.e. being able to match the present day demand and also being reliable. One such convincing technology is "Fuel cell technology". The necessity for this technology has been widely accepted globally in the energy and power sectors of the many emerging technologies such as biomass fuels, liquid-bio fuels, geothermal energy, Photo-voltaic, Hydro-electric power, solar thermal-electricity, tidal-energy and wind-energy. Fuel cell technology has been much considered more advantages comparative with other technologies, because it has the practicability of being used in many mechanical, electronic devices, and hence this seems to be the futuristic technology[1]

Solid polymer electrolyte membrane fuel cells are promising candidates as power generators for zero emission vehicles in place of conventional combustion engines. These cells use PEM such as nafion as electrolyte. But nafion is very costly so we need to develop a new conducting polymer electrolyte membrane as alternative to existing membrane (nafion) systems with improved physical, chemical, mechanical and electrical characteristics with low cost. At present, conducting nano crystalline PEO complexed with sodium bicarbonate based PEM are fairly developed/fabricated and have been successfully used in $H_2/O_2$, fuel cell. Solid electrolyte PEM requires water to maintain their ionic conductivity. The absorption, diffusion coefficient and electro-osmotic drag of water and proton/ionic conductivity in PEMs and inter related and strongly affected by the cell operating conditions[2,-6]. This problem gets aggregated when the fuel cell is operated at higher temperature (above 70°C) water content in PEM developed so far has been indirectly managed by humidifying the reactant gases. The electrochemical performance of polymer electrolytes has been improved by the addition of inorganic fillers[7]. The resulting composite polymer electrolytes discharged enhanced conductivity, mechanical stability and improved interfacial stability towards electrode materials[8-12].

In recent years an attempt to investigate the possibility of fabricating PEM fuel cell based on other polymer electrolytes[8] Some researchers Studied and reported on polymer electrolyte membrane fuel cells based on Nafion/Nafion +Silica +Phospotungstic[1] The Present work examines a new conducting polymer electrolyte system, namely nano crystalline PEO based conducting polymer electrolyte system, that is ($PEO+NaHCO_3$). Using this solid electrolyte, a PEM fuel cell stack has been fabricated and its I-V characteristics studied.

## EXPERIMENTAL:

Polymer films (thickness ≅ 100-150 μm) of pure PEO (Aldrich ~ $6x10^5$) and various compositions of complexed film of nano crystalline PEO with $NaHCo_3$ salt was prepared in wt. ratios (90:10); (80:20) and (70:30) by a Sol-gel technique using methanol (water free) as solvent. The infrared (IR) spectra in these films have been recorded with the help of JASCO FT / IR– 53000–spectrophotometer in the range 400-4000 $cm^{-1}$.The dc conductivity has been measured using the lab made conductivity setup[11] in the temperature range 303-368 K using a Keithley Electro meter (Model 614].

Solid state polymer electrolyte membrane (PEM) fuel cell stack was fabricated in the configuration electrode /solid polymer electrolyte / cathode. The readings were taken with the high purity cylinder gases and the specification design of the PEM fuel cells was reported. The details about the fabrication of the fuel cells are given elsewhere[12 -14]. Finally the I-V characteristics of these fuel cells were monitored for a constant load of 0.5Ω.

## RESULTS AND DISCUSSION:

The variation in dc conductivity (σ) as a function of $NaHCO_3$ composition in PEO at room temperature ($R_T$) i.e.,303K and 368K is given in Figure.1(Composition dependence of ($PEO + NaHCO_3$) polymer electrolyte system at different temperatures).The conductivity of pure PEO is approximately $10^{-10}$ $Scm^{-1}$ at room temperature ($R_T$) and its value increases sharply to $10^{-7}$ $Scm^{-1}$ on complexing with 10 wt % $NaHCO_3$. The increase in conductivity becomes slower on further addition of $NaHCO_3$ to the polymer. This behavior has been explained by various researchers, who have studied PVP and PEO based polymer electrolyte in terms of ion association and the formation of charge multipliers [15-21].

The complex of the polymer PEO and salt $NaHCO_3$ were confirmed by using IR spectroscopy. The IR spectra of pure PEO, PEO complexed with $NaHCO_3$ with different weight ratios (90:10), (80:20) and (70:30) were recorded with the help of JASCO FT/IR–5300 spectrophotometer in the range 400-4000 $cm^{-1}$ and are shown in **Figure-2.** The intensity of the aliphatic C-H stretching vibrations band observed around 2950$cm^{-1}$ in PEO was found to decrease with the increase in the concentration of $NaHCO_3$ salt in the polymer. The width of the C-O stretching band observed at around 1100$cm^{-1}$ in PEO also showed an increase in the salt concentration in the polymer. Also the appearance of new peaks along with changes in existing peaks (and/or their disappearance) in the IR-spectra directly indicates the complexation of PEO with $NaHCO_3$. This IR data clearly establishes the complexation of $NaHCO_3$ with different weight ratios of the polymer PEO.

**Table-1:D.C. Conductivity and Activation energies of (PEO+$NaHCO_3$) electrolyte System**

| Films | Conductivity at 303 K($R_T$) ($Scm^{-1}$) | Conductivity at 368 K ($Scm^{-1}$) | Activation energies (eV) | |
|---|---|---|---|---|
| | | | Region-I | Region –II |
| Pure PEO | $6.78x10^{-10}$ | $1.58x10^{-7}$ | 0.34 | 0.59 |
| (PEO+$NaHCO_3$) (90:10) | $1.55x10^{-7}$ | $5.11x10^{-6}$ | 0.32 | 0.48 |
| (PEO+$NaHCO_3$) (80:20) | $1.62x10^{-7}$ | $5.91x10^{-6}$ | 0.25 | 0.33 |
| (PEO+$NaHCO_3$) (70:30) | $1.65x10^{-7}$ | $6.33x10^{-6}$ | 0.19 | 0.28 |

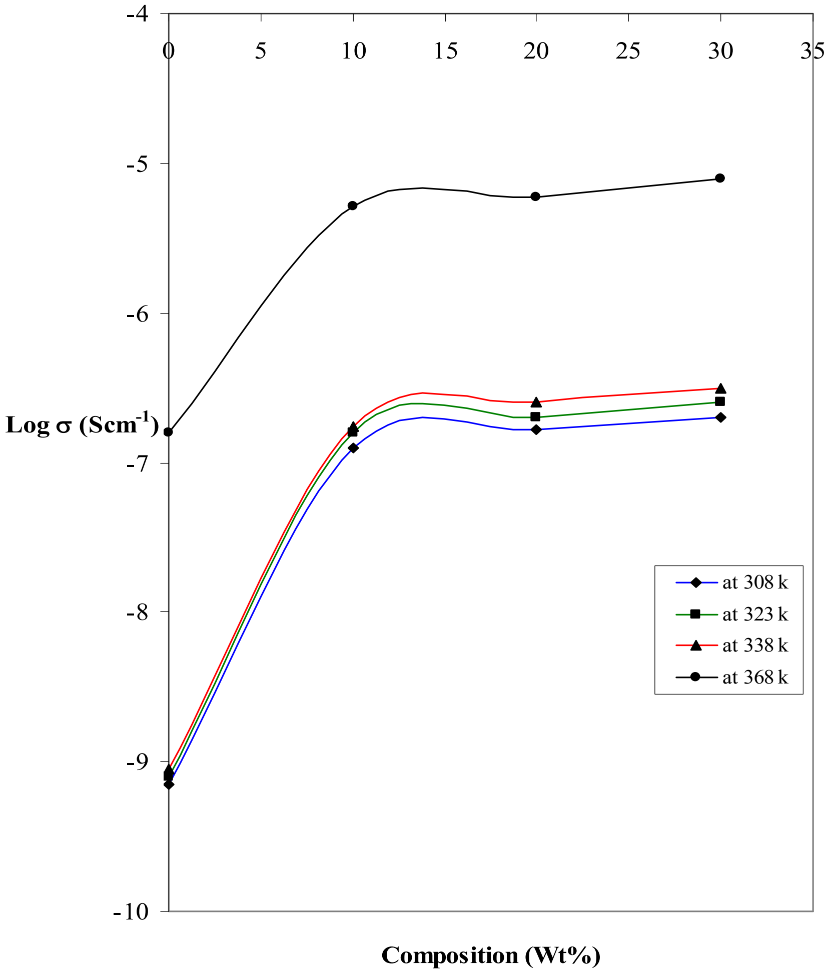

**Figure.1: composition dependence of (PEO+$NaHCO_3$) polymer electrolyte systems at different temperatures.**

The variation in conductivity as a function of temperature for pure PEO with different compositions of (PEO + $NaHCO_3$) polymer electrolytes over the temperature range of 303-368 K is shown in Figure-3. The conductivity versus temperature (log σT versus $10^3/T$) plots follows the Arrhenius nature throughout, but with two different activation energies (Table-1 ($E_a$ in ev)) above and below melting point ($T_m$) of the polymer. In region- I (that is, below $T_m$), the conductivity of pure PEO increases slowly with temperature up to 65°C. At 65°C there is a sudden increase in conductivity. In region- II (that is, above $T_m$), the conductivity again increases with temperature.

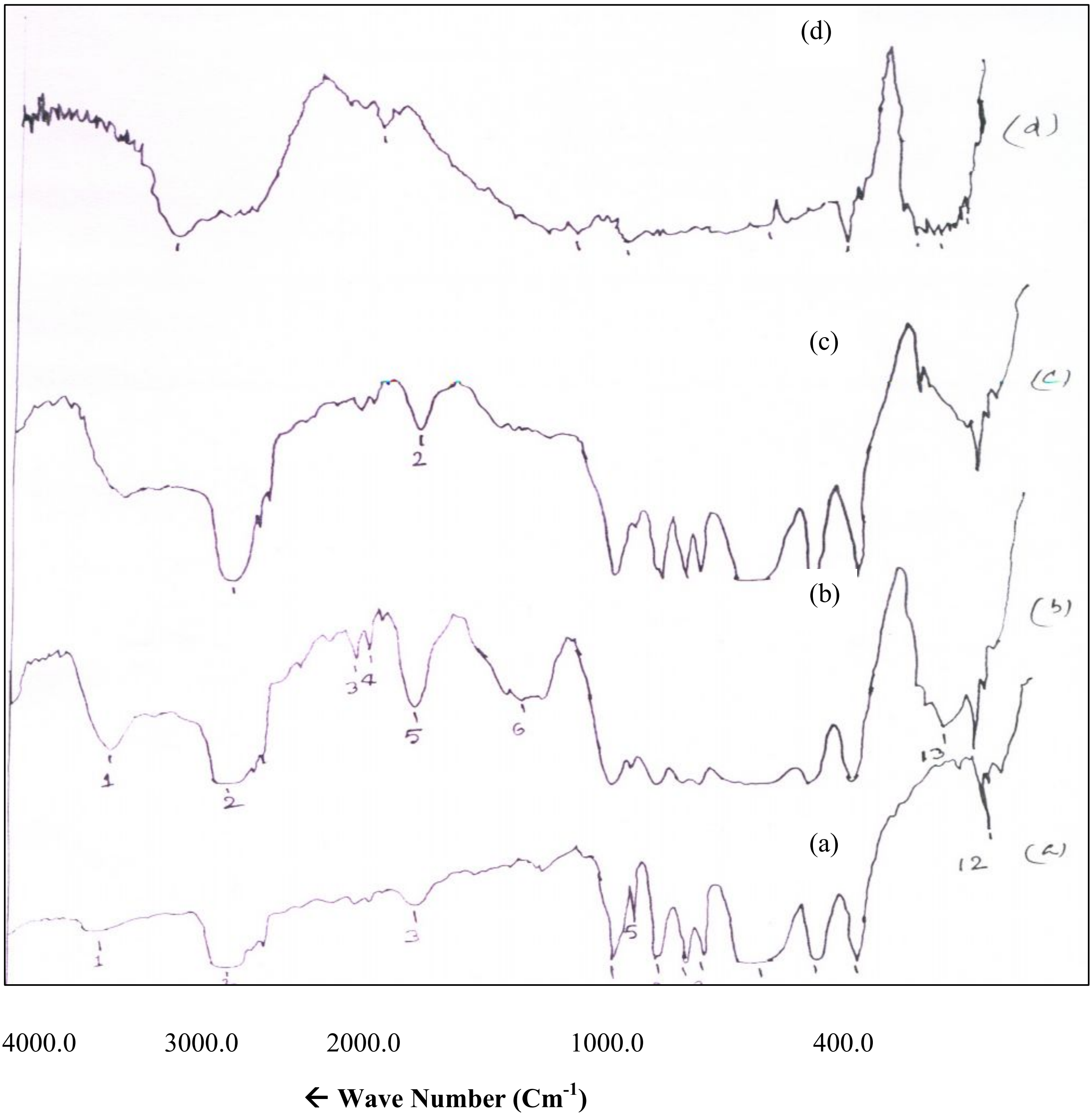

**Figure.2: IR-Spectra of (a) PURE PEO; (b) PEO + $NaHCO_3$ (90:10); (c) PEO+$NaHCO_3$ (70:30); (d) $NaHCO_3$**

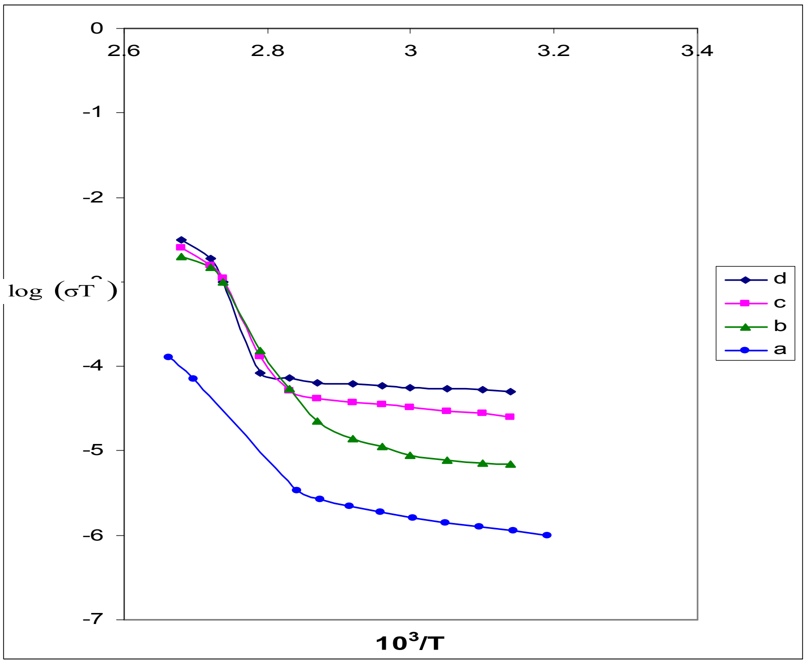

**Figure:3: The temperature dependence of D.C. conductivity**
**a) Pure PEO, b) PEO + $NaHCO_3$ (90:10), c) PEO +$NaHCO_3$ (80:20), d) PEO + $NaHCO_3$ (70:30)**

The calculated conductivity (σ) at room temperature, at 368K and activation energies ($E_a$ in ev) for pure PEO and (PEO+$NaHCO_3$) electrolyte systems are given in Table-1, that is ($E_a$ in ev). The conductivity of pure PEO is ~ $6.78 \times 10^{-8}$ $Scm^{-1}$ at room temperature and its value increases sharply to ~$10^{-7}$ $Scm^{-1}$ on complexing with 10 wt % of $NaHCO_3$. The increase in conductivity becomes slower on further addition of $NaHCO_3$ to the polymer. This behavior has been explained by various researchers, who have studied PMMA and PEO-based polymer electrolyte, in terms of ion association and formation of charge multiples[22-25].The conductivity increases with temperature in pure PEO and in all the compositions of the (PEO+$NaHCO_3$) polymer electrolyte system. The ionic conductivity in the polymer complexes may be interpreted on the basis of a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chains; these are essential to assure high ionic conductivity of the electrolyte [26, 29] The basic design of the cell, which consists of a solid electrolyte ion-exchange membrane, electro catalysts and gas feed fuels is illustrated in Figure.4.

The two electrodes, which consist of the electro catalyst and a plastic material for water-proofing the electrode, are in the form of fine metallic wire screens. They are bonded on either side of the electrolyte layer. The wire screen material is titanium or platinum. Metallic current collectors are ribbed onto each electrode. The hydrogen compartment of the cell is enclosed; the hydrogen gas enters this compartment through a small inlet and circulates throughout the ribbed current collectors and distributes itself evenly over the electrode. On the opposite side oxygen or air enters the compartment, coolant tubes run through the ribs of the current collectors. On the oxygen side, the current collectors also hold wicks which absorb water, the product of fuel-cell reaction and carry it over by capillary action. The water leaves the cell through an exit from the oxygen compartment. Oxygen is prevented from leaving its compartment by the inclusion of a differential pressure water-separation system. The distinctive feature of this cell is that it uses a solid polymer electrolyte in the form of an ion-exchange membrane. The membrane is non-permeable to the reactant gases, hydrogen and oxygen, which thus prevents them from coming into contact. The membrane is however; permeable to hydrogen ions[10] which are the current carriers in the electrolyte .The desired properties of polymer electrolyte membrane are high ionic conductivity, low permeability of fuel and oxidant, Very low electronic conductivity, high resistance to its oxidation or hydrolysis and Mechanical stability[30] .

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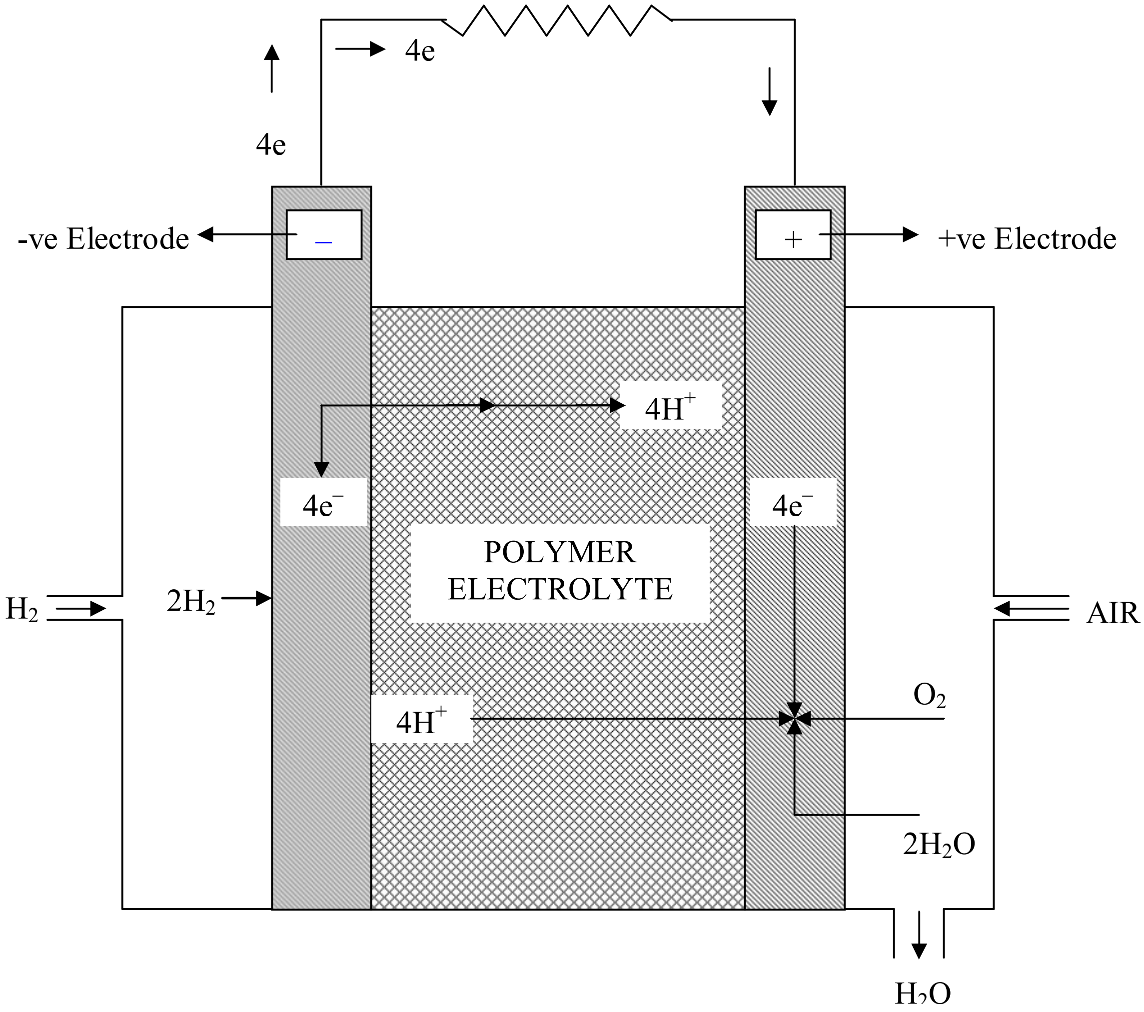

**Figure.4: Polymer electrolyte Membrane Fuel cell (PEMFC)**

The ion-exchange membrane electrolyte is acidic and the current carriers in solution are hydrogen ions. The hydrogen ions are produced by the reaction at anode according to,

$2H_2 \rightarrow 4H^+ + 4e^-$

These ions are then transported to the cathode through the electrolyte and the electrons reach the cathode via the external circuit. At the cathode, oxygen is reduced producing water as represented by:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

This cell operates at about 40 – 70°C.

The single cell1 with the configuration Anode / ($PEO+NaHCO_3$) (90:10)/ Cathode was assembled with the specifications and the first readings were taken with the cylinder gases. The specifications of the single fuel cell 1 with the configuration Anode / ($PEO+NaHCO_3$) (90:10)/ Cathode polymer electrolyte are given in Table-2 that is Specifications for single cell 1. The resistor 0.5Ω were added in series to the circuit to gain an increase in voltage. Subsequently it was achieved. The open circuit voltage was found to be 0.95 V.

**Table-2: Specifications for Single Cell 1**

| | |
|---|---|
| Electrodes | 20% carbon anode and cathode |
| Polymer Electrolyte | ($PEO+NaHCO_3$) (90:10) |
| Type of graphite rates | Porous 1 no. and non-porous 1 no. |
| Concentrating $NaBH_4$ | 10% |
| Fuel | $H_2$ & $O_2$ (from cylinders) |

The single cell 2 and single cell 3 with the configurations anode/($PEO+NaHCO_3$) (80:20)/ cathode and anode/($PEO+NaHCO_3$) (70:30) (Table 3 and 4**)** were assembled with the specifications. The specification design of the PEM fuel cell2, cell 3 was given in Table-3 and 4 respectively. The observations were taken with the cylinder gases. The resistor 0.5Ω was connected in series to the circuit. It is observed that, when the cell current increases, cell voltage slightly decreases[30] up to 0.61 volt due to concentration of sodium boro hydride.

After testing successfully with the single cell, a three cell stack was assembled (that is, the three single cells are connected in series). The material require for this assembly is similar to that of the single cell, but the quantity of the material required for assembly is given in Table-5**.**

**Table-3: Specifications for Single Cell 2**

| | |
|---|---|
| Electrodes | 20% carbon anode and cathode |
| Polymer Electrolyte | ($PEO+NaHCO_3$) (80:20) |
| Type of graphite rates | Porous 1 no. and non-porous 1 no. |
| Concentrating $NaBH_4$ | 15% |
| Fuel | $H_2$ & $O_2$ (from cylinders) |

**Table-4: Specifications for SCell 3**

| | |
|---|---|
| Electrodes | 20% carbon anode and cathode |
| Polymer Electrolyte | ($PEO+NaHCO_3$) (70:30) |
| Type of graphite rates | Porous 1 no. and non-porous 1 no. |
| Concentrating $NaBH_4$ | 20% |
| Fuel | $H_2$ & $O_2$ (from cylinders) |

**Table-5: Specifications for the THREE PEM Fuel cells stack**

| | |
|---|---|
| (a) Electrodes | : 20% carbon electrodes no. 6 |
| (b) Electrolytes | : $PEO + NaHCO_3$ (90:10)<br>$PEO + NaHCO_3$ (80:20)<br>$PEO + NaHCO_3$ (70:30) |
| (c) Electrolyte chamber thickness | : 4 mm (3) |
| (d) Electrolyte temperature | : 65°C |
| (e) Graphite plates | : non-porus (4)<br>Mono-polar - 2 no.<br>Bi-polar – 2 no. |
| (f) Concentration of sodium borohydride | : 30% |
| (g) Hydrogen and Oxygen | : Completely running on cylinder Gases |

For the three cell stack we used non-porous, bi-porous graphite plates. The three design aspects of the PEM fuel cell system under fabrication are (1) the hydrogen on demand generation system (that is. hydrogen reformer system) and (2) the air scrubber system (i.e. the fuel cell assembly).The incorporation of the above three designs completes the fuel cell system[31]. Using this conducting polymer electrolyte thin film systems, a three fuel cell stack have been fabricated and I-V Characteristics studied and the results were subsequently summarized.

The basic design of the cell, which consists of a solid polymer electrolyte ion-exchange membrane, electro catalysts and gas fuel tubes. Hydrogen was generated from sodium borohydride ($NaBH_4$) and air was scrubbed using the initial setup of the air scrubber. The fuel cell system was run on a completely on generated gases. The distinctive feature of this cell is that it uses a solid electrolyte in the form of an ion-exchange membrane. The membrane is non-permeable to the reactant gases hydrogen and oxygen, which this prevents them from coming into contact. The membrane is however, permeable to hydrogen ions [32] which are the current carriers in the polymer electrolyte. This cell operates at around 40-70$^o$C.

Polymer electrolyte fuel cells are assembled in the configuration (anode) / (polymer electrolyte) / (Cathode) and studied their I-V characteristics. The main function of the electrolyte in PEMFC is to carry the $O^{2-}$ ions from the cathode to the anode and also it separates the fuel from the oxidant inside the cell. The high ionic electrolytes are independent of oxygen partial pressure. In PEMFC the ($PEO+NaHCO_3$) electrolyte system is typically chosen as the base line material. And also most of the polymer electrolyte systems have good mechanical strength, fracture toughness, better ionic conductivity and lesser chemical reactivity with the cathode, anode and inter connectors[30] .

The current voltage characteristics of the single cell1, single cell2 and single cell3 are shown in Figure.5. From the figure it is observed that, when current of the cell increases, the developed voltage of the cell gradually decreases. The three fuel cell stack, I-V characteristics are also studied and it is shown in Figure.6.The voltage of the fuel cell stack gradually decreases with increase of current. The open circuit voltage of these fuel cells has been measured for different compositions of various polymer electrolyte systems. It is observed that the open circuit voltage was found to be in range 0.95 V to 1.1 V it may be due to used electrolyte membrane type, electro catalysts and Concentration of sodium borohydride.

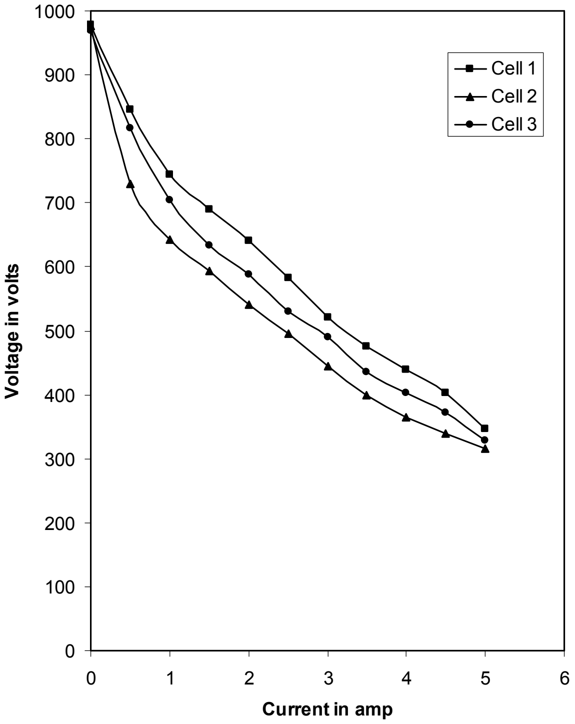

**Figure.5: I-V Characteristics of a single cell 1, 2 and 3 of a ($PEO + NaHO_3$) based PEM fuel cell**

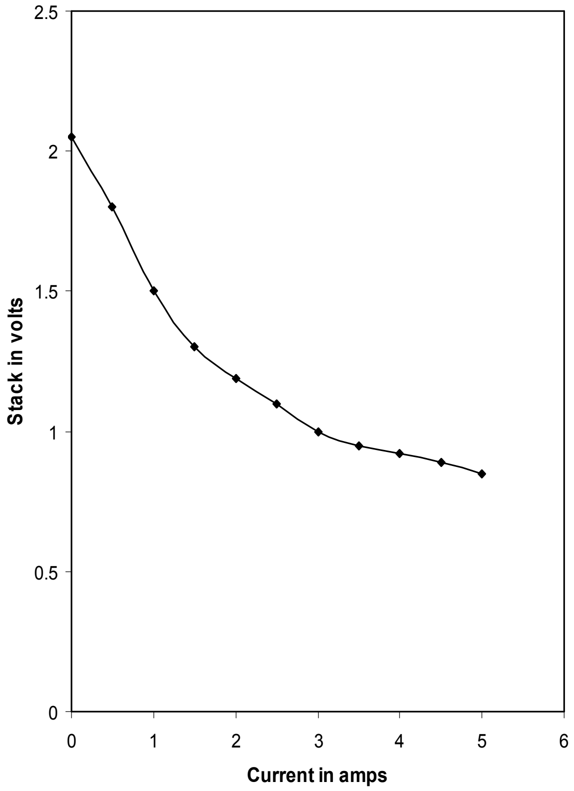

**Figure.6: I-V Characteristics of a three PEM Fuel cell stack**

## Conclusion:

i. The fuel cell stack is found to be better performance as compared to a single cell fuel cell.
ii. [PEO+$NaHCO_3$] three cell stack wattage is found to be 4.25 watt with a stack voltage of 0.85 volt. The fuel cell characteristics like I-V characteristics, Open circuit voltage, power density etc. mainly depends on nature of electrolyte, the generated gases and its purity. But it is observed that the volt-ampere characteristics, efficiency of these fuel cells are very low. Further work has to be done to improve the fuel cell efficiency by proper choosing of solid polymer electrolytes along with the electrodes.
iii. The improve power density, current density of the fuel cell mainly depends up on the nature of catalyst used in the fabrication. Among all the electrodes, platinum is a very good catalyst but, its cost is very high. Therefore studies of other catalyst materials in the place of platinum are needed.

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