

Short Communication

Anodic Generation of Hydrogen Peroxide by Using Manganese(III) Oxide Based Catalyst

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Electrochemical synthesis of hydrogen peroxide (H₂O₂) during oxidation of water oxidation could present a valuable method to generate this powerful oxidant. A simply structured Mn based electrode over a carbon polymer composite substrate (Mn(III)oxide/C) was manufactured by a thermal compression bonding method. The electrode was then used for water electrolysis at different electrode potentials and the amount of hydrogen peroxide generated was determined in an undivided electrochemical cell. The results show that the optimal values for H₂O₂ synthesis are anodic potentials of +0.5 V, +0.6 V and +0.7 V vs. Hg/HgO and producing H₂O₂ up to 11 ppm in an undivided cell.

Keywords: carbon polymer, hydrogen peroxide, Mn based electrodes, water oxidation

1. INTRODUCTION

Hydrogen peroxide (H₂O₂) is a valuable molecular specie that decomposes to molecular oxygen, free radicals and water. It has been widely utilized for many industrial applications like the synthesis of organic compounds, paper bleaching, wastewater treatment, and detoxification of hazardous organic residues. One of the most beneficial applications of H₂O₂ is the reagent for the classical Fenton's based process for the degradation of toxic organic free radicals and molecular compounds from wastewater. Fenton's reagent forms by mixing H₂O₂ and Fe²⁺, which generates the hydroxyl radical with an oxidation potential of 2.33 V vs. NHE [1], which can then be used to oxidase recalcitrant organic compounds in wastewater.

Electrogenerated hydrogen peroxide is typically produced via the reduction of oxygen at carbonaceous electrodes such as reticulated vitreous carbon (RVC) [2]. The electrochemical method offers a number of advantages over the current industrial method of production by anthraquinone oxidation, such as its lower cost and the ability to produce the oxidant on-site [3].

Hydrogen peroxide production by the reduction of dissolved oxygen has been demonstrated as a reliable method for oxidation of organics [4]. Another possible route for the electrochemical generation of H₂O₂ is via dual electron water splitting as shown in equation 1.



This reaction competes with the four-electron O₂ evolution reaction (2) and the production of the hydroxyl •OH radical involving single electron oxidation reaction (3). Much of the current literature focuses on the O₂ evolution reaction and the •OH radical generation with little emphasis on the feasibility of H₂O₂ electrosynthesis [5].



Previous works have also suggested that predominantly two-electron water oxidation to H₂O₂ might be possible if a catalyst with low overpotential for H₂O to H₂O₂ can be developed to promote the synthesis of H₂O₂ over O₂ evolution [6]. Some metal oxides have been shown to favour two-electron electrochemical water oxidation reaction, including MnO_x [7], TiO₂[8] and BiVO₄[9]. A number of theoretical studies have also highlighted these materials as being close to, but not yet at, the theoretical maximum for H₂O₂ electrosynthesis activity [10,11]. Here we present a novel Mn(III)oxide/C based coating towards water oxidation for H₂O₂ synthesis in an undivided electrochemical cell.

2. EXPERIMENTAL DETAILS

The materials used are: bipolar plates made of extended graphite (C-polymer PV-15) from SGL group, C black VULCAN[®] XC72R from Cabot, Reagent grade, manganese (III) oxide, 99 % oxalic acid and Nafion[®] perfluorinated resin solution from Sigma Aldrich, and isopropanol, sodium sulphate, acetone from Fischer scientific. All the materials were used as received.

2.1 Preparation of the ink and fabrication of the Mn based (Mn(III)oxide/C) Anode

C-polymer PV-15 was pretreated with 10% oxalic acid at 50 °C for 20 minutes and left overnight in DI water. Printable ink was formed by mixing Manganese (III) oxide (preheated at 300 °C) with Nafion and iso-propanol in 70:10:10. The shear blade mixer was used at 7000 rpm for 20

minutes. Further, 10% C black was added in the ink and stirred simultaneously at $3000 \text{ rev sec}^{-1}$ with a radius of 0.03 cm, 0.5 cm in length coated with PTFE, over a stirrer with cylindrical shape (Fischer GMBH). The ink was rolled on both sides of the hydrophobic C black to form a flat sheet coating. The flat coating was thermo-laminated in a hot press to 0.1 mm thickness at 10 MPa pressure and $60 \text{ }^\circ\text{C}$. The Mn (III) based coating on composite carbon polymer electrode Mn(III)oxide/C fabrication procedure is shown in Figure 1.

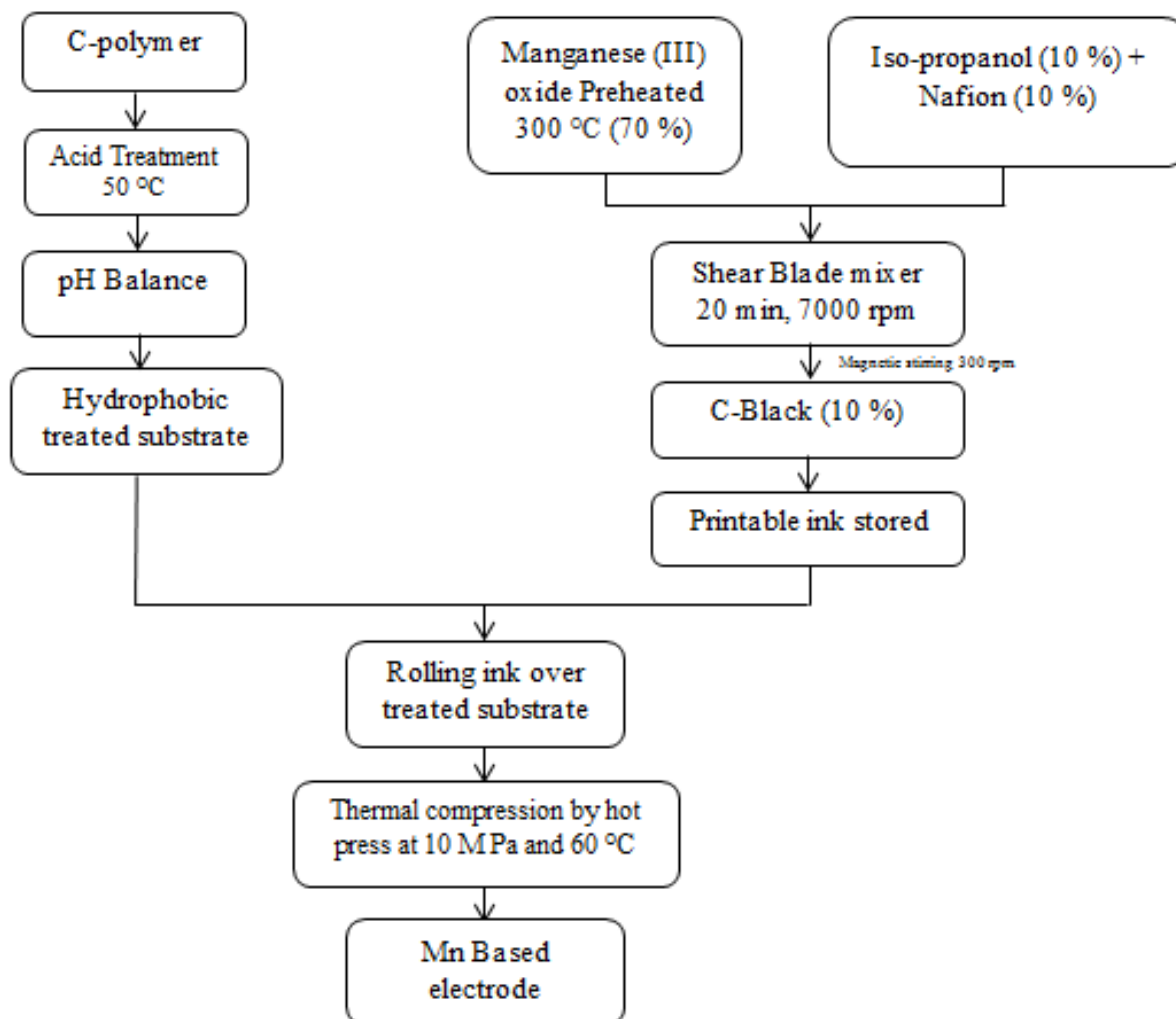


Figure 1. Schematic diagram for the fabrication of Mn (III) based coating Mn(III)oxide/C for the anodic production of hydrogen peroxide

2.2 Electrochemical studies

The electrochemical experiments were performed using a Ivium potentiostat/galvanostat from Alvatech U.K using Ivium Soft Channel 1 software.

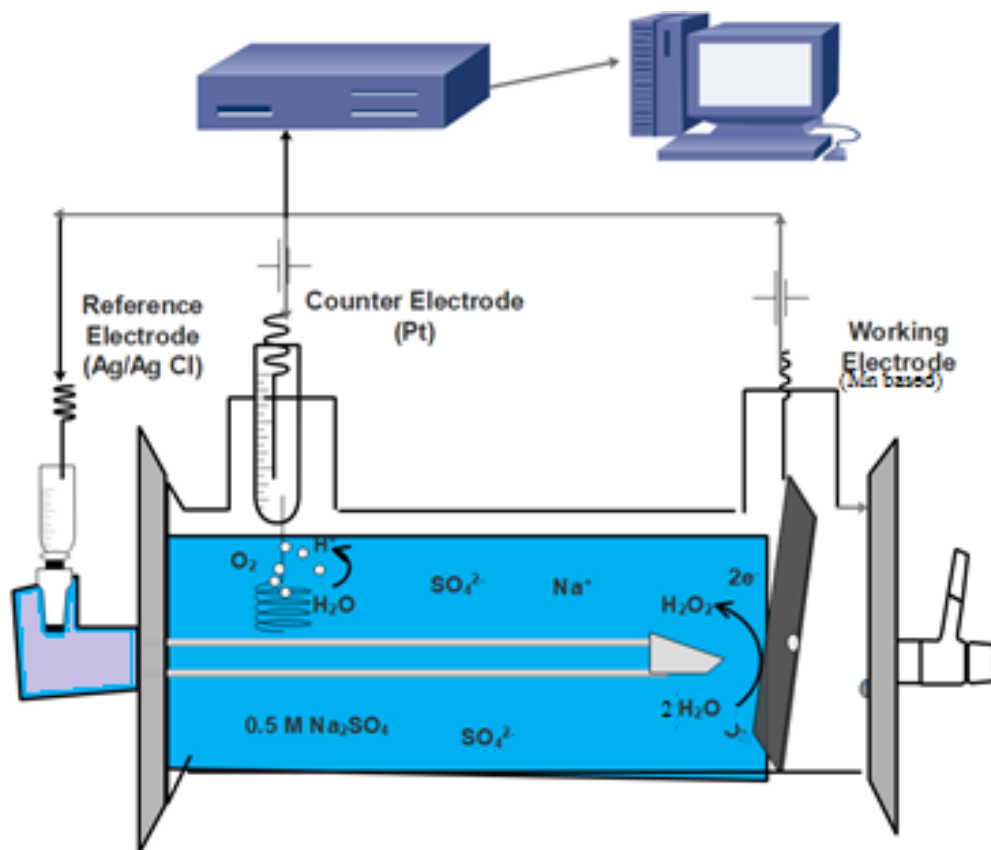


Figure 2. Schematic diagram of undivided three-electrode cell equipped with a Mn(III)oxide/C working electrode anode, Pt as counter electrode with Hg/HgO as reference electrode inserted into a Luggin capillary used under constant potential electrolysis of 100 cm³ of a 0.5 M Na₂SO₄.

The as obtained Mn(III)oxide/C based coating was cleaned with ultra-pure water, dried with nitrogen gas and used as an anode in an undivided electrochemical type of cell as shown in Figure 2. A 100 mL of solution having 0.5 mol dm⁻³ of sodium sulfate was used as the electrolyte for all electro-generation of hydrogen peroxide studies. A platinum type mesh (1.5 cm × 1.5 cm) with a Hg/HgO (1.0 g L⁻¹ NaOH) were employed as a counter type of electrode and reference type of electrode respectively.

2.3 Determination of H₂O₂

Samples of 0.5 mL were obtained at known periods of time during the electro-generation and the concentration was measured by an UV–VIS spectrophotometer by the ammonium metavanadate method [10]. The phase change on the sample colors obtained while the electrolysis was seen with the reason of the generation of a dark red peroxovanadium ion obtained due to the chemical conversion between hydrogen peroxide in the sample and ammonium type of metavanadate at acidic conditions. The absorbance was measured in the region of 450 nm.

3. RESULTS AND DISCUSSION

In neutral solutions, H_2O_2 was synthesized by water electrolysis at the anode according to reaction (1). The polarization curves showed transitory current response with respect to the applied anodic potential. The curve in Figure 3 demonstrates that after 0.5 V vs. Hg/HgO, the anodic current density fluctuates proportionally with the applied electrode potential. It is assumed that water electrolysis to H_2O_2 as depicted in reaction 1 occurs low overpotentials and O_2 evolution (reaction 2) takes place predominantly after 0.7 V vs. Hg/HgO. As the potential becomes more positive oxygen evolution becomes more evident.

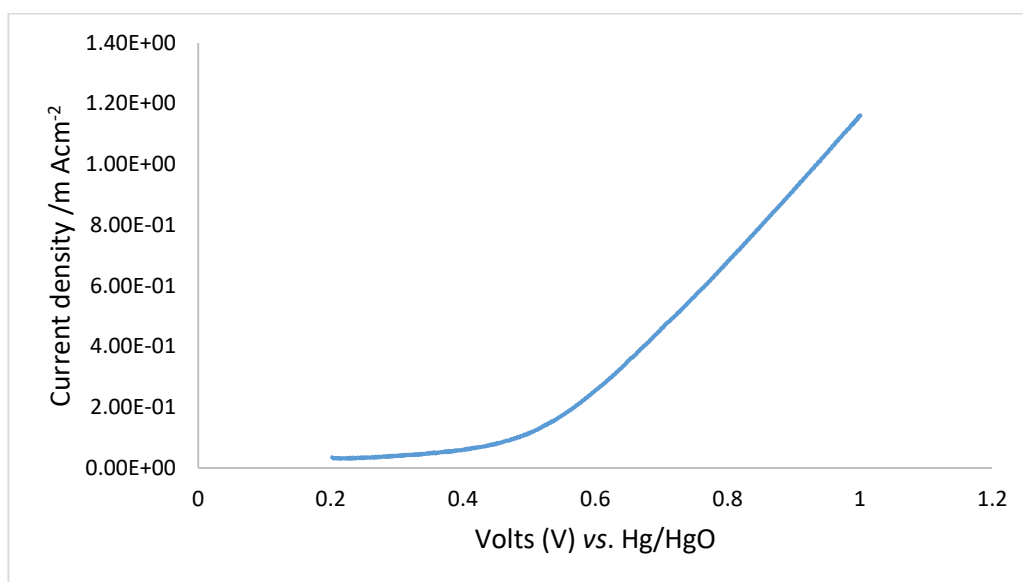


Figure 3. Polarization curve by using Mn(III)oxide/C based anode coating in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ background electrolyte; rate at which potential swept = 0.1 mV s^{-1} and temperature: 298K.

For electrodes under consideration, the Faradaic efficiency (%FE) can be defined as the experimental electric current consumed by the desired electrochemical reaction (H_2O_2 synthesis) over the total electric current passed [11]. In one of the similar studies authors report H_2O_2 production over gas diffusion cathodes the reported maximum value of $0.003 \text{ mol dm}^{-3}$ at more negative potential by constant supply of oxygen [12]. In another studies H_2O_2 was generated on gas diffusion electrodes with the constant supply of air at a current density of 15 mA cm^{-2} . The H_2O_2 yield was observed to be more than 500 mg/L . The reported catalyst was carbon based fine structures over the current collector [13]. Similarly, in another studies electro-generation of H_2O_2 was conducted in an advanced type of assembly which reported more than 700 mg/L of H_2O_2 .

The current efficiency was reported at exceeding value of 40% [14]. However, in this study we reported the production of H_2O_2 without any additional supply of oxygen or any other gas at Mn(III)oxide/C based catalyst at a constant potential electrolysis of 0.5 V vs. Hg/HgO .

$$\%CE = \frac{i_{\text{H}_2\text{O}_2}}{i_{\text{total}}} \quad (4)$$

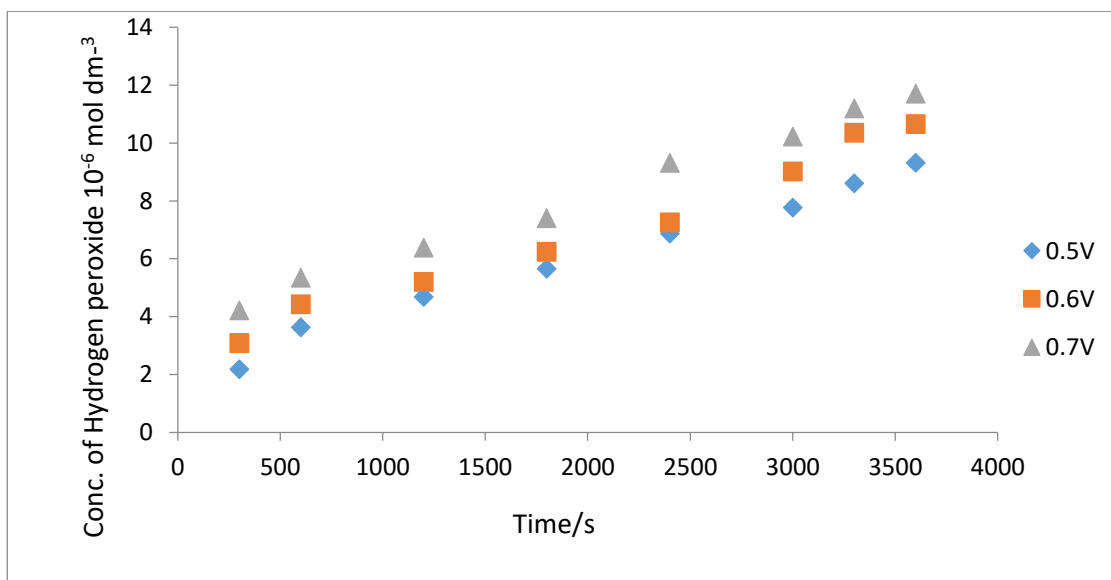
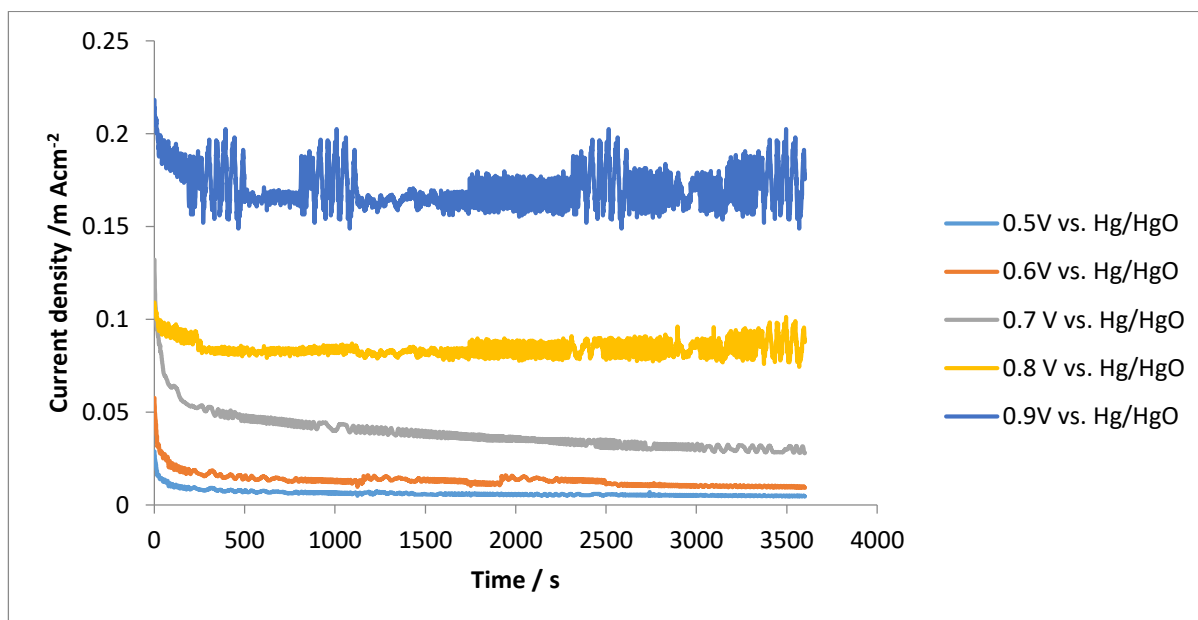


Figure 4. Anodic generation of hydrogen peroxide at 0.5, 0.6 V & 0.7 V vs. Hg/HgO in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at Mn(III)oxide/C oxide based anode at pH = 7 and Temperature: 298K.

The effect of anodic potential on the electro-generation of hydrogen peroxide was investigated from 0.5 V to 0.9 V vs. Hg/HgO.



Figures 5. Constant Potential electrolysis (Chronoamperometry) results for anodic production of hydrogen peroxide at 0.5, 0.6, 0.7, 0.8 & 0.9 V vs. Hg/HgO in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at Mn(III)oxide/C based anode at pH = 7 and Temperature: 298K.

Figure 4 shows the concentration of H_2O_2 versus time at three different applied potentials, while Figures 5 and 6 show the corresponding current density and %CE attained during electrolysis respectively. In one of the study in literature, the H_2O_2 generated is strongly influenced by the side reactions which actually utilize more energy due to the presence of other competing species. The reported energy consumption was 22.1 kWh kg^{-1} by applying a constant potential electrolysis of $-2.25 \text{ V vs. Ag/AgCl}$, this actually corresponds to the presence of other species which actually taken out energy and causing current loss. The reported H_2O_2 generation was only 294 mg/L which showed the occurrence of side reactions during the reduction of oxygen at more negative potential electrolysis [15]. Other peers also reported the electro-generation of H_2O_2 at an energy consumption of 118 kWh kg^{-1} at an applied current density of 75 mA cm^{-2} , this phenomenon is actually a continuity of side reactions involved during the electrolysis process which competes over the equilibrium conditions during the actual reduction reaction pathways [16].

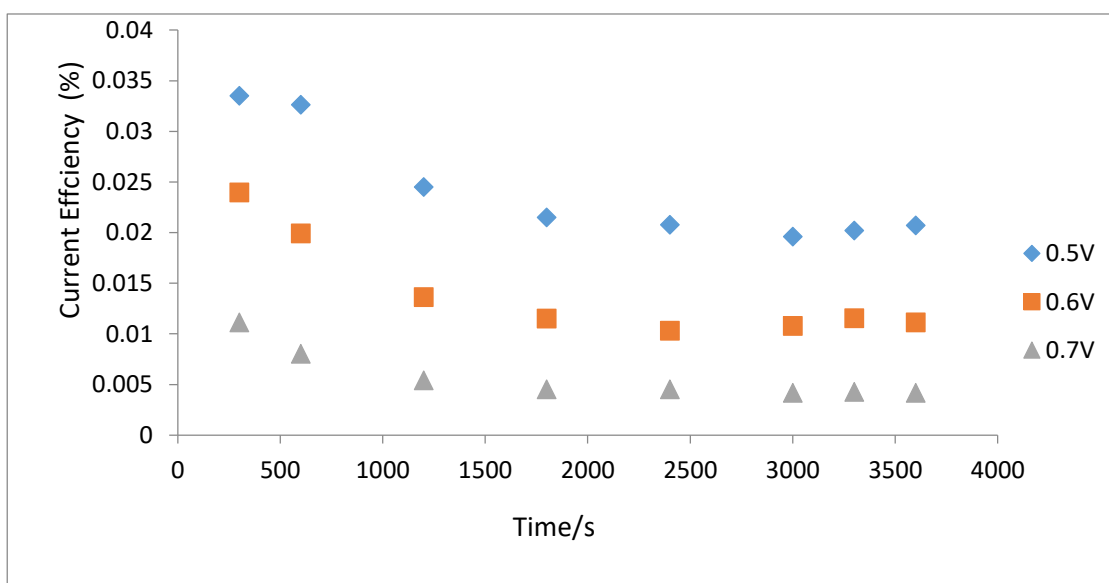


Figure 6. Current efficiency results for anodic production of hydrogen peroxide at 0.5, 0.6 & 0.7 *vs.* Hg/HgO in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at Mn(III)oxide/C oxide based anode pH = 7 and Temperature 298K.

The results show that H_2O_2 generation improves linearly at an applied potential of $0.5 \text{ V} \leq E_A \leq 0.7 \text{ V vs. Hg/HgO}$. Figure 4 suggest that at 0.7 V vs. Hg/HgO , there is a slight rise in the current density with electrochemical reaction time. At potentials greater than 0.8 V vs. Hg/HgO no hydrogen peroxide was detected and oxygen evolution was evident at the anode. High E_A causes decomposition of H_2O_2 together with the unwanted secondary oxygen evolution reaction [17].

The overall %CE is presented in Figure 6 is very low for all the electrode potentials. The maximum current efficiency was obtained at 0.5 V vs. Hg/HgO but decreases with time for all applied potentials. However these results are found to be novel in terms of previous studies as there is no

external specie like added oxygen flow or any kind of catalyst to synthesize hydrogen peroxide at reasonable cost in anodic electrochemical process.

4. CONCLUSIONS

We have shown that H₂O₂ can be electrochemically synthesized through water oxidation using Mn(III)oxide/C catalyst in an undivided cell. The H₂O₂ generation was optimally seen at 0.5 V vs. Hg/HgO and the concentration of H₂O₂ was enhanced by increasing the potential up to 0.7 V vs. Hg/HgO. However further increase in potential negatively impacted the electro-synthesis of H₂O₂ due to the competing oxygen evolution reaction at such a high potentials. This study indicated that the electrochemical pathways reflected in this experimental work can be further improved for H₂O₂ production in a more complex system. The electrodes exhibited by this methodology represented reasonable stability during electrochemical water oxidation in an undivided cell. These trends showed that this process is helpful for advanced industrial applications in the evolution of novel electrode surfaces for diversified applications.

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