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Research Article

Effect of Embedding Ion Exchange Stack Layer in PEM Fuel Cell on Electrode Corrosion

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Abstract: Fuel cell based electrical energy is sustainable, environment friendly, and economical. Among different fuel cell categories like proton exchange membrane (PEM), alkaline, direct methanol, phosphoric acid, molten carbonate, solid, and microbial fuel cells, PEM fuel cell is the most suitable for rural areas as it does not require any material other than water for generating electrical power. Using the same cell in electrolysis mode, the input water can be dissociated into hydrogen and oxygen using solar energy. The gases liberated may be stored for generating electrical power whenever there is a need. But the main problem of using water in rural areas for generating hydrogen and oxygen is the electrode corrosion as the water found in these areas is not pure. The impurities accumulated inside the system degrade the performance of the cell. A novel technique based on ion exchange stack layer made up of Tin(IV) arsenatungstate has been proposed and investigated in this paper for reducing the effect of corrosion on the electrodes. The analysis of the results based on pH measurements, visual inspection of the electrodes, and XRD studies shows that the proposed technique is capable of reducing the effect of impurities on the fuel cell electrodes.

Keywords: Fuel cell, water impurities, pH modification, ion exchange, ion exchange stack layer, PEM fuel cell.

1. Introduction

The uncontrolled use of power and energy has triggering the process of depletion of energy resources on earth. Deteriorating climatic changes and rapid depletion of fossil fuels has further exaggerated the problem. Combustion of fossil fuels is slowly affecting the atmosphere and in near future, it may lead to climatic disasters. There is a time to search for alternative sources of energy like green energy [1]. An alternative for reducing some of these problems may be the emphasis on the use of a fuel cell for generating electrical power. The fuel cell converts chemical energy of fuel directly into electrical energy [2], [3]. There are several types of fuel cells like proton exchange membrane (PEM) fuel cell, alkaline acid fuel cell, direct methanol fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, solid oxide fuel cell and microbial fuel cell. [4-6].

Each type of fuel cell has its own advantages and disadvantages. Alkaline fuel cell uses potassium hydroxide (KOH) as the electrolyte and operates at 70-90^{o}C with conversion efficiency up to 70% [7], [8]. Direct methanol fuel cells operate at 120-190^{o}C with efficiency up to 40% [9]. Phosphoric acid fuel cell uses liquid phosphoric acid as the electrolyte and operates at 160-220^{o}C with efficiency varying from 40% to 80% [6]. Molten carbonate fuel cell uses molten carbonate and operates at 600-700^{o}C [10] with efficiency ranging from 60-70%. Solid fuel cell uses a hard non porous ceramic compound as the electrolyte and operates at 700^{o}C to 1000^{o}C with efficiency around 80% [11], [12]. Microbial fuel cell uses the catalytic reaction of micro organisms to convert organic materials into electric power at 50% efficiency [13-15].

PEM fuel cell uses a polymer electrolyte membrane and platinum electrodes. The efficiency of the cell ranges from 40-60% [16]. The main advantage of the cell is the low operating range (50^{o}C to 100^{o}C) leading to high power density in the fuel cell stacks, thereby, making the technology potentially attractive for automotive applications [17], [18].

PEM based fuel cell is a better choice for remote areas where supply of fuel is difficult. The fuel of the cell is simply the hydrogen and oxygen, which can be easily obtained from electrolysis of water using the same fuel cell in reverse mode. The problem with this choice is the corrosion of electrodes due to impurities in the water. Several researchers are working on handling the problem of electrode corrosion. M. A. Deyab et al. [19] investigated the use of polyaniline/Zn-Porphyrin composites coatings on Grade 303 stainless steel electrodes for protection against corrosion. The coating resulted in decreased corrosion and also led to increased output power of the PEM fuel cell. T. Wilberforce et al. [20] employed 316L stainless steel coated withSS316L and reported appreciable results with coated plates using potentiostatic test. M. G. Kadhim et al. [21] after reviewing literature on different types of corrosions in oil field and flow line equipments under the presence of corrosive gases (CO_2, H_2S, etc.) concluded that inorganic or organic inhibitors are efficient in reducing the corrosion. J. Xu et al. [22] investigated the electrode Ti-641-4V coated with ZrCN using double cathode discharge technique and reported that the coating resulted in low surface wettability than uncoated Ti-641-4V alloy leading to improved corrosion resistance. S. Frangini et al.

[23], after reviewing corrosion protection methods for electrodes of different fuel cells suggested the use of sol-gel derived oxide ceramic coatings as a relatively better option for fuel cells working at high temperature.

S. A. Muhmed et al. [24] after reviewing literature on PEM fuel cells, suggested that green material natural polymers (like chitosan and cellulose) as electrolytes a novel approach with respect to clean energy. S.-Y. Moon et al. [25] investigated the effect of Tris (40-Trifluorovinyloxyphenyl) Ethane on physical and electrochemical properties for fuel cells. It was reported that branched structure of Sulfonation of PBS-40Bx provides efficient ion channels by allowing the sulfonic acids to aggregate on water uptake and proton conductivity. The main advantage is the flexibility of controlling the physical and electrochemical properties by the degree of branching. P. D. Luca et al. [26] reported after investigating the use of ETS-10 zeolite for filtering zinc based pollutants that ETS-10 has better efficiency for the removal of lead, zinc, and manganese based impurities.

S. S. Kumar et al.[27], after reviewing different techniques for energy generation suggested PEM based fuel cell a better choice as it can act in both configurations i.e. as electrolyser and fuel cell as well. Similar observations were drawn by H. A. Miller et al. [28]. Y. Budak et al. [29], after comparative investigations reported that methanol electrolyzer can produce 27% more H_2 than the water electrolyzer. H. Chang et al. [30], on the basis of mathematical modelling reported that higher efficiency can also be achieved in PEM fuel cells at higher heating value for developing hybrid energy systems. A. Pashaei et al. [31] reported the use of PEM electrolysis cell even at higher pressure (20 bar), but it was also reported that the performance decreases as the pressure increases. Y. Guo et al. [32], studied working principles of the two kinds of electrolyzers: alkaline and PEM. It was concluded that although alkaline water hydrogen production technology is economical, however, it has the disadvantages of slow start-up, corrosion, and complicated maintenance. On the other hand, PEM hydrogen production technology has the advantages of fast start-up, no corrosion, simple maintenance, and requiring fewer components.

It has been observed that the problem of corrosion and efficiency of the fuel cells is a hot area of research and there is a scope for further enhancing the performance of the fuel cells, particularly PEM based fuel cells. The main advantage of these fuel cells is the ease of getting raw material (water) for generating the energy. The problem of impurities in the water may be tackled using a two level process. In the first level, the common methods of filtering like sedimentation can be used to separate out the most of the visible impurities. In second level, the micro impurities can be taken care. The objective of this research is to incorporate an ion exchange stack layer in PEM fuel cell to filter out the ionic impurities in the water, i.e., allowing only pure water to reach the electrolyzer electrodes. The details of the ion exchange process are described in the following section. The overall methodology of the proposed system is described in Section III. The results and conclusions are presented in the subsequent sections.

2. Ion exchange based filtering

Ion exchange is a commonly used technique for filtering of proteins, polypeptides, nucleic acids, and other charged molecules. It separates ions and polar molecules based on their affinity to the ions present in the ion exchange resin. Ion exchange is also known as demineralization or deionisation. Ion exchange resins are insoluble cross linked long chain organic polymers with a micro porous structure [33]. The functional group attached to the chain are responsible for the ion exchanging properties. The resins with pH less than 7 (acidic) functional groups are capable of exchanging H^+ ions. Similarly, the resins with basic functional groups are capable of exchanging OH^- ions. There are several types of ions exchange resins and mostly, commercial resins are made of polystyrene. Sulfonate ion exchange resins are widely used in separation, purification, and decontamination of liquids. Some resins are highly effective in biodiesel filtration [34]. For water purification, ion exchange resins are used to remove poisonous and heavy metal ions from the solutions, replacing with more innocuous ions, such as sodium and potassium. Some ion exchange resins remove chloride and organic contaminants from water using an activated charcoal filter mixed with the resins [35]. Ion exchange based filters are very efficient in replacing magnesium and calcium ion resulting in softening of the water. When the resin is fresh, it contains sodium ions at its active sites. When in contact with a solution containing magnesium and calcium, ions preferentially migrate out of the solution to the active sites on the resin and are replaced in the solution by the sodium ions. This process reaches equilibrium with a much lower concentration of magnesium and calcium ions in solution [36].

Broadly, the ion exchange resins may be categorized as anion and cation exchange resins. Anion resins attract negatively charged ions (Cl^{1-}, SO^{2-}_4, CO^{2-}_3) and cation resins attract positively charged ions [34] ($Ca^{2+,}$ Mg^{2+}) from the liquid. The process of exchanging ions is shown graphically in Figure 1.

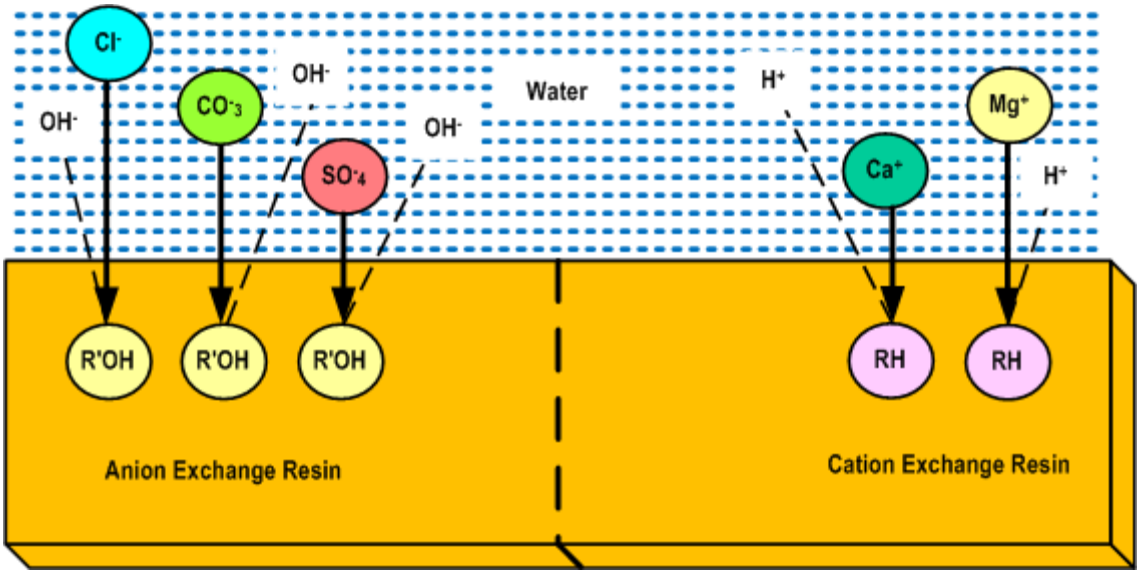

Fig. 1. Demonstration of ion exchange process for anion and cation resins.

In ion exchange process, hard water is allowed to pass through both cation and anion exchange resins. Cation exchange resin removes $Ca^{2+}$and Mg^{2+} ions by exchanging equivalent amount of H^+ ions as follows

Cation exchange resin's reaction:
$2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$
$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$
(RH^+ = Cation exchange resin)

Anion exchange resin removes bicarbonates, chlorides, and sulphate by exchanging equivalent amount of OH^- ions as follows

Anion exchange resin's reaction
$R'OH^- + Cl^{1-} \rightarrow R'Cl + OH^-$
$2R'OH^- + SO_4^{2-} \rightarrow R_2'SO^{2-}_4 + 2OH^-$
$2R'OH^- + CO_3^{2-} \rightarrow R_2'CO^{2-}_3 + 2OH^-$
(R'OH = Anion exchange resin)

H^+ / OH^- ions released in water from respective cation /anion exchange resin get combined to produce water molecules resulting in reduced concentration of impurities in the filtered water.

$H^+ + OH^- \rightarrow H_2O$

After some time, resin capacity of producing H^+/ OH^- ions is exhausted due to ion exchange and recharging of the resin becomes mandatory. Recharging, in case of cations / anions is carries out by using dilute H_2SO_4/NaOH as per the following reactions [37].
$R_2'Ca^{2+} + 2H^+ \rightarrow 2RH^+ + Ca^{2+}$
$R_2'SO_4^{2-} + 2OH^- \rightarrow 2R'OH^- + SO_4^{2-}$

3. Methodology

The overall diagram of the proposed fuel cell structure is shown in Figure 2. It consists of four sections: ion exchange stack layer, consisting of three sub layers (L1, L2, and L3), anode, PEM membrane, and the cathode. The PEM fuel cell can work in dual mode: electrolyser and electric current generator. The water is given as input to the PEM fuel cell working in electrolysis mode. The ion exchange layers remove the impurities and help in protecting the electrodes, especially the anode. The filtered water from the ion exchange layer is decomposed into hydrogen and oxygen gases. The gases are stored for future use of the fuel cell as electrical current generator. For that, Hydrogen is entered through the anode of the cell and O_2 through the cathode. H_2 is split into protons and electrons. Oxygen entered through the cathode reacts with protons coming through the PEM membrane to generate water. The electrons follows the external circuit and produce electricity.

For quantifying the effect of extra layer on the performance of the fuel cell, two investigations are conducted. In the first investigation, the filtering capabilities of the ion exchange layer are studied. In second investigation, the effect of water impurities on the anode has been studied.

Tin(IV) Arsenatungstate is used as ion exchange stack layer. It is synthesized by adding 0.25 M tin(N) chloride solution to a mixture of 0.25 M sodium arsenate and 0.25 M sodium tungstate in the volume ratio 2: l: l. The dried mixer (40 g) was treated with 100 ml of 1.0 M of nitric acid [38].

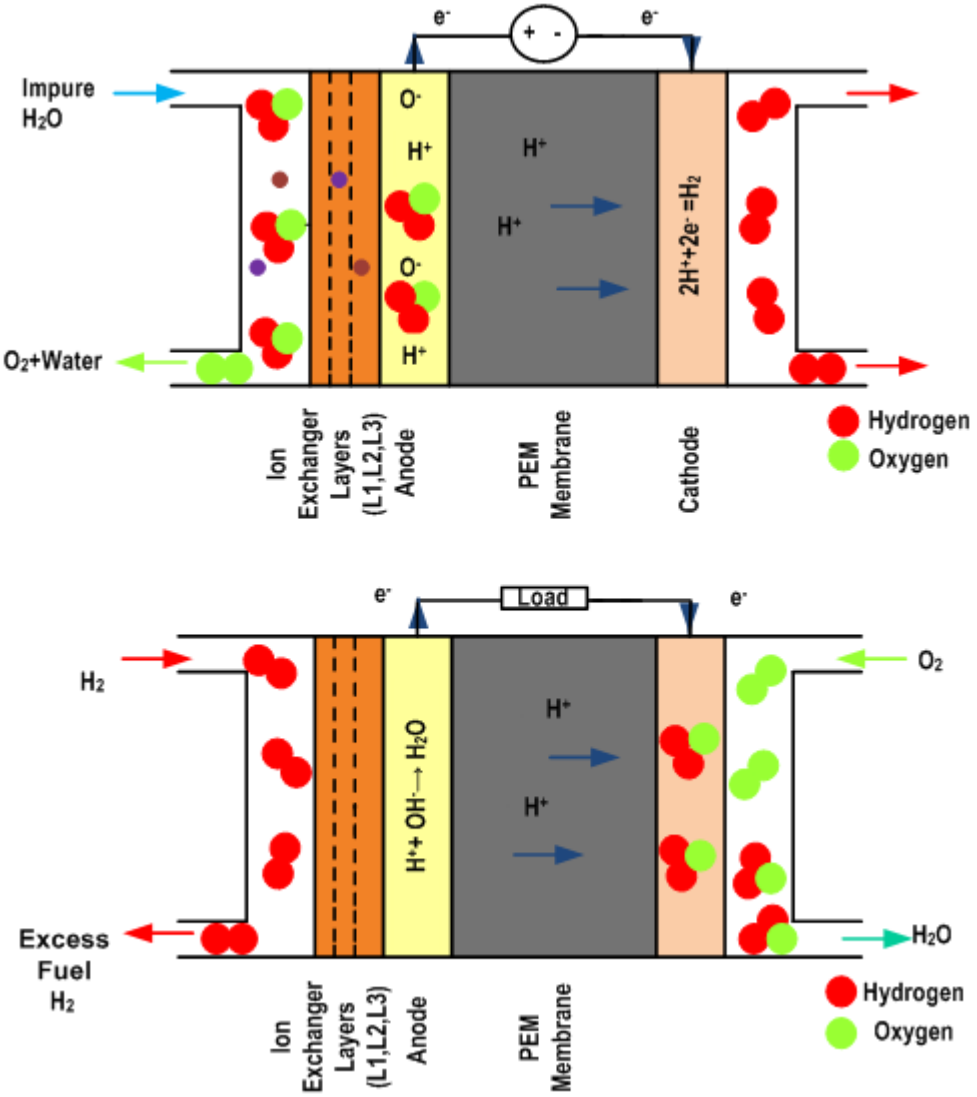

Fig. 2. The modes of PEM fuel cell. a) Electrolyzer, b) Fuel cell.

Presence of impurities may disturb the pH of the water depending upon their nature. Some impurities may lead to acidic water and others may lead to basic water. The change of behaviour from neutral to acidic or basic affects the life of the electrodes in the fuel cell. Few drops of acid (HCL) or weak base (ethanol) were added to the water to slightly vary its pH. The solution is filtrated by the ion exchange layer and pH of the filtered water was evaluated. The effect of impurities on the electrodes is further investigated by visual inspection and XRD testing.

4. Results and discussion

The results of pH correction by the ion exchange layer stack are shown in Figure 3.In the figure; x-axis represents the ion exchange stack layers L1, L2, and L3. The pH of the solvent is shown along y-axis. It is clear from the figure that each layer reduces the pH of the liquid given at its input. The input of the L1 has pH of 7.20 and the pH of the output becomes 6.93 Figure 3(a). The final pH at the output of L3 becomes 7.00. In case of acidic input water, the pH increases from 6.67 to 6.74 at the first layer (L1). Similarly, L2 increases the pH to 6.88 and finally, L3 makes the pH of the filtered water as 6.93 as shown in Figure 3(b).

Investigations were also conducted using four layers of ion exchange membrane and the results are shown in Figure 4(a, b). The histograms confirm that the efficiency of the ion exchange stack improves as the number of

layers is increased. For four layers, the pH of the filtered water becomes almost near to 7.00, i.e. pH of the neutral water.

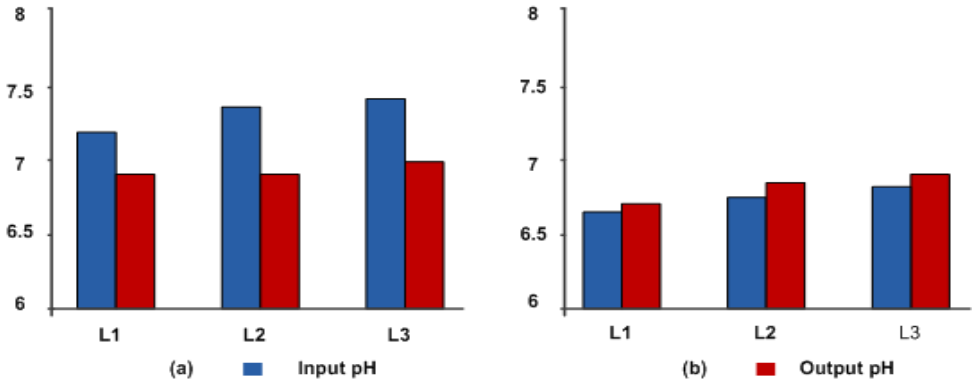

Fig. 3. Experimentally value of pH for acidic and basic for three layers

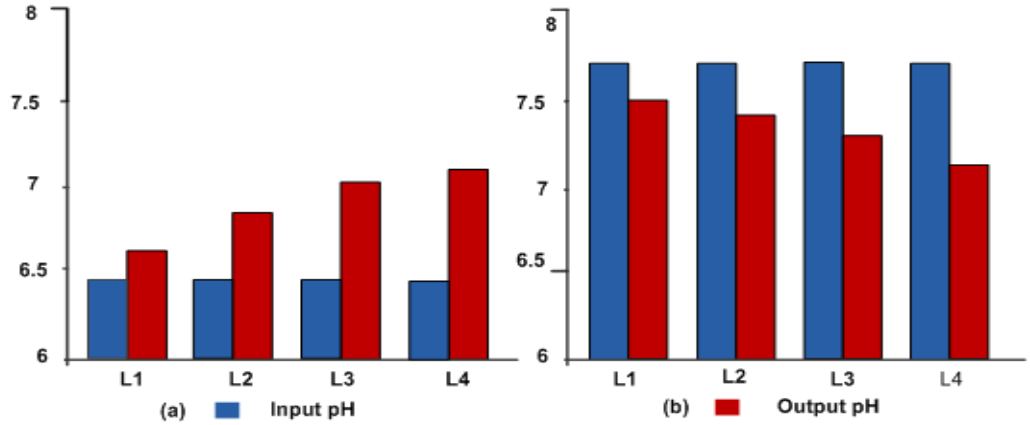

Fig. 4. Experimentally value of pH for acidic and basic for four layers.

The effect of water on the anode mesh is shown in Figure 5. First row shows the newly installed set of electrodes. The images in the row were taken from different sites on the mesh to include multiple defects if any. Second row shows the images of the mesh sections after 15 days of use with unfiltered water. The images in the third row correspond to filtered water through the ion exchange stack. All the images were taken using microscope with 10X magnification. The visual analysis of the images shows that ion exchange stack reduces the damage of the electrodes and hence, the proposed structure of the fuel cell leads to increased life of the electrodes. Also, the active area of the electrodes does not reduce because of decrease in the impurities and hence, the efficiency of the fuel cell also increases.

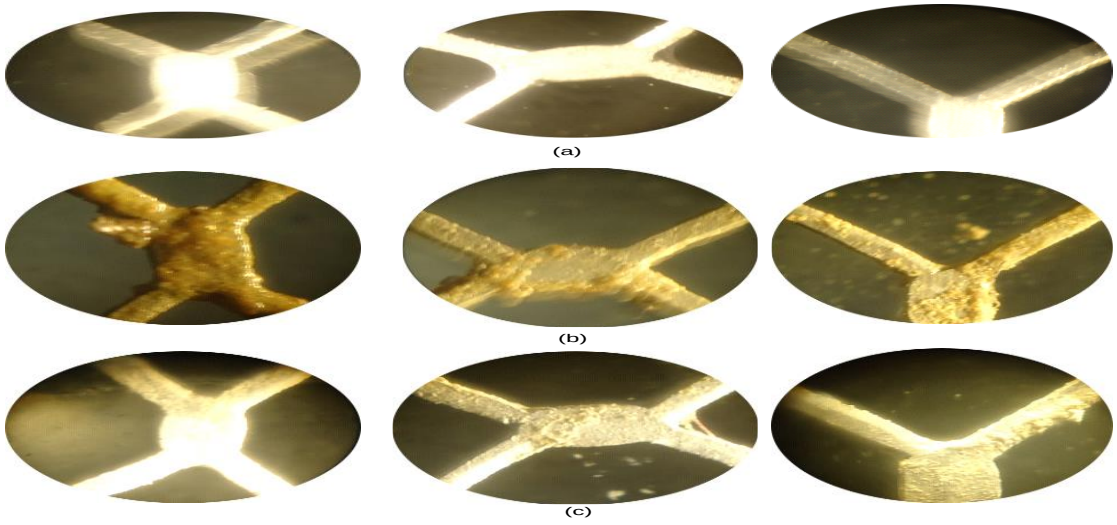

Fig. 5. Images of the electrodes taken from microscope (a) original electrode, (b) 15 days of use with unfiltered water, (c) 15 days of use with filtered water through the ion exchange stack.

For investigating the impurity deposits on the electrodes, XRD of the electrodes was carried out. The XRD of the newly installed mesh electrode is shown in Figure 6(a). The XRD of the electrode treated with unfiltered water for 15 days is shown in Figure 6(b) and XRD of the electrode treated with filtered water using ion exchange stack is shown in Figure 6(c). The plots in the figure show diffraction patterns of intensities against the angle of the detector (2Theta). The diffraction peaks positions depend upon the wavelength. Prominent peaks are observed at 40^0 and 45^0 in the newly installed electrodes. The XRD of electrodes treated with unfiltered water shows multiple peaks at 40^0, 45^0, 68^0, 69^0, 70^0, and 79^0. The peaks get reduced in the XRD of the water filtered using ion exchange stack, indicating that ion exchange stack reduces the impurities of the water passing through it and resulting in enhanced working of the fuel cell.

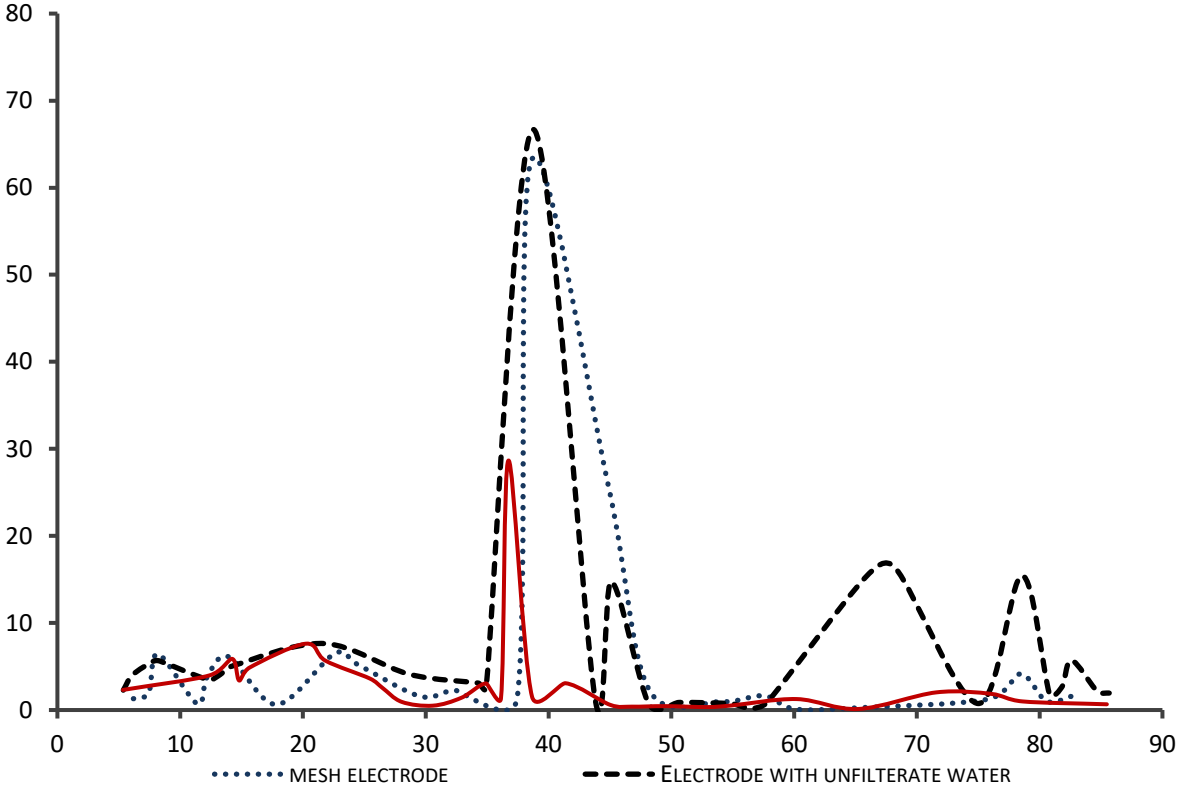

Fig. 6. XRD of the electrode a) original, b) treated with unfiltered water for 15 days, and c) treated with filtered water using ion exchange stack

5. Conclusions and future scope

The investigations in the present paper were carried out for studying the effect of ion exchange stack included as an extra layer in PEM based fuel cells. The proposed cell structure is proposed to be used for rural areas where availabi (a) pure water for generation of H_2 and O_2 us (b) ctrolysis is difficult. The investigations were carried out using pH measurement of the filtered water by the hange stack layer, visual analysis of the electrodes, and XRD for estimating the chemical deposition on the electrodes due to impurities in the water. Investigations have shown that inclusion of ion exchange layer in the PEM fuel cell enhances its performance because of reduced effect of impurities on the electrodes. The PEM fuel cells having inbuilt ability of reducing the effect of impurities in the input water has a lot of applications not only in rural areas but in transportation vehicles as well.

Investigations related to extended physical and chemical structure of the ion exchange stack are on the agenda for future work.

6. Acknowledgement

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