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Development of Polymeric Layer on Anode for Enhanced Hydrogen Generation in Microbial Electrolysis Cell†

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Hydrogen is a green fuel with low carbon footprints and is gaining importance as a replacement for petroleum products. Majority of hydrogen production is from fossil fuels that may exhaust in near future. Producing hydrogen using microbial electrolysis cell is a novel approach which utilizes organic matter including waste water. The anode used in a conventional microbial electrolysis cell is usually graphite felt/cloth/plate. This work concentrates on exploring the option for coating a polymeric layer on electrode surface used as anode that boosts the affinity of microbes towards electrode and its impact on hydrogen production in microbial electrolysis cell. Conducting polymer material, polyaniline was synthesized on the surface of graphite felt anode. Experiments were conducted to evaluate the performance of the modified graphite anode in microbial electrolysis cell. The results proved that the microbial electrolysis cell having the modified anode is 30 % more efficient than the microbial electrolysis cell having conventional anode.

Keywords: Microbial electrolysis cell, Graphite anode, Polyaniline.

INTRODUCTION

Microbial electrolysis cell produces hydrogen from wastewater by application of electric current. The electric current would ideally be produced by a renewable source of energy. Microbes consume the organic matter present in wastewater for the metabolic activities releasing carbon dioxide, protons and electrons. Formation of hydrogen gas by reduction of protons is thermodynamically unfavourable and hence an additional voltage is required which is supplied to the microbial electrolysis cell from an external source. As part of the energy for this reduction is derived from bacterial activity, the electrical energy that has to be supplied is less than that of electrolysis of water in the absence of microbes. Hydrogen production has reached up to 3.12 m^3 H_2/m^3d with an input voltage of 0.8 volts [1]. The efficiency of hydrogen production depends on which organic substances are used. Lactic and acetic acid as substrates have achieved 82 % efficiency, while the values for untreated cellulose or glucose are close to 63 % [2]. The efficiency of normal water electrolysis is 60-70 %. Sugarcane wastewater when used directly in microbial electrolysis cell for a span of 21 days has given a hydrogen recovery of 22.9 % and upon adding *Pseudomonas aeruginosa* to the same substrate has led to doubling of the volume of gas generated [2]. Platinum (cathode) and graphite (anode) are normally used as electrodes in a conventional microbial electrolysis cell. There has been several works where the cost effective cathodes like stainless steel [3], metal oxide coated stainless steel [4], biocathode [5], *etc*. have been used. Work has also been carried out on using alternative anodes or modified graphite electrode. Use of a conducting polymer coated graphite anode in a microbial fuel cell (MFC) [6], has resulted in higher current density compared to the conventional microbial fuel cell due to better adhesion of microbes on the coated graphite felt. Microbial fuel cell and microbial electrolysis cell have similar construction, so the electrodes used in a microbial fuel cell can also be used in a microbial electrolysis cell. This work concentrates on using polymer coated graphite felt as anode in a microbial electrolysis cell and comparing its result with the conventional microbial electrolysis cell.

EXPERIMENTAL

Synthesis of polymeric layer on graphite felts

Synthesis of polyaniline: Solution 1 was prepared by adding 4 mL of aniline to100 mL of 1 M HCl (8.62 mL of

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HCl in 100 mL water) in a 250 mL beaker. Solution 2 was prepared by adding 5 g of ammonium per sulphate to 100 mL of 1 M HCl in a 250 mL beaker. Solutions 1 and 2 were mixed in a 500 mL beaker and a graphite felt was immersed into the solution and stirred continuously for 7 h using a magnetic stirrer. A green colour solution was obtained. After 7 h of stirring the graphite felt was taken out from the solution and dried at 70 °C for a period of 24 h, a green coating was developed on the surface of the graphite felt [6]. Fig. 1 shows the polyaniline coated graphite felt.

Fig. 1. Polyaniline coated graphite felt

Preparation of synthetic wastewater: Microbes consume the organic matter in the wastewater leading to the formation of acetate which combines with water to form carbon dioxide, electrons and protons [7]. Hence synthetic wastewater was prepared by adding 6 g of sodium acetate to1200 mL of distilled water, leading to a COD of 500 g/L.

Buffer preparation: A pH of 7 should be maintained for the microbes to survive in the cell and phosphate buffer was used for this purpose. Phosphate buffer was prepared by mixing 30.5 mL of 0.2 M dibasic sodium phosphate with 19.5 mL of 0.2 M monobasic sodium phosphate. It was diluted to 100 mL in a volumetric flask using double distilled water. The pH was checked using pH strip and was found to be 7 [8]. 10 mL of this buffer was added to the prepared synthetic wastewater.

Microbial inoculation: Pure culture of *P. aeruginosa* was selected for the preparation of microbial culture and placed inside the laminar air flow chamber. The nutrient broth was inoculated with the microbes from the petri-plates using Streaking method. The streaker is made up of a material which can be heated and cooled at a rapid rate. Once the streaking is done, the streaker is placed on the burner to remove all the remaining microorganisms, if any. After the microbes had been transferred to the media, the media was kept in the orbital shaker for a duration of 24 h. The clear solution of the media then turned turbid which indicated that the *Pseudomonas aeruginosa* microbes had grown. This solution was then stored in the refrigerator. The culture prepared had a yellow-green fluorescence as shown in Fig. 2.

Fig. 2. Prepared *Pseudomonas aeruginosa* inoculum

Fabrication of microbial electrolysis cell: Microbial electrolysis cell was fabricated using acrylic sheets. The anode and cathode chambers were separated by CPI 7000 cation exchange membrane as shown in Fig. 3. Synthetic wastewater

Fig. 3. Microbial electrolysis cell in operation with an electrode spacing of 4cm and electrode potential of 0.8 V

was added into the anode chamber of the microbial electrolysis cell followed by 15 mL of culture media of *Pseudomonas aeruginosa* and 10 mL of buffer solution to maintain the pH in anode. The cathode chamber was filled with distilled water. Polymeric coated felt was immersed in the anode chamber and stainless steel was immersed in the cathode chamber. The anode was connected to the positive terminal and the cathode was connected to the negative terminal of the DC power supply. The lid was closed and sealed. The power supply was switched on and voltage was set to 0.8 V. The hydrogen gas produced was collected in a downward displacement of water setup to measure the amount of hydrogen produced. Two microbial electrolysis cells, one using the conventional anode (graphite felt) and the other using modified anode (polyaniline coated graphite felt). The parameters like voltage, spacing between the electrodes and pH of the solution were maintained same for both microbial electrolysis cells.

RESULTS AND DISCUSSION

Conductivity of polymeric coating: The conductivity of the synthesized polymer was measured using Agilent conductivity meter and was compared with the conductivity of the non-coated graphite felt. Fig. 4 shows that the synthesized polymer is conducting and its conductivity is better than non-coated graphite felt.

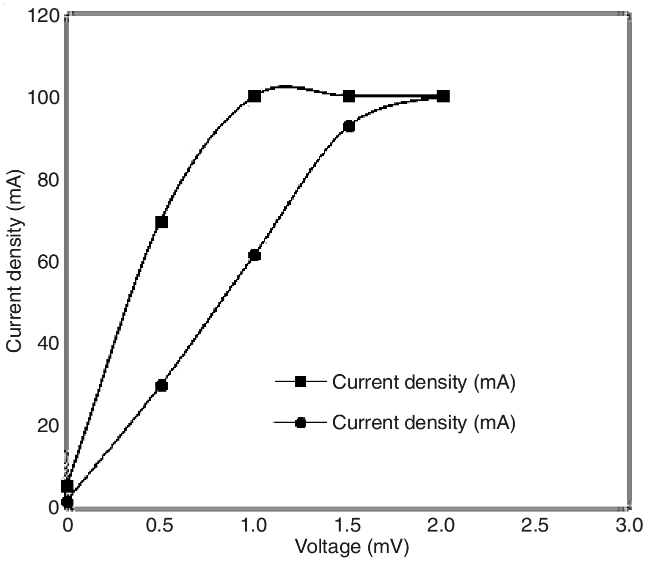

Fig. 4. Drop in resistance of graphite felt due to addition of conducting polymeric layer

From plots in Fig. 4, resistances are obtained such as 42.10 Ω for graphite felt and 18.37 Ω for polyaniline. It is visible that the resistance offered by the material for the flow of current is reduced by coating the graphite with the polymeric layer. Since, the conductance is reciprocal of resistance it can be inferred that the conductivity of the electrode is increased by the addition of polymeric layer.

Presence of required functional groups: Fig. 5 depicts the FTIR spectrum of polyaniline. According to literature, peaks in 3335-3000 cm^{-1} region indicate the presence of NH group [9,10]. Fig. 5 shows the presence of only NH group in polyaniline at 3100 cm^{-1}. Hence, confirms the polyaniline coating and the method of synthesis has been proven to be correct.

Enhanced hydrogen generation in microbial electrolysis cell: Fig. 6 compares hydrogen generation in a microbial electrolysis cell having conventional graphite felt anode microbial electrolysis cell having polyaniline coated graphite felt anode. Plots clearly show that there is an enhancement in the volume of gases generated in presence of polyaniline coating. There is a 30 % enhancement in the volume of gases generated. This increase in volume of gases generated can be attributed to the enhanced activity of the microbes at the anode which leads to efficient transfer of electrons to anode.

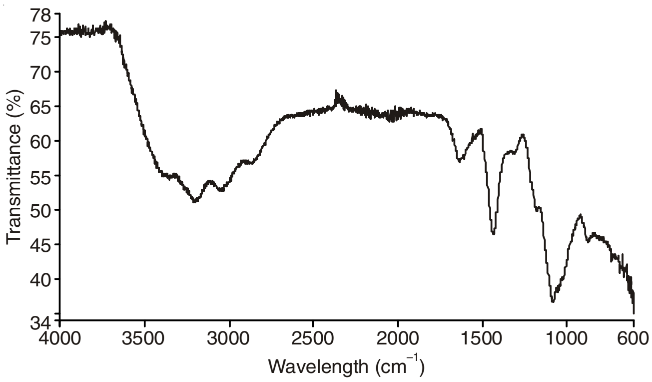

Fig. 5. FTIR spectrum of polyaniline

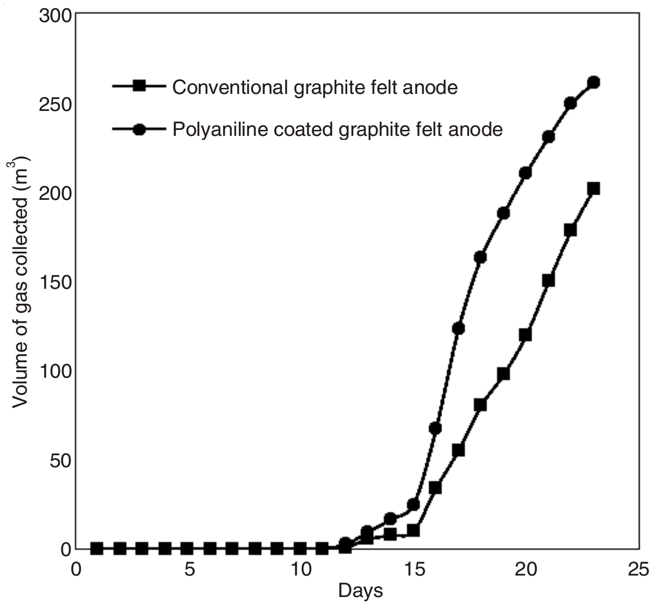

Fig. 6. Volume of gases collected in microbial electrolysis cells with conventional graphite felt anode and polyaniline coated anode

Conclusion

Conductive polymers were successfully synthesized and coated on the surface of the graphite felt. Use of polyaniline coated graphite felt as anode in microbial electrolysis cell proved that there is an enhancement of 30 % in the volume of gases generated when compared with a microbial electrolysis cell using conventional graphite felt without polyaniline coating.

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