Int. J. Electrochem. Sci., 3 **(2008)** 1348 - 1363

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Oxidative Stress and Parkinson's Disease: Electrochemical Behavior of Hydrogen Peroxide in Aqueous Sodium Chloride

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Received: 18 September 2008 / *Accepted:* 12 October 2008 / *Published:* 17 November 2008

Excessive reactive oxygen species, such as hydrogen peroxide (H_2O_2), seems to have a deleterious effect in patients with Parkinson's disease. The electrochemical behavior of this molecule in the presence of the most common biological electrolyte, sodium chloride, over a concentration range of 0.02 – 1.0 M, was investigated by cyclic voltammetry. The 'normal' and the 'activated' or 'autocatalytic' H_2O_2 reduction were observed. The 'normal' H_2O_2 reduction current at high cathodic potentials was nearly the same for scans 2 and 3. A slightly higher current for scan 1 was observed compared to the subsequent scans. On the other hand, the 'autocatalytic' H_2O_2 reduction current increased with increasing number of scans and increasing sweep to higher cathodic potentials. A slight cathodic shift in the peak was also observed with increasing number of scans. Also a strong cathodic current was observed on reversing the scan from -1.0 V to less cathodic potentials. With increasing concentration of H_2O_2, there was a slight cathodic shift in the cyclic voltammetric peak observed for the 'autocatalytic' H_2O_2 reduction. A new cathodic shoulder peak before the 'autocatalytic' H_2O_2 reduction was observed for the first time. The autocatalytic process was not observed for peroxide in 0.1 M HCl. Current oscillations were observed in 0.04 M NaOH. Addition of traces of chloride enhanced the autocatalytic cathodic current in basic medium. Both the 'normal' and 'autocatalytic' H_2O_2 reductions were observed in 0.1 M Na_2SO_4 and 0.1 M $NaClO_4$. The catalytic activity was highest in the presence of sulfate and least with perchlorate. We conclude that the 'autocatalytic' H_2O_2 reduction process is sensitive to the range of the sweep potential, concentration of H_2O_2, NaCl concentration, and pH. The multiple equilibria involved in the H_2O_2 redox process were evident in the observed cyclic voltammograms.

Keywords: Parkinson's disease, hydrogen peroxide, spatiotemporal oscillations, activated or autocatalytic reduction, cyclic voltammetry

1. INTRODUCTION

The appearance of oxygen in the atmosphere is associated with a great expansion of the varieties and the number of complex living forms. Oxygen is the source for the emergence of respiratory metabolism and energy efficiency. It is also a source of free radicals, such as hydroxyl and superoxide, and reactive species, such as hydrogen peroxide and singlet oxygen. It is known that hydrogen peroxide, a product of metabolism, is a source of oxidative stress and can adversely affect the local conformations of DNA, RNA and proteins in cells. However the beneficial aspects of hydrogen peroxide in regulating signal transduction in a number of cellular processes are only beginning to emerge. For example, neurons as well as brain macrophages produce superoxide in pathological situations and the hydrogen peroxide produced from superoxide is known to increase gap junctional communication in astrocytes [1]. The dismutation of superoxide produces hydrogen peroxide as well as singlet oxygen. Other examples involved in signaling processes include the overoxidation of the peroxidatic cysteine in peroxiredoxins from the cysteine sulfenic acid to cysteine sulfinic acid as well as the overoxidation of methionine residues in proteins to methionine sulfoxide [2, 3].

Hydrogen peroxide exhibits a variety of oscillations and synchronized spatiotemporal reaction waves under potentiostatic conditions [4-8]. We have reported a variety of biological systems that exhibit oscillations and unique impedance behavior [9]. The mitochondrial oscillation reactions support the emerging electron transport chain [10]. While the energy advantage of oxygen metabolism forms a stimulus to such growth, we are also interested in the contribution of the periodic oscillation which peroxide brings to physico-chemical systems. Spatiotemporal oscillations in a system allow the intricate electronics of alternating current circuits and long range signals.

Past electrochemical impedance measurements of hydrogen peroxide have concentrated on the oscillatory behavior at fairly high concentrations and at high acidities [4-8, 11]. Cyclic voltammograms obtained using polycrystalline silver in 0.02 M H_2O_2 and 0.1 M $HClO_4$ have been explained using ‘normal’ and ‘activated’ or ‘autocatalytic’ H_2O_2 reduction mechanisms [7]. Current oscillations have also been observed during H_2O_2 reduction in alkaline solutions using gold (100) electrode as well as p-type copper-containing semiconductors [12-16].

We want to briefly mention the electrolytes and the electrodes used in some of the previous investigations of peroxide. These include $HClO_4$ and H_2SO_4 (0.5-1.0 M) [6, 11, 17], 2 x 10^{-3} -1.0 M KOH [16], 0.1 M NaOH [14], 1 M Na_2SO_4 in borate buffer of 0.1 M H_3BO_3 (pH adjusted with NaOH or KOH) [13, 18], Merck Titrisol buffer of pH 9 containing 0.5 M KCl [12], and 0.3 M H_2SO_4 [19]. It has also been stated that support electrolytes, such as 1 M Na_2SO_4, 1 M KCl, and 2 M $NaNO_3$, do not play an essential role in the H_2O_2 reduction process in basic solutions [18]. On the other hand, additions of small amounts of halide ions to 0.3 M H_2SO_4 has produced a new type of oscillation for peroxide on a platinum electrode [20]. The electrodes used for many of these investigations include Pt, Ag, Au(100) and semiconductor electrodes p-$CuInSe_2$ and n-GaAs.

Our recent electrochemical experience with simple electrolytes and simple biological molecules has shown that the structure of the electrical double layer is very sensitive to the orientation effects of water around ions [21-24]. Also our investigation of peroxomolybdate indicated spatiotemporal oscillations [25]. The purpose of the present investigation is to bring focus on the electronic properties of this unique molecule, H_2O_2. We have focused our studies on the oscillatory behavior at low concentrations of H_2O_2 in the presence of the most common biological electrolyte, sodium chloride, and around neutral pH. It is increasingly evident that cell signaling takes place when there is a rapid increase in the concentration of H_2O_2. In order to probe this, we have investigated the effects of concentration of H_2O_2 on its electronic properties. In this study we have focused our attention on the cyclic voltammogram of H_2O_2 in the presence of electrolytes. In a subsequent paper, we plan to report the results of frequency response analysis and its impact on the deep brain stimulation treatment of Parkinson's disease.

2. EXPERIMENTAL PART

The EG &G PARC Model 303A SMDE trielectrode system (mercury working electrode, platinum counter electrode and Ag/AgCl saturated KCl reference electrode) along with the Autolab ecochemie was used for cyclic voltammetric and electrochemical impedance measurements.

Analytical grade salts, HCl, NaOH, J.T. Baker 31.3% H_2O_2, and distilled water were used for all the experiments. H_2O_2 was standardized by titration in the presence of 1 M H_2SO_4 with standard potassium permanganate. Solutions were purged with N_2 before experiment.

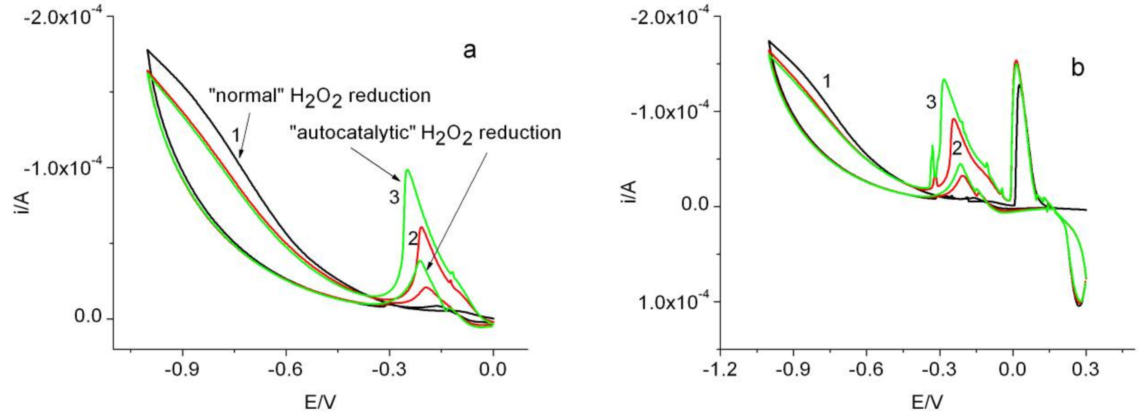
3. RESULTS AND DISCUSSION

Cyclic Voltammetry

The results of all the cyclic voltammetric data will be discussed in section 4.

3.1. Influence of scanning potential

The general characteristics of the cyclic voltammograms of 88 mM H_2O_2 in 0.10 M NaCl for the first 3 sweeps in the potential range 0 to -1.0 V, 0.3 to -1.0 V and 1.0 to -1.0 V are shown in Figures 1 a, 1b, and 1c. We are fully aware of the fact that mercury passivation may begin to interfere at potentials beyond 0.0 V. In all the three cases, sweeps 2 and 3 gave nearly the same current for the 'normal' H_2O_2 reduction at most cathodic potentials, with slightly higher currents for the first sweep. For the sweeps in the range of 0.3 to -1.0 V, the chloride peak appeared and it became more fully developed reduction and oxidation peaks in the 1.0 to -1.0 V scan. We also noticed a cathodic spike during the second and third sweeps. In all the three cases, the initial 'activated' or 'autocatalytic' reduction peak of H_2O_2 was evident for sweeps 2 and 3. It is remarkable that in all the three cases, a strong cathodic current was observed on the reverse scan from -1.0 V to less cathodic potentials, an unusual feature rarely observed for other systems. This current became stronger and stronger with increasing number of sweeps.



Figures 1a, 1b Cyclic voltammetry of 0.10 M NaCl, 88 mM H_2O_2, pH ~ 6.0, 0.1 V/s, 1) scan 1 2) scan 2 3) scan 3; a) sweep 0 to -1.0 V and back; b) sweep 0.3 to -1.0 V and back

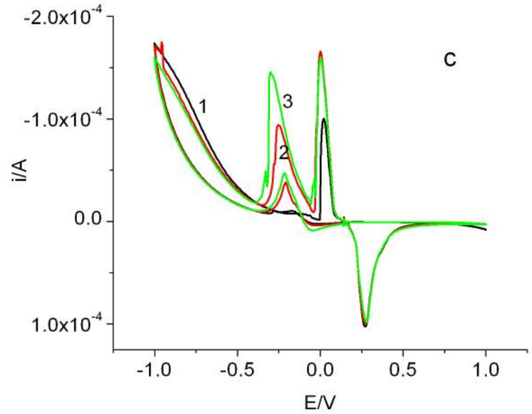
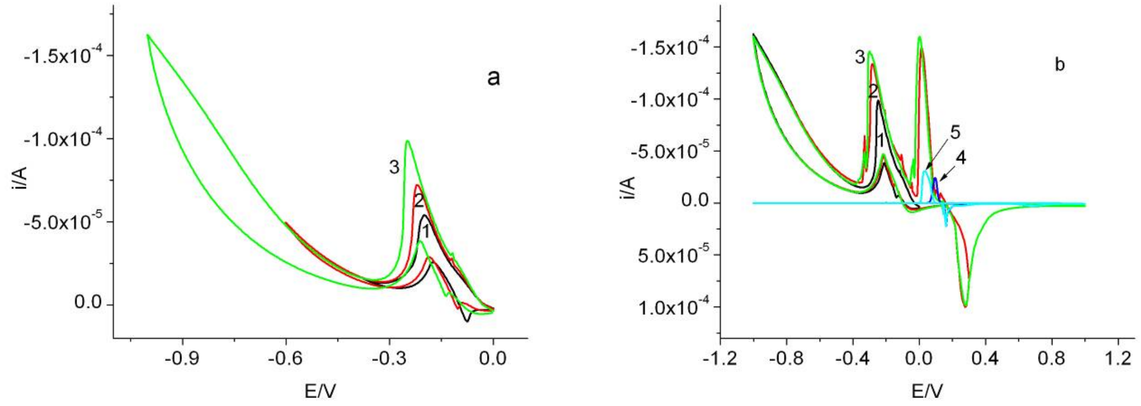


Figure 1c Cyclic voltammetry of 0.10 M NaCl, 88 mM H_2O_2, pH ~ 6.0, 0.1V/s, 1) scan 1 2) scan 2 3) scan 3; sweep 1.0 to -1.0 V and back



Figures 2a, 2b Cyclic voltammetry of 0.10 M NaCl, 88 mM H_2O_2, pH ~ 6.0, 0.1V/s, scan 3; a) sweep 1) 0 to -0.4 V and back 2) 0 to -0.6 V and back 3) 0 to -1.0 V and back; b) sweep 1) 0 to -1.0 V and back 2) 0.3 to -1.0 V and back 3) 1.0 to -1.0 V and back; NaCl 0.10 M, no H_2O_2, sweep 4) 0.3 to -1.0 V and back 5) 1.0 to -1.0 V and back

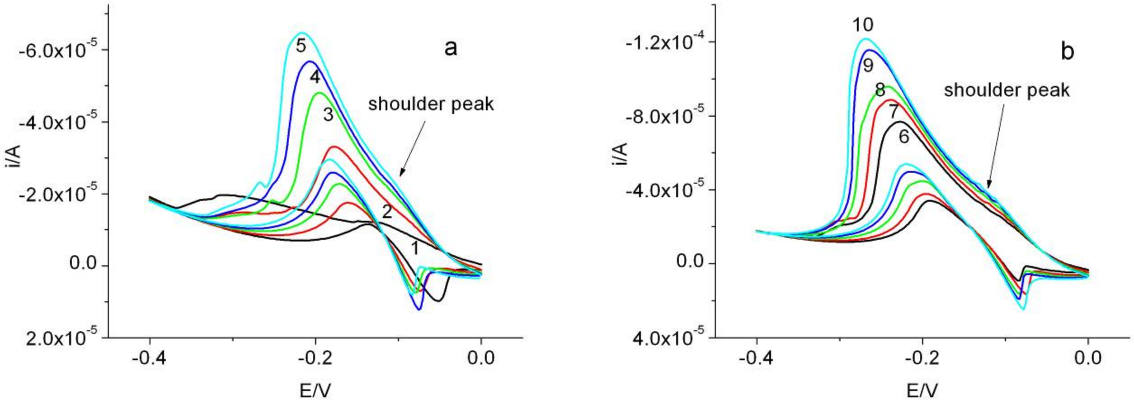
The influence of the cathodic potential or the influence of the 'normal' H_2O_2 reduction on the 'activated' H_2O_2 reduction is shown in Figure 2a for the third sweep. As the sweep voltage was changed from 0 to -0.4 V, then from 0 to -0.6 V, and then from 0 to -1.0 V, the 'activated' H_2O_2 reduction current also increased in the same order with a corresponding slight shift in the cathodic peak potential. Figure 2b shows the influence of the anodic potential on the 'activated' H_2O_2 reduction. Here again as the starting potential of the sweep changed from 0 V to 0.3 V and to 1.0 V, there was an increase in the 'activated' H_2O_2 reduction current with a slight shift in the cathodic peak potential. This shift in peak potential was less than that observed for increasing the final cathodic potential.

In Figure 2b the data for 0.10 M NaCl in the absence of H_2O_2 is also shown. As observed before, there was a slight cathodic peak shift but no anodic peak shift when the starting sweep potential was changed from 0.3 to 1.0 V (curve 4 and 5) [22]. More importantly, in the presence of H_2O_2, the chloride cathodic and anodic peak currents were much higher. Also there was a slight shift of the cathodic peak to more cathodic potential and a more obvious shift of the anodic peak to more anodic potential.

Cyclic voltammograms, in Figures 1-2 also indicate a slight cathodic shoulder before the 'activated' H_2O_2 reduction peak and a corresponding anodic peak. This finding has not been reported before.

3.2. Influence of number of scans or sweeps on the 'activated' or 'autocatalytic' H_2O_2 reduction

The influence of number of sweeps on the 'activated' H_2O_2 reduction is shown in Figures 3a and 3b for 10 scans. For the sake of clarity, scans 1-5 and 6-10 are shown separately. As observed earlier, the first scan was different than others. More importantly, with increasing number of sweeps, the reduction current became higher and higher with a corresponding slight peak shift to more cathodic potentials. Also the strong cathodic current observed on the reverse scans from -1.0 V to less cathodic potentials became stronger with each scan with a corresponding slight cathodic shift of the peak potential.



Figures 3a, 3b Cyclic voltammograms of 0.10 M NaCl, 88 mM H_2O_2, pH ~ 6.0, 0.1V/s, scans a) 1-5 b) 6-10

3.3. Influence of scan or sweep rate on ‘activated’ or ‘autocatalytic’ H_2O_2 reduction

The influence of different sweep rates on the ‘activated’ H_2O_2 reduction is shown in Figure 4. The shoulder peak before the ‘activated’ H_2O_2 reduction peak became more and more obvious with slower sweep rates. Also the ‘activated’ H_2O_2 reduction peak shifted more and more cathodic with slower and slower sweeps with a corresponding increase in the reduction currents. The strong cathodic current observed on the reverse scans from -0.4 V to less cathodic potentials became stronger with slower sweeps with a corresponding cathodic shift of the peak potential.

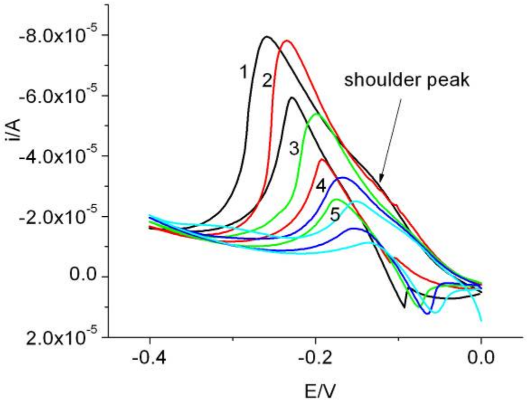
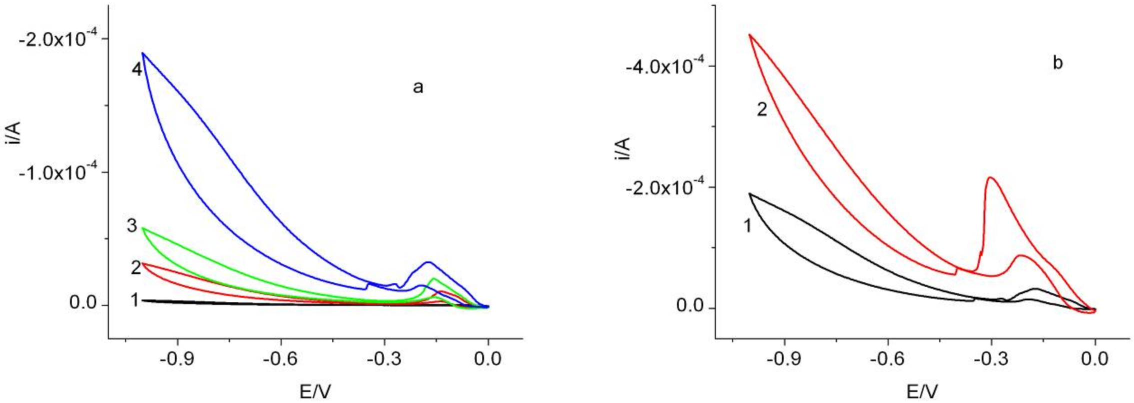


Figure 4. Cyclic voltammograms of 0.10 M NaCl, 88mM H_2O_2, pH ~ 6.0, scan 3, sweep rates, (1) 0.01 (2) 0.05 (3) 0.1 (4) 0.2 (5) 0.3 V/s



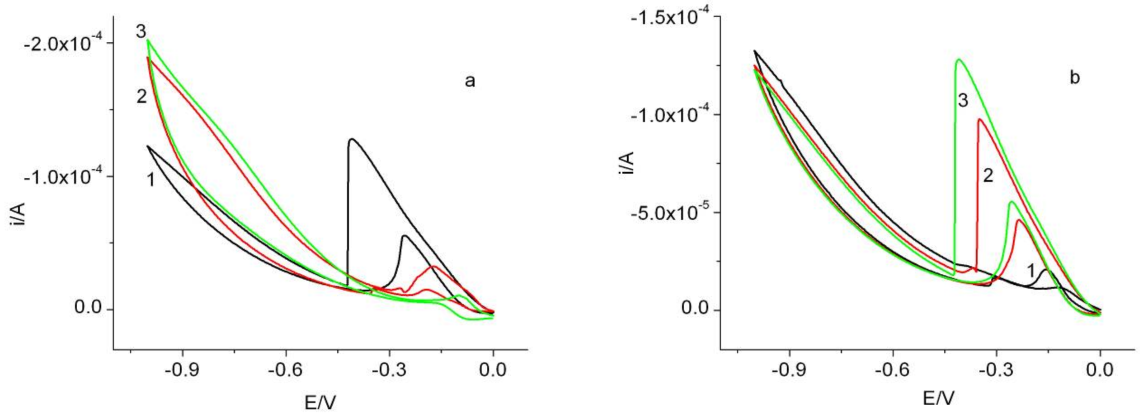
Figures 5a, 5b Cyclic voltammetry of a) 0.1 M NaCl with 1) 0.88 mM 2) 8.8 mM 3) 17.6 mM 4) 88 mM H_2O_2; b) 1) 88 mM 2) 352 mM H_2O_2; all with pH ~ 6.0, scan 3, sweep 0 to –1 V and back, 0.1 V/s

3.4. Effect of H_2O_2 concentration on the ‘activated’ or ‘autocatalytic’ H_2O_2 reduction

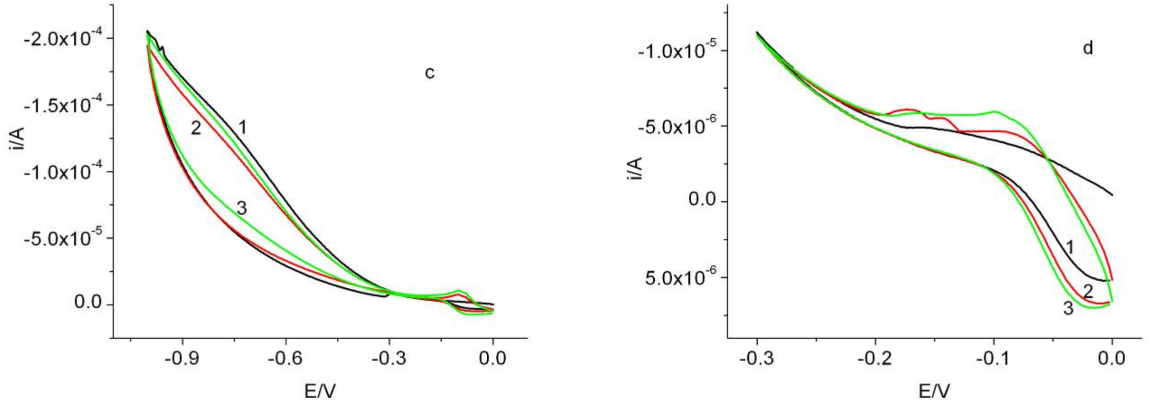
The cyclic voltammograms of 0.10 M NaCl in the presence of different concentrations of H_2O_2 are given in Figure 5a. For the sake of clarity, the highest concentrations are shown in Figure 5b. At the lowest concentration of H_2O_2, there was a region of ‘autocatalytic’ H_2O_2 reduction, even though it was not clear from the compressed figure. Both the 'normal' as well as the 'autocatalytic' H_2O_2 reduction currents were higher with increasing concentration of H_2O_2 . The cathodic 'autocatalytic' H_2O_2 reduction peak also shifted more cathodic with increasing concentration of H_2O_2.

3.5. Effect of NaCl concentration on 'activated' or 'autocatalytic' H_2O_2 reduction

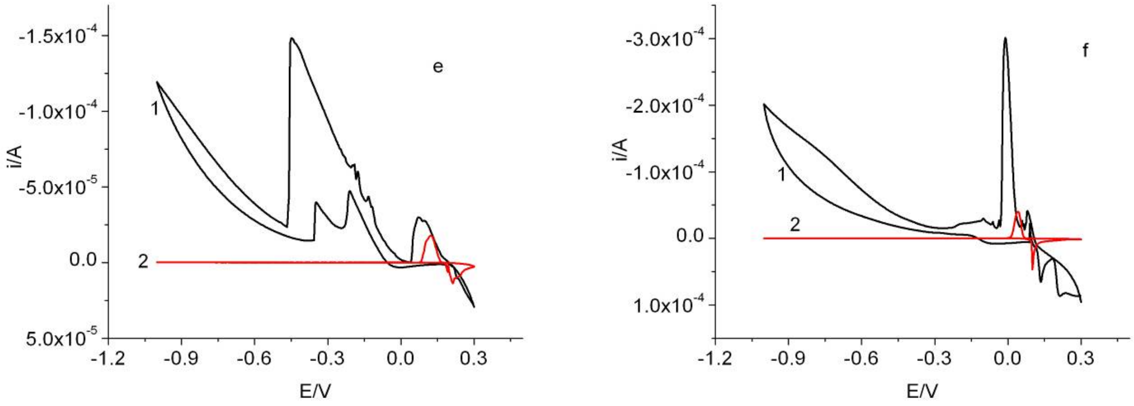
It was not obvious from the literature as to the particular choice of supporting electrolyte or its concentration. Contradictory roles for chloride, one inducing new electrochemical oscillations [20] while the other poisoning the electrode and inhibiting the oscillations [7] have been reported. In order to gain some information on the influence of the ratio of H_2O_2 to NaCl, the concentration of NaCl was varied while keeping constant concentration of H_2O_2. The results are shown in Figures 6a-6f.



Figures 6a, 6b Cyclic voltammetry of 88 mM H_2O_2 with a, 1) 0.02 M NaCl 2) 0.1 M NaCl 3) 1.0 M NaCl; with b) 0.02 M NaCl 1) scan 1 2) scan 2 3) scan 3; 0.1 V/s, all with pH ~ 6.0



Figures 6c, 6d Cyclic voltammetry of 1.0 M NaCl, 88 mM H_2O_2, pH ~ 6.0, 0.1V/s, 1) scan 1 2) scan 2 3) scan 3; c, scan 0 to -1.0V and back; d, scan 0 to -0.3V and back



Figures 6e, 6f Cyclic voltammetry of 0.02 M NaCl, , pH ~ 6.0, 0.1 V/s, scan 3, e) 1) with 88 mM H_2O_2 2) no H_2O_2 f) cyclic voltammetry of 1.0 M NaCl, , pH ~ 6.0, 0.1 V/s, scan 3, 1) with 88 mM H_2O_2 2) no H_2O_2

Figure 6a indicates that the ‘normal’ H_2O_2 reduction increases with increasing concentration of NaCl whereas the ‘activated’ H_2O_2 reduction is significantly favored at lower concentrations of NaCl. Also the lower the concentration of NaCl, the higher is the cathodic shift of the ‘activated’ H_2O_2 reduction peak. Figure 6b more clearly demonstrates the “activated’ H_2O_2 reduction process including the cathodic peak when the potential is swept from the most cathodic to the least cathodic. Figures 6c and 6d demonstrate that the ‘autocatalytic’ reduction of H_2O_2 is favored less with the highest concentration of 1.0 M NaCl. Figures 6e and 6f indicate that H_2O_2 catalyzes both the cathodic and anodic currents due to the mercury-chloride interaction. Also the cathodic peak was shifted more cathodic and the anodic peak was shifted more anodic in the presence of H_2O_2, similar to the behavior in the presence of 0.10 M NaCl in the presence of H_2O_2.

For the third sweep from 0.0 to -1.0 V and back, the initial cathodic peak due to the ‘autocatalytic’ H_2O_2 reduction was at -0.08, -0.13, -0.16 and -0.17 V with increasing H_2O_2 concentration from 0.88, 8.8, 17.6, to 88 mM (Figure 5). For the third sweep from 0.0 to -1.0 V and back, the initial cathodic peak due to the ‘autocatalytic’ H_2O_2 reduction on increasing NaCl concentration from 0.02 M to 0.1 M and then to 1.0 M at constant 88 mM H_2O_2 concentration shifted from -0.41 to -0.17 and to -0.10V (Figure 6).

3.6. Influence of pH on ‘activated’ or ‘autocatalytic’ H_2O_2 reduction

Most of the investigations on reduction have been carried out in either highly acidic or highly basic medium. Our focus is from a biological point of view and therefore we have chosen a pH close to biological pH so that no other electrolyte is needed except the one under investigation. We have varied the pH mildly by using HCl or NaOH. The cyclic voltammograms obtained at different pH values are given in Figure 7a-7d. The potential is swept only from 0.0 to -1.0 V and back. For comparison of results at different pH values, the results for the third sweep are shown in Figure 7e.

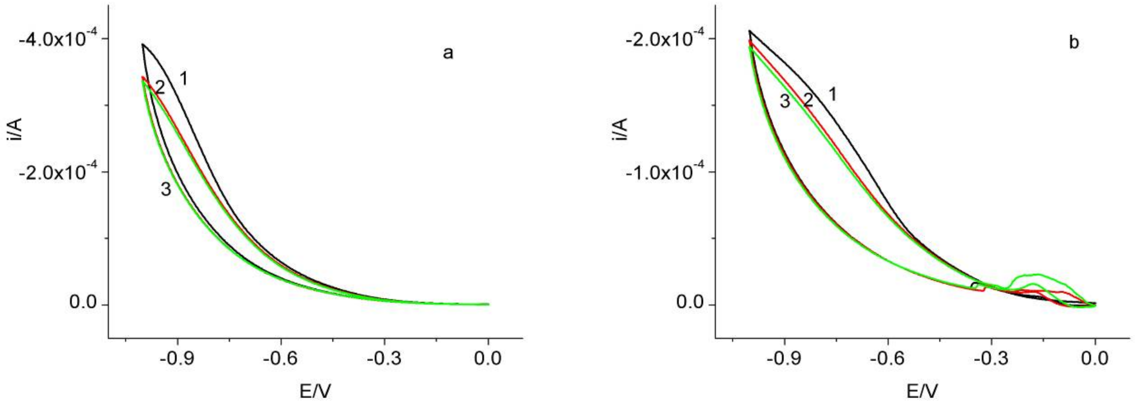


Figure 7a, 7b Cyclic voltammetry of 88 mM H_2O_2 in a) 0.10 M HCl, pH 1.35, 0.1 V/s, 1) scan1 2) scan 2 3) scan 3, sweep 0.0 to -1.0 V and back; b) 0.10 M NaCl, 1 mM HCl, pH 3.05, 0.1 V/s, 1) scan1 2) scan 2 3) scan 3, sweep 0.0 to -1.0 V and back

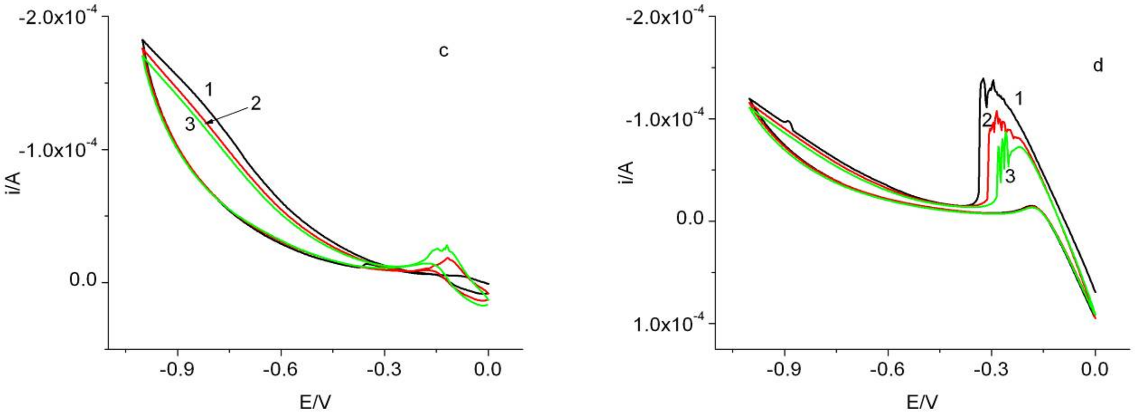
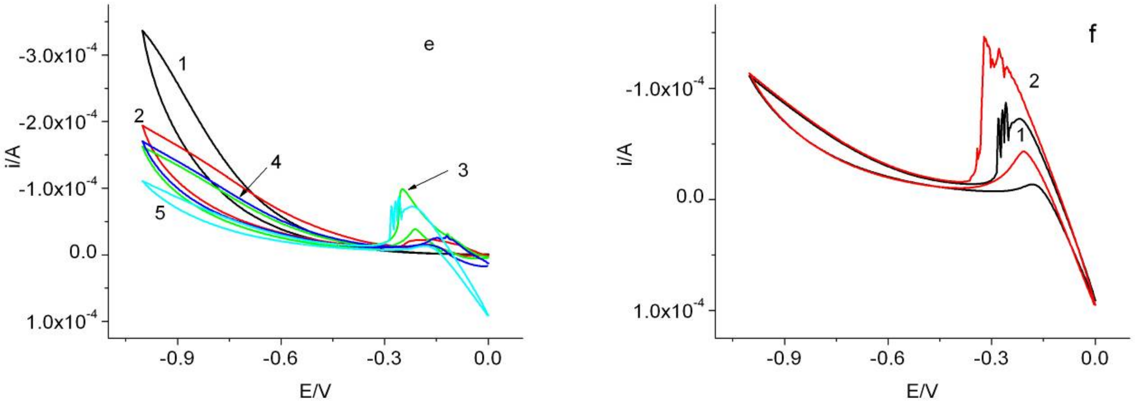


Figure 7c, 7d Cyclic voltammetry of 88 mM H_2O_2 in c) 0.10 M NaCl, 1 mM NaOH, pH 9.28, 0.1 V/s, 1) scan1 2) scan 2 3) scan 3, sweep 0.0 to -1.0 V and back; d) 0.04 M NaOH, pH 11.13, 0.1 V/s, 1) scan1 2) scan 2 3) scan 3, sweep 0.0 to -1.0 V and back



Figures 7e, 7f Cyclic voltammetry of 88 mM H_2O_2 at pH e) 1) 1.35 2) 3.05 3) 6.01 4) 9.28 5) 11.13; scan 3, 0.1V/s, concentrations are the same as in Figure 7 a-d; f) scan 3, 0.1 V/s 1) 0.04 M NaOH, pH11.13 2) with added 1 mM NaCl

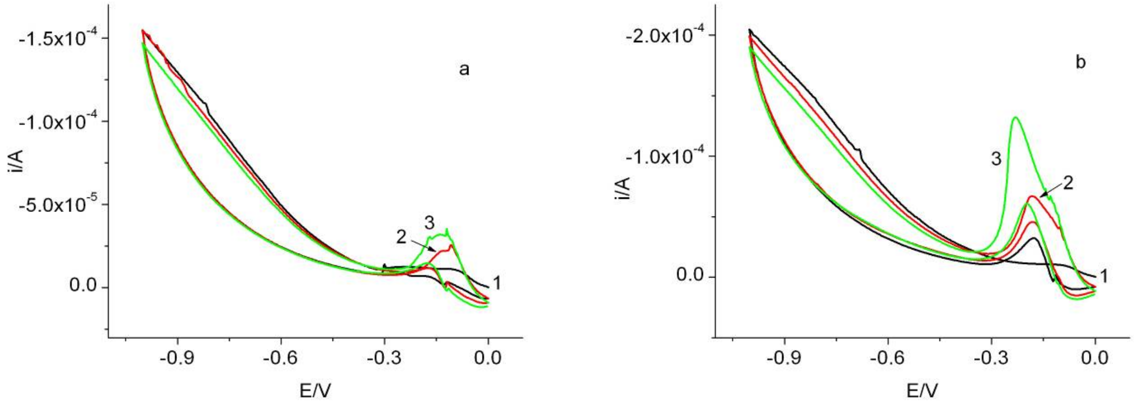
It was clear from Figure 7a, that there was no indication of any ‘activated’ or ‘autocatalytic’ H_2O_2 reduction at this pH of 1.35 but only the ‘normal’ H_2O_2 reduction. The data at pH 3.05 and 9.28 shown in Figure 7b and 7c indicated that the characteristics of the curves were similar to that observed at pH 6.0. Figure 7e also indicated that the ‘normal’ H_2O_2 reduction process became less efficient with increasing pH.

There were significant differences in the behavior of H_2O_2 reduction at pH 11.13. The ‘normal’ H_2O_2 reduction current was the least in this case. The other major difference was that with increasing the scan or sweep from 1 to 2 and then to 3, the ‘autocatalytic’ H_2O_2 reduction peak current became less and less compared to the opposite effect observed at other pH values. Also the cathodic current observed on sweep from most cathodic to less cathodic potentials was almost the same for all the three sweeps compared to the behavior at other pH values where this cathodic current also increased with increasing number of sweeps. There was also no shift to slightly more cathodic potentials for this sweep. Another significant difference was that current oscillations were observed for every sweep at the cathodic ‘autocatalytic’ H_2O_2 reduction peak. These oscillations were similar to the ones observed for H_2O_2 reduction on Au(100) in 0.1 M NaOH containing 1 mM H_2O_2.

We have investigated the influence of traces of chloride at the high pH of 11.13 (with 0.04 M NaOH and 88 mM H_2O_2) by adding 1 mM NaCl and the results are compared in Figure 7f. The catalytic effect of chloride was evident from the increase in the ‘autocatalytic’ H_2O_2 reduction peak current. There was also a stronger cathodic current on reversing the sweep to the positive direction from – 1.0 V.

3.7. H_2O_2 reduction in the presence of Na_2SO_4 and $NaClO_4$

In order to assess whether our current data are unique with respect to NaCl, we have investigated the cyclic voltammetric behavior of 88 mM H_2O_2 in 0.10 M $NaClO_4$ as well as 0.1 M Na_2SO_4. The results are shown in Figures 8a and 8b.



Figures 8a, 8b Cyclic voltammetry of 88 mM H_2O_2, pH 6.14, 0.1 V/s, 1) scan 1 2) scan 2 3) scan 3, sweep 0 to -1.0 V and back; in a) 0.10 M $NaClO_4$ b) 0.10 M Na_2SO_4

The comparison data for the third sweep from 0.0 to -1.0 V and back for 88 mM H_2O_2 in 0.1 M NaCl, 0.10 M $NaClO_4$ and 0.10 M Na_2SO_4 are shown in Figure 8c. This has indicated that the catalytic activity for both the 'normal' and 'activated' or 'autocatalytic' H_2O_2 reduction was the highest for sulfate and least for perchlorate. However, the cathodic shift in the 'autocatalytic' H_2O_2 reduction peak was the most for chloride and least for perchlorate. This was also true for the cathodic current on reversing the sweep from -1.0 V to the positive direction.

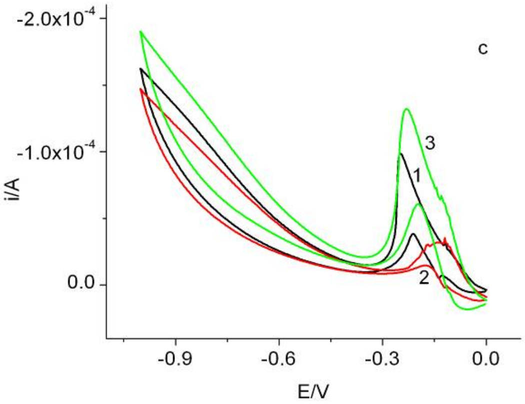


Figure 8c Cyclic voltammetry of 88 mM H2O2, scan 3, 0.1 V/s, sweep 0.0 to -1.0 V and back in 1) 0.10 M NaCl 2) 0.1 M $NaClO_4$ 3) 0.10 M Na_2SO_4

4. COMPLEXITY OF H_2O_2 REDOX PROCESSES

The nature of the cyclic voltammograms reported here in Figure 1, in the scan or sweep range of 0 to –1V is very similar to that observed for H_2O_2 (0.02 M) reduction in 0.1 M $HClO_4$ on thoroughly cleaned polycrystalline silver electrodes [7]. It is generally accepted that the current in the extreme cathodic region is due to the 'normal' H_2O_2 reduction [7, 26-27]. The peak at less cathodic potentials is attributed to the 'activated' or 'autocatalytic' mechanism of H_2O_2 reduction [7].

It has been suggested that the following reaction takes place at the metal/solution interface [28]:

$$H_2O_2 + e^-_{metal} = {}^{\cdot}OH + OH^- \quad (1)$$

$${}^{\cdot}OH + H_2O_2 = H_2O + HO_2^{\cdot} \quad (2)$$

$$O_2^{\cdot-} + H^+ = HO_2^{\cdot} \quad (3)$$

$$O_2^{\cdot-} + H_2O_2 = {}^{\cdot}OH + OH^- + O_2 \quad (4)$$

In reaction (1), H_2O_2 is an oxidizing agent. In alkaline solutions, it acts as a reducing agent.

$$HO_2^- + H^+ = H_2O_2 \quad (5)$$

$$HO_2^- = HO_2^{\cdot} + e^-_{metal} \quad (6)$$

Based on Franck-Condon principle, the possibility of a significant amount of the following reaction has been ruled out [29].

$$H_2O_2 + 2e^-_{metal} = 2OH^- \qquad (7)$$

The chain reactions 2 and 4 may be partially offset by the following chain breaking reactions by a negative potential [28].

$$^{\cdot}OH + e^-_{metal} = OH^- \qquad (8)$$

$$HO_2^{\cdot} + e\text{-}_{metal} = HO_2^- \qquad (9)$$

$$^{\cdot}OH + HO_2^{\cdot} = O_2 + H_2O \qquad (10)$$

In the 'autocatalytic' mechanism, the involvement of an activating adsorbate, generated autocatalytically, is suggested. The numerous types of electrochemical oscillations observed for H_2O_2 [4-8, 11-16] is attributed to the complex dynamics of formation and reduction of this activating adsorbate [7].

As observed earlier with silver electrode [7], we have also observed that the first sweep (the so called inactive state) is different from the following sweeps. A strong cathodic current flow at less cathodic potentials is observed during scan in the positive direction. Our data, shown in Figure 3 with 10 scans showed that this cathodic current became increasingly stronger with subsequent scans. This has been attributed to the 'activated' or autocatalytic reduction. It has been demonstrated that O_2 dissolved in the electrolyte does not affect this autocatalytic reduction region [7] and thus the contribution from the disproportionation reaction,

$$2H_2O_2 = 2H_2O + O_2 \qquad (11)$$

was excluded.

The 'activated' reduction current was not observed for gold electrode or silver in the presence of chloride or sulfate [7]. It has also been reported that support electrolytes such as 1 M Na_2SO_4, 1 M KCl, and 2 M $NaNO_3$, do not play an essential role in the H_2O_2 reduction process in basic solutions [18]. This is in contrast with our present observations. Our experiments at pH 11.13 (Figure 7f) have indicated that the addition of 1 mM NaCl enhanced the 'activated' or autocatalytic H_2O_2 reduction current. This was in agreement with the observation that additions of small amounts of halide ions to 0.3 M H_2SO_4 could produce a new type of oscillations for peroxide on a platinum electrode [20].

The formation of adsorbate OH_{ad} or chemisorbed OH [14, 27, 29] is postulated.

$$H_2O_2 + H^+ + e^- \rightarrow OH_{ad} + H_2O \qquad (12)$$

The formation of OH_{ad} accelerates the following reaction rate and further increases the coverage.

$$H_2O_2 + H^+ + e^- + OH_{ad} \rightarrow 2\,OH_{ad} + H_2O \qquad (13)$$

This results in the final reduction reaction.

$$OH_{ad} + H^+ + e^- \rightarrow H_2O \qquad (14)$$

Our data has supported these suggestions and demonstrated that the coverage increases with increasing concentration of H_2O_2, and with increase in the number of sweeps or scans.

Anodic processes assumed in electrolysis [29] may also have some relevance during the anodic sweep.

$$2^{\cdot}OH = H_2O + O \qquad (15)$$
$$H_2O_2 + O = O_2 + H_2O \qquad (16)$$

Hydrogen peroxide is a weak acid [30].

$$H_2O_2 = H^+ + HO_2^- \qquad K_{20}^o = 1.5 \times 10^{-12} \qquad (17)$$

Its redox reactions indicate that it is an oxidizing agent in both acidic and basic solutions [30].

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad E^o = 1.77V \qquad (18)$$
$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad E^o = 0.68V \qquad (19)$$
$$HO_2^- + H_2O + 2e^- = 3OH^- \qquad E^o = 0.87V \qquad (20)$$

The auto oxidation reduction or disproportionation reaction (equation 11) is quite slow in acidic solutions and fast in basic solutions.

We know that in biological systems the following reactions take place in the presence of the enzyme, myeloperoxidase

$$H_2O_2 + Cl^- \rightarrow H_2O + OCl^- \qquad (21)$$
$$OCl^- + H_2O_2 \rightarrow H_2O + Cl^- + {}^1O_2 \qquad (22)$$

Phagocytosis stimulates glycolysis-linked respiration, generating hydrogen peroxide in neutrophils. The generation of HOCl (and singlet oxygen, ${}^1O_2$) from myeloperoxidase-H_2O_2-Cl^- system is optimal at 0.1M Cl^- at pH 4-6 in the presence of the enzymatic H_2O_2 generating system. It is not clear whether OCl^- and singlet oxygen are produced electrochemically under our present experimental conditions.

The superoxide radical involved in reactions 3 and 4 can undergo spontaneous dismutation to produce singlet oxygen.

$$O_2^{\cdot -} + O_2^{\cdot -} + 2H^+ \rightarrow H_2O_2 + {}^1O_2 \qquad (23)$$

The superoxide is a powerful oxidizing agent and it reacts vigorously with water [30]

$$2O_2^- + H_2O = O_2 + HO_2^- + OH^- \quad (24)$$
$$2HO_2^- = 2OH^- + O_2 \text{ (slow)} \quad (25)$$

We have used platinum counter electrode for all of our experiments. Platinum is well known as a catalyst for decomposition of peroxide. We did notice some bubble formation on the counter electrode, especially in the presence of peroxide in basic solutions and at higher concentrations of peroxide. However, this slight bubble formation does not seem to affect the consistency of our data. Also during experiments with solutions around pH 6.0, we noticed an increase in pH when checked after the experiment. This is consistent with reaction 4. In order to maintain nearly the same concentration of H_2O_2 throughout the experiment, we often replenished with fresh solution. It must be pointed out that platinum has been used as a working electrode for galvanostatic reduction of H_2O_2 in 0.1 M H_2SO_4 [17] and chronopotentiometric investigation of H_2O_2 and 0.5 M $HClO_4$ and 0.5 M H_2SO_4 [11]. Also solutions containing 0.02 M H_2O_2 in 0.1M HClO4 saturated with O_2 and with no O_2 gave identical results in the region of the 'activated' or autocatalytic reduction of H_2O_2 [7].

Occasionally we have noticed a bubble at or near the mercury drop. This will reduce the concentration of H_2O_2 at that area participating in the reaction. It has been reported that on gold and platinum electrodes, traces of oxygen induced the reduction of H_2O_2 at potentials at which H_2O_2 is 'not or very slowly reduced' [31, 32].

$$O_2 + e^- \rightarrow O_2^{\cdot-} \quad (26)$$
$$O_2^{\cdot-} + e^- \rightarrow O_2^{2-} \quad (27)$$

The $O_2^{\cdot-}$ ion so formed reacts as per reaction 4 and $^{\cdot}OH$ is formed as one of the products.

$$^{\cdot}OH + e^- = OH^- \quad (28)$$

The net reaction of 4 and 28 being

$$O_2^{\cdot-} + H_2O_2 + e^- \rightarrow 2OH^- + O_2 \quad (29)$$

The cathodic doublet observed on repeated cathodic and anodic cycling of the electrode is attributed to this catalytic reduction of H_2O_2 by the oxygen produced by disproportionation [11]. We want to point out that the doublet observed in these chronopotentiometry curves on repeated cathodic and anodic cycling can be compared to the 'normal' and 'activated' or autocatalytic' cathodic H_2O_2 reduction observed in the present studies as well as the one for silver electrode in 0.1 M $HClO_4$ [7].

The involvement of another adsorbate, H_{ad} or chemisorbed H contributing to the oscillatory behavior of H_2O_2 reduction has also been presented [12].

$$\text{Metal} + H^+ + e^- \rightarrow H_{ad} \quad (30)$$
$$H_{ad} + H^+ + e^- \rightarrow H_2 \quad (31)$$
$$H_{ad} + OH_{ad} \rightarrow 2\text{ Metal} + H_2O \quad (32)$$

Since the surface area is reduced by the adsorption of hydrogen, H_{ad} acts as an inhibitor of H_2O_2 reduction (equations 12-14). The autocatalytic generation of free surface area by the recombination reaction 32 introduces instability in the system leading to oscillations. We have observed oscillations only in alkaline medium. However our frequency response analysis data reported in the following paper indicate negative differential resistance, a characteristic often associated with instabilities and bifurcation phenomena.

5. CONCLUSIONS

Cyclic voltammetric behavior of H_2O_2, was investigated in the presence of the most common biological electrolyte, sodium chloride (0.02 – 1.0 M). The 'normal' as well as the 'autocatalytic' H_2O_2 reduction was observed. The 'normal' H_2O_2 reduction current at high cathodic potentials was nearly the same for scans 2 and 3. A slightly higher current for scan 1 was observed compared to the subsequent scans. On the other hand, the 'autocatalytic' H_2O_2 reduction current increased with increasing number of scans and increasing the sweep to higher cathodic potentials. A slight cathodic shift in the peak was also observed. A strong cathodic current was observed on the reverse scans from -1.0 V to less cathodic potentials. With increasing concentration of H_2O_2, there was a slight cathodic shift in the cyclic voltammetric peak observed for the 'autocatalytic' H_2O_2 reduction. A new cathodic shoulder peak before the 'autocatalytic' H_2O_2 reduction was observed for the first time. The autocatalytic process was not observed for peroxide in 0.1 M HCl. Current oscillations were observed in 0.04 M NaOH. Addition of traces of chloride enhanced the autocatalytic cathodic current in basic medium. Both the 'normal' and 'autocatalytic' H_2O_2 reductions were observed in 0.1 M Na_2SO_4 and 0.1 M $NaClO_4$. We conclude that the 'autocatalytic' H_2O_2 reduction process was sensitive to the range of the sweep potential, concentration of H_2O_2, NaCl concentration, and pH. The multiple equilibria involved in the H_2O_2 redox process were evident in the observed cyclic voltammograms.

We have attempted to bridge the information gap on the H_2O_2 redox processes between acidic and basic solutions by choosing a pH ~ 6.0, which is close to the biological pH, and the most common biological electrolyte, NaCl. By carefully controlling the supporting electrolyte concentration, our data have demonstrated the need for strict control of the supporting electrolyte and its concentration in order to arrive at meaningful mechanisms of electrochemical processes. The need for investigating several sweeps of the potentials, the need for careful selection of the potential range for the sweep as well as the importance of the starting potential before the potential sweep are clearly demonstrated.

ACKNOWLEDGEMENT

Benjamin Chu gratefully acknowledges partial support of this work provided by the Basic Energy Sciences, Department of Energy (DEFG0286ER45237)

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