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Enhancing biohydrogen production from sugar industry effluent by metal oxide coatings on nickel foam cathode in Microbial Electrolysis Cell

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ABSTRACT

Development of low cost cathode materials is one of the crucial challenge in Microbial Electrolysis Cell (MEC) for hydrogen production. In this study, MEC hydrogen production through various catalyst coatings on Nickel foam (NF) template cathode was investigated using sugar industry effluent. NF has proved a better performance than other cathodes in dual chamber MEC using sugar industry effluents. Various catalysts are of oxides of Nickel and Cobalt synthesised using simple precipitation and calcination techniques. The hydrogen evolution performance of Nickel Oxide/ Nickel foam and Cobalt oxide/Nickel Foam was conducted in MECs which were significantly superior to NF. Electrochemical Characterization were conducted on the three cathodes and the stability of the cathode coatings were also studied. Similar to LSV trends, current density and hydrogen production rate were obtained. At an applied voltage of 1.0 V, the maximum hydrogen production rate (HPR) was achieved in MEC with NiO/NF, nearly twice than NF and 1.12 times higher than other metal oxide cathode. The MEC performance using the three cathodes based on the production of hydrogen, coloumbic efficiency, hydrogen recoveries and COD removal efficiency were also in the order as same as the HPR. The hydrogen gas collected from the MEC was confirmed of high purity using GC analysis. These results demonstrate the high-efficient and low cost cathodes materials for biohydrogen production in MECs.

Keywords: *Hydrogen production; MEC; Nickel Foam; catalyst; sugar industry effluent.*

1 INTRODUCTION

Microbial Electrolysis Cell (MEC) is the bio-electrochemical technology involving microorganisms for production of hydrogen from organic matter in wastewater. With energy recovery on focus, wastewater fed MEC are gaining more interest rather than synthetic substrates fed MEC[1,2]. Hydrogen generation through MEC technology has attained added benefits of simultaneous treatment even with industrial effluents[3–5]. Sugar industry, being food based industry let out its effluents with characteristics which are significant in harnessing hydrogen through MEC technology. MEC employing sugar industry effluent with Nickel foam (NF) cathode has been demonstrated with higher performance than Stainless Steel mesh and Nickel plate cathode[6]. Nowadays, NF has enticed researchers especially in the field of MEC, as low cost alternative to precious metals like Platinum (Pt) and with 3D scaffold porous structure. To enhance the performance of NF, additions of materials in form coating, electrodeposition or other methods are done for increasing the catalytic activity[7–10]. And nickel and cobalt have been extensively researched for catalysts enhancing fast HER[11–14]. In this study, the performance of metal oxide catalysts namely Nickel oxide and Cobalt oxide have been investigated with NF electrode in the cathode side of the MEC using sugar industry effluent.

2 METHODS AND MATERIALS

2.1 Characteristics of wastewater

Sugar industry effluent was collected from Erode, Tamilnadu. By appearance it was brown in colour and less turbid in nature. The important characteristics of the wastewater were measured using multiparameter analysis kit (PCD650, Eutech Instruments) and listed as initial COD 4000 ppm, TDS 2300 ppm, pH-4.4, salinity 2980 ppm, resistance 10.5 Ω and conductivity 205 mS.

2.2 MEC construction and operation

Three dual chamber rectangular box type MEC separated by Nafion 117 membrane were fabricated as previously reported in Samsudeen et al[15]. A DC power supply (Bestmach Make) was used for the addition voltage to reactor the setup. A 10 Ω resistor was connected across the circuit to measure the current flowing, and recorded continuously. In the anode compartment, the substrate used was sugar industry wastewater without any dilution and the catholyte used was phosphate buffer (50 mM) solution. The graphite electrode was used as anode while NF and two coated NF were used as cathode in three reactors respectively. The metal oxides of nickel and cobalt were prepared by converting their respective chlorides into hydroxides, and finally calcination was done. The metal oxide was bound to the surface of NF with Polyvinyl alcohol (PVA) polymer binder. Nickel oxide coated Nickel Foam and Cobalt oxide coated Nickel foam were designated as NNF and CNF respectively. All electrodes were cut into 6 x 4 cm^2 and interspacing distance from the membrane was maintained at 1.5cm. After stabilisation of the systems, the experimentation was done in triplication at the room temperature.

2.3 Characterisation studies:

XRD patterns of the two metal oxides were obtained on 2θ range from 10° to 90°and step size 2° in Cu-kα radiation mode (Rigaku X-ray diffractometer). SEM images were acquired for the two catalysts coated electrode materials

(VEGA3 TESCAN with Oxford Instruments). Linear Scan Voltammetry(LSV) studies were made in three electrode system for the two fabricated cathodes along with the uncoated NF over a potential range of 1.0 V to -1.0 V at a scan rate of 50 mV/s (Amteksi).

2.4 Calculation & Analyses:

Standard potassium dichromate close reflux method was used to determine the substrate COD using digestive spectrophotometry. Gas Chromatography analysis was performed with Thermal Conductivity Detector (TCD) using Nitrogen (N2) as carrier gas for clear identification of peak of hydrogen (Thermofisher). The performance of MEC were reported in terms of Hydrogen production rate (HPR), COD removal Efficiency, Coloumbic Efficiency (CE), Cathodic Hydrogen Recovery (CHR), Overall Hydrogen Recovery (OHR) and Energy recovery (ŋE). The voltage across 10Ω resistor was connected using multimeter and the current was recorded in Data Acquisition system.

3 RESULT AND DISCUSSIONS

3.1 Chemical Characterizations:

The structural characterisation of the two synthesised materials was obtained as the XRD patterns of both catalysts. The crystalline nature of nickel oxide and cobalt oxide were clearly evident in the figure 1(a) & 1(b). The characteristics peaks of both metal oxides were confirmed for NiO and Co_3O_4.

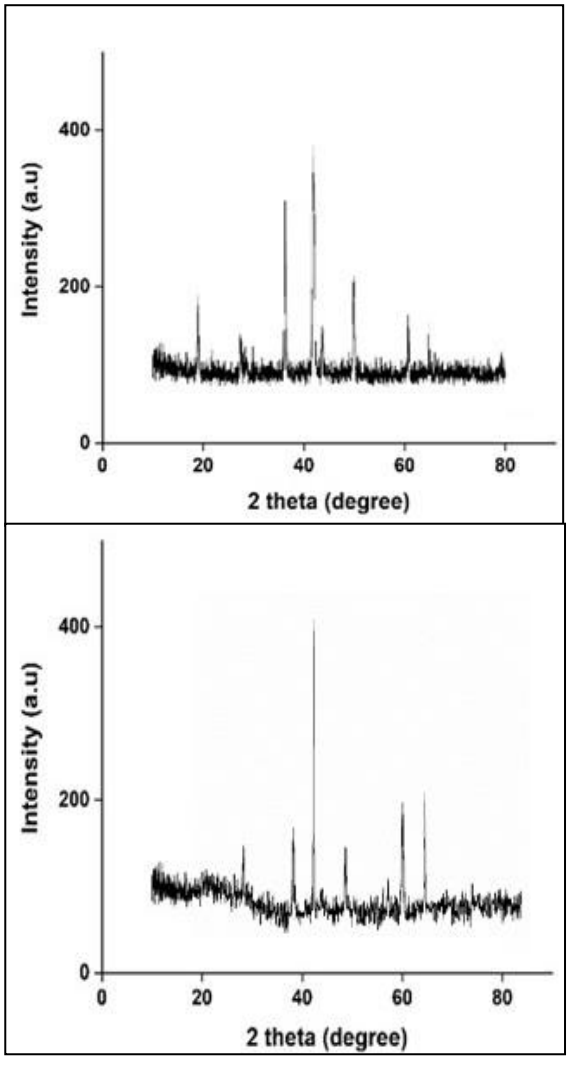

Figure 1(a) &1 (b) : XRD pattern of Nickel and Cobalt oxide catalysts

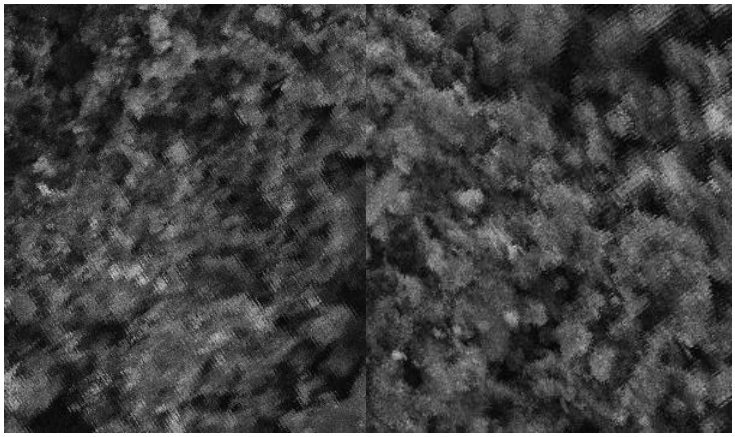

Figure 2(a) and 2(b): SEM images of Nickel oxide and Cobalt oxide

SEM images clearly depicted the catalyst material coated on NF with help of polymer binder. Both Cobalt and nickel oxides synthesised were very crystalline in appearance under SEM images. Figure 2(a) &2(b) represents the micrographs of the metal oxide coated NF.

3.2 Linear sweep voltammetry:

LSV revealed a lower onset potential for NiO than Co_3O_4 coated cathodes but NF had a higher onset potential for NNF cathode, an increase in current density is evident around at − 500 mV, while for CNF cathode it was around at − 550 and − 600 mV for NF respectively. This deviation of onset potential on contrast with uncoated NF directly described the improvement of electrocatalytic property which is responsible for HER. Additionally, the current densities at 1.0 V of NF, CNF and NNF were 1.1 A/m^2, 1.08 A/m^2 and 1.20 A/m^2 respectively.

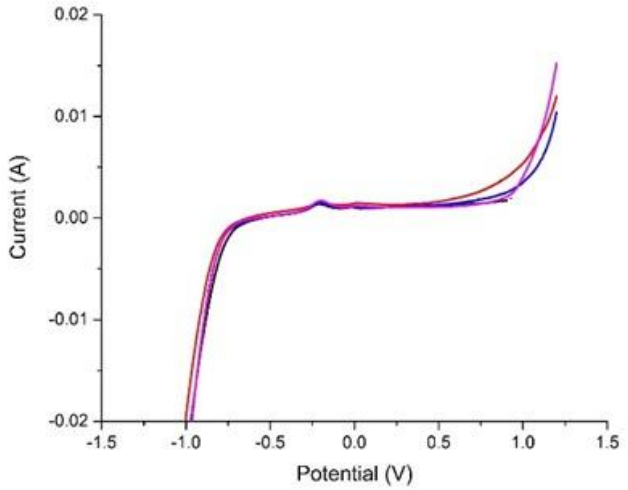

Figure 3: LSV of NF, CNF, NNF with reference electrode (Ag/AgCl) and counter electrode (Pt) with PB electrolyte

3.3 Performance of MEC

3.3.1 Hydrogen Production rate:

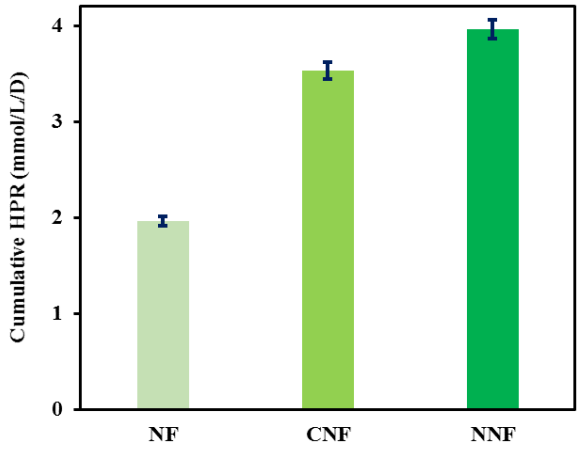

Figure 4: Cumulative Hydrogen production rate in all three MECs.

After achieving stable operation of all three MEC using different electrodes, hydrogen production was monitored for the batch cycle of 5 days, operated at the applied voltage of 1.0 V (triplication). The maximum hydrogen production was attained by NNF which was equal to 3.95 mmol/L/D and followed by 3.28 mmol/L/D in CNF cathode used MEC. The control NF MEC produced 1.96 mmol/L/D of hydrogen during the batch operation. From figure 4, NNF showed 9.4% and 50.4% higher HPR than CNF and NF in the sugar industry effluent respectively. Similar coatings and electrodeposits had improved hydrogen productions compared with uncoated cathodes[16,17].

3.3.2 Performance of the three MECs:

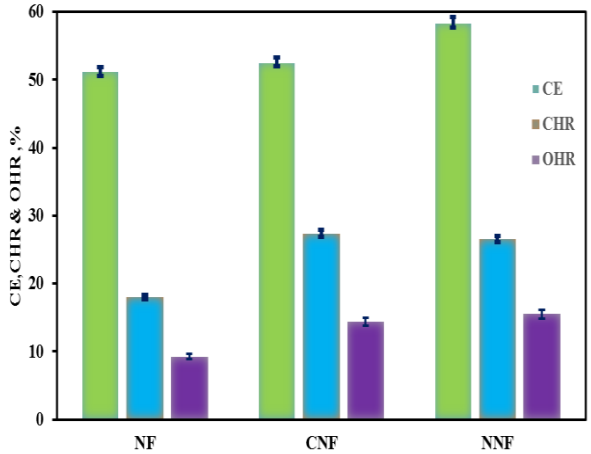

Figure 5: Performance of the two metal oxide/NF cathode compared with NF

As shown in figure 5, the performance of the MEC reactor evaluated based on various expressions were reported also followed the similar trend of NNF>CNF>NF in the order. Coulombic Efficiency of the MECs using NF, NNF and CNF cathodes were 51% %, 54%, and 58 % respectively. Based on the batch hydrogen production against the measured current, Cathodic Hydrogen recovery of NF, CNF, NNF were 18.02%, 27.39% and 26.56% correspondingly. Similarly, the OHR exhibited by NF was 9%, which was 4% and 6% lower than CNF and NNF accordingly. Hydrogen recoveries and columbic efficiency were low when compared to acetate fed MEC. But MEC operating with industrial and domestic wastewater had similar type of HPR and other performances. This was mainly ascribed by the non-usage of targeted microorganisms in place of inherent organisms of the sugar industry effluents that could enhance hydrogen production[6].

3.3.3 Substrate degradation:

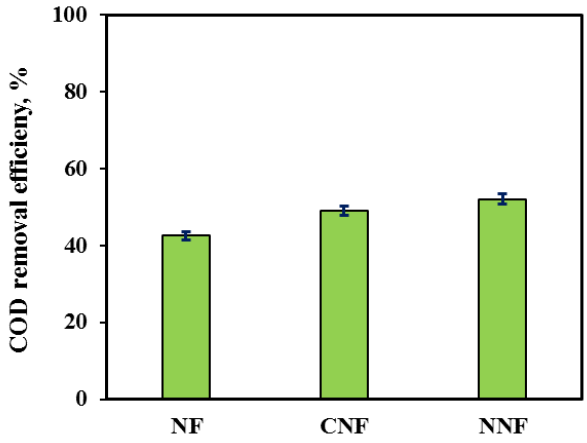

Figure 6: COD removal efficiency in the three MECs

COD removal efficiency of the three MECs were calculated based on the substrate COD before and after every batch operation. Considering all three nearly 50% of substrate degradation of the sugar industry effluent were achieved implying the responsible microorganisms active in the effluent for production of hydrogen. The MEC setup had demonstrated the removal efficiency of 42.5%, 49% and 52% in employing NF, CNF and NNF cathodes When using hydrogen producing pure culture, nearly 90% removal of COD could be attained[18]. Use of catalyst metal oxide had improved the current density and were responsible for 7-10% deviation in improvement of substrate degradation for enhancing hydrogen production from Sugar industry effluent.

4 CONCLUSION

This present study had investigated improving the production of bio-hydrogen from sugar industry effluent using two metal oxide catalysts coated on NF cathode in dual chamber MEC reactor. NiO and Co_3O_4 catalysts were synthesized and decorated on NF using simple manual coating. Both catalysts had similar properties in structure and electrochemical characterisations. The performance evaluation of these catalysts were presented in terms of coloumbic efficiency, cathodic hydrogen recovery and overall hydrogen recovery. At the operating conditions of room temperature and applied voltage 1.0 V, the maximum hydrogen production rate was 3.95 mmol/L/D by NiO coating with 58% CE, 27% CHR, 15% OHR and 52% substrate degradation. Metal catalysts

other than precious materials have to be investigated for higher HER demonstrating the high-efficient and low cost materials for biohydrogen production in MECs. Simultaneous treatment of industrial effluents with energy recovery in mind with this technology would nurture mankind towards sustainable environment and future.

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