ROLE OF SUPPORTING ELECTROLYTES FOR HYDROGEN PEROXIDE GENERATION ON GRAPHITE CATHODE

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Abstract— **The use of hydrogen peroxide for water decontamination is encouraged by many researchers being a green chemical in nature. The influence of supporting electrolytes on continuous in-situ generation of H2O2 was studied in this work. Four common supporting electrolytes (SEs) i.e. NaCl, NaNO3, Na2SO4 and Na2ClO4 were investigated in acidic solution. An undivided electrochemical reactor with graphite/Ti-TiO2 as cathode/anode electrode was used. The highest current efficiency of 42 % was noted with NaCl. NaClO4 gave the lowest current efficiency due to formation of titanyl ion. The limiting current was varied from 150 to 230 mA. The volume of the reaction zones were found to be between 0.07 and 0.2 cm3.**

Keywords— current efficiency, supporting electrolyte, diffusional resistance

I. Introduction

H2O2 is known as a "clean oxidizing" agent in a wide range of industrial processes as it does not leave any hazardous residues. The main applications for water treatment are in Fenton, electro-Fenton and photo-Fenton processes. In 1894, the reaction between H2O2 and metal as a homogeneous catalyst in dark condition was proposed first by H. J. H. Fenton, is recognized as Fenton reaction. Later, in 1934 Haber and Weiss realized that OH• is responsible for Fenton reaction which is based on OH• radical under dark condition [1].

In electro-Fenton, H2O2 and Fe2+ are on-site generated electrochemically, either separately or concurrently. H2O2 is electro-generated by the reduction of dissolved oxygen (1) and Fe2+ regenerated by Fe3+ reduction (2) or oxidation of a sacrificial iron-anode [2]. Electro-Fenton process is operated using different types of two- and three-electrode in divided and undivided cells.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.67\text{-}68 \text{Vvs SHE} \quad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^0 = 0.77 \text{ V vs SHE} \quad (2)$$

The SEs in electro-Fenton reaction enhances specially the solution conductivity and accelerates the electron transfer.

Generally, sodium sulphate, sodium perchlorate, sodium chloride, sodium nitrate and potassium chloride are used as the supporting electrolytes. Ghoneim et al. showed that the decolorization rate of azodye is faster in SO_4^{2-} solutions than in Cl^- electrolyte at the same concentration [3]. Approximately 100% removal of azodye occurs in 120, 180 and 180 min in Department of Chemical Engineering, IIT Guwahati, Assam-781039, INDIA

Corresponding author: animes@iitg.ernet.in, †Presenting author Na2SO4, NaCl and KCl
solution, respectively. Daneshvar et al. reported that the removal efficiency of Orange II in different electrolyte media follows the order as $ClO_4^{2-} \rightarrow Cl^- \rightarrow SO_4^{2-}$ at 0.05 M electrolyte concentration. The increase in NaClO4 concentration from 0.05 to 0.1 M does not have any effect in Orange II degradation [4]. Diagne et al. got a faster Methyl parathion degradation rate in presence of NO_3^- than that of SO_4^{2-} [5].

In addition, the concentration of electrolyte also affects the efficiency of the process. Higher Na2SO4 concentration leads to higher current density, which is resulted in faster and higher production of H2O2 [6]. This work uncovers the

dependency of NaCl, NaNO3, Na2SO4 and Na2ClO4 as SEs on H2O2 electro generation at fixed –Ecat=0.5 V vs Ag/AgCl at high pure graphite surface.

II. Experimental Section
A. *Materials*
All chemicals used were of analytical grade. NaCl (assay min 99.5%), NaNO3 (assay ≥99%), H2SO4, (assay 95-98%) and NaOH pellets (assay min 98%) were purchased from M/s Merck, Mumbai, India. NaSO4 (assay min 98%) and NaClO4.H2O (assay 98-102%) were from M/s LOBA Chemie, Mumbai, India. TiO2 powder (assay min 99.5%) was purchased from M/s LOBA Chemie, Mumbai, India, to make Ti2(SO4) solution for H2O2 analysis. The graphite electrode was supplied by M/s GraphiteStore.com, Inc., USA and Ti-TiO2 was procured from M/s Titanium antalum Products Ltd. Chennai, India. Milli-Q water (M/s Millipore USA, model: Elix 3) was used to prepare the all reagents and solutions.

B. *Analytical techniques*
The concentration of H2O2 was determined using colorimetric method. The H2O2-Ti(IV) yellow colour complex was formed in presence of acidic reagent of Ti2(SO4). The absorbance was measured at 410 nm wavelength using a double beam UV-Vis spectrophotometer purchased of M/s Thermo-Fisher Scientific India (model: UV 2300). A high precision bi-potentiostat/galvanostat of M/s Metrohm (model: 302N) was employed to maintain the cathode potential (-Ecat) within ±0.4 μV vs. Ag/AgCl as reference electrode. A pH meter (model: ION 2700) purchased of M/s EUTECH instruments, Malaysia was used to adjust the solution pH. The dissolved oxygen (DO) was measured by a DO meter (Model: HI 2400) made of M/s Hanna Instruments.
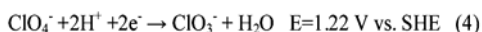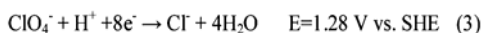
C. *Experimental procedure*
The experiments were performed in an undivided cell of 4 L capacity using 2 L electrolyte at pH 2.5 in batch mode with constant agitation on a magnetic stirrer (M/s Tarsons Products Pvt. Ltd, model: MC 02) at 300 rpm. Solution pH was adjusted either using H2SO4 or NaOH of 2 M. The –Ecat was fixed at 0.5 V vs. Ag/AgCl and electrode spacing was 2 cm. The SEs was taken as 0.08M. Prior to electrolysis, oxygen was sparged at 4 LPM flow rate for 15 min for presaturation of DO. O2 was sparged continuously during experiment to supply the necessary O2 for the electrochemical reaction. The test was carried 2 h and the samples withdrawn at every 20 min for the analysis of H2O2 concentration, pH and DO values.

III. Results and Discussion
The role of SEs on the amount of H2O2 formed was studied at –Ec=0.5 V vs. Ag/AgCl and the results with the time of electrolysis is illustrated in Figure 1. A steady initial rate of H2O2 formation was observed noted and then it fell down. Even though the rate was the highest with NaClO4 at the beginning however, it fell down with progressively with electrolysis time. Ti0 was oxidized to Ti3+ (next stable oxidation state) which was susceptible to react with strong chelating anion perchlorate (ClO4-) to form a yellow colored titanyl ion complex. The standard reduction potentials [7] for the halfreactions (3 and 4) clearly indicate that reductions to chloride or chlorate are very favorable from a thermodynamic standpoint:

$$ClO_4^- + H^+ + 8e^- \rightarrow Cl^- + 4H_2O \quad E=1.28 \text{ V vs. SHE} \quad (3)$$

$$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O \quad E=1.22 \text{ V vs. SHE} \quad (4)$$

Perchloric acid also could oxidize water to oxygen because the water-oxygen couple has an oxidation potential of –1.229 V (5) [7].

$$2H_2O + \Leftrightarrow 4H^+ + O_2 \quad (5)$$

Duke and Quinney published the first rigorous study on the reaction of titanium(III) and perchlorate (6) [8]. They found that the reaction proceeds through an initial complexation, after which Ti(III) is oxidized to a titanyl ion, TiO^{2+} (7).

$$8Ti^{3+} + ClO_4^- + 8H^+ \rightarrow 8Ti^{4+} + Cl^- + 4H_2O \quad (6)$$
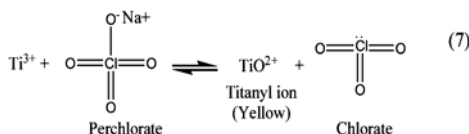
NaCl showed a reasonably steady formation of H2O2 with graphite/Ti-TiO2 system. Around 36.8, 27.6, 26.3, and 17.2 mg/L H2O2 was determined in 2 h with NaCl, Na2SO4, NaNO3 and Na2ClO4, respectively.

Current efficiency (CE) is expressed by the ratio of electrical current consumed by a desired electrode reaction to total current supplied through the cell. The performance of an electrode reaction is typically determined in terms of CE as in
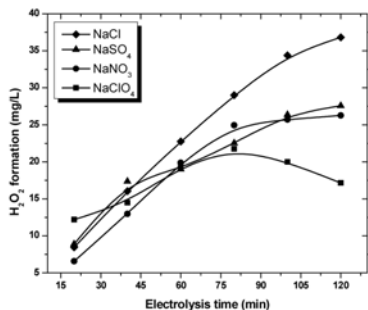
Figure 1. Formation of H2O2 with electrolysis time using equimolar electrolyte concentration of 0.08 M at –Ecat= 0.5 vs Ag/AgCl, pH 2.5, rpm 300 and solution volume 2 L.

$$CE = \frac{nFM}{\int_0^t Idt} \times 100, \% \tag{8}$$

where, n = stoichiometric number of electrons transfer for a reaction, F = Faraday's constant (96485 C/mol), M = mole of a desired reacting species formed/consumed, I= cell current (A) supplied for the time period of t (s). The results imply that CE decreased gradually with the time of electrolysis (Figure 2). The initial higher CE could be attributed to preadsorption DO at the cathode surface leading to higher cell current (Figure 3). The preadsorbed DO was almost exhausted within 5 min as in Figure 3. It indicates that the cell current limited by the diffusional resistance of DO in the film.

The rate of H2O2 formation is governed by DO transport from the bulk to the cathode surface. The highest rate of a desired reaction at CDO,surface= 0, is called limiting current (iL) can be expressed as in (9).

$$i_L = k_m nFAC_{DO,bulk} \tag{9}$$

where, km is mass transfer coefficient (m/s),A is effective cathode electrode area (m2) and CDO,bulk is bulk DO concentration (mol/ m).

The volume of the cathode zone, where cathode reaction occurs, depends on the thickness, δ (m) of the diffusion layer. δ is related to km and diffusivity, D (m2/s) following macroscopic approach as shown below (10).

$$\delta = \frac{D}{k_m} \tag{10}$$

DO concentration at the cathode surface became negligible at ≥5 min and a steady current was observer thereafter. The variation of mass transfer coefficient and the volume of 3 cathode reaction zone are shown in Figure 4. The diffusivity of O2 in aqueous solution was taken as D=2×10-9 m2 s-1 [9]. The order of thickness

of diffusion layer with NaCl, Na2SO4, NaNO3 and Na2ClO4 were in line with H2O2 formation using graphite/ti-TiO2 electrode system.
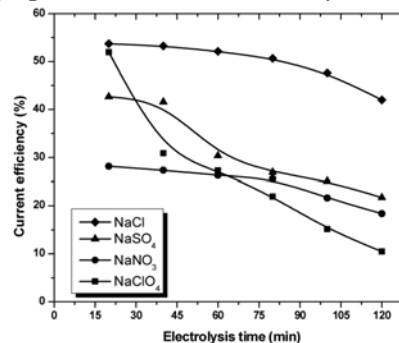

Figure 2. Current efficiency of H2O2 formation with electrolysis time using equimolar electrolyte concentration of 0.08 M at –Ecat= 0.5 vs Ag/AgCl, pH 2.5, rpm 300 and solution volume 2 L.
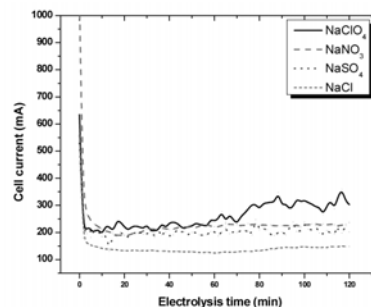

Figure 3. Variation of cell current with electrolysis time using equimolar electrolyte concentration of 0.08 M at –Ecat= 0.5 vs Ag/AgCl, pH 2.5, rpm 300 and solution volume 2 L.

IV. Conclusions

The selection of suitable SEs is a crucial parameter for maximizing electrogeneration of H2O2 with graphite/Ti-TiO2 electrode system. The order of amount of H2O2 formation was found to be as NaCl>Na2SO4>NaNO3>Na2ClO4. The results were in accordance with thickness of the diffusional film at the cathode surface. The highest cell current efficiency of 42% was observed with 0.08M NaCl at min of electrolysis at Ecat=0.5 vs Ag/AgCl, pH 2.5.
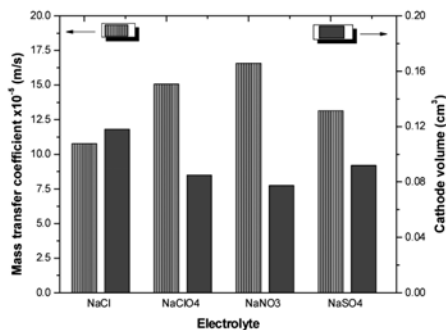
Figure 4. Influence of different electrolyte on cathode reaction volume with electrolysis time using equimolar electrolyte concentration of 0.08 M at –Ecat 0.5 vs Ag/AgCl, pH 2.5, rpm 300 and volume 2 L.

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