ELECTROCATALYTIC ACTIVITY OF CHEMISORBED HYDROXYL ION TOWARDS OXIDATION OF HYDROGEN PEROXIDE ANION IN ALKALINE MEDIA

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ABSTRACT

In situ chemisorbed hydroxyl ion (OH^-) onto clean polycrystalline gold (Au (poly)) electrode showed an extraordinary enhanced electrocatalytic activity towards oxidation of hydrogen peroxide anion (HO_2^-) in alkaline media. The oxidation of HO_2^- at the fabricated electrode was found to be a diffusion controlled process. The anodic transfer coefficient of the oxidation reaction was estimated as 0.47. Chloride ion (Cl^-) replaced the chemisorbed OH^- from the surface of the modified Au (poly) (OH^-|Au (poly)) electrode leading to diminishing the observed electrocatalytic activity. The optimized concentration of KOH solution for the highest catalytic activity was found to be ca. 0.1 M. A linear calibration curve for various concentrations of HO_2^- in the range of 0.5 to 5 mM was obtained having sensitivity equal to 1.028 A cm^{-2} M^{-1}.

Key words: Chemisorption of OH^-, Surface coverage, Hydrogen peroxide oxidation, Electrocatalysis, Competitive adsorption, Calibration curve

INTRODUCTION

HO_2^- is one of the most consumed chemicals in various sectors such as food, clinical, pharmaceutical, industrial and environmental analysis etc. Detection of its proper level of concentration is very important and hence has received considerable scientific interests since long. Electrochemical sensing is one of the promising techniques towards the detection of HO_2^-. HO_2^- can be detected by both of its electrochemical oxidation and reduction but the latter has received less attention. This is because of lack of suitable electrode materials as they undergo oxidative degradation by HO_2^- and positive applied potential. Different electrode materials have been utilized for oxidation of HO_2^-. For examples, platinized (Pt-black) electrode (V. Badets *et al*. 2016), Pt (E. Nouri-Nigjeh *et al*. 2012), gold nano-particles (C.-H. Lin *et al*. 2015), film of microspheres MnO_2 and Nafion composite fabricated on glassy carbon electrode and flower like copper oxide (L. Zhang *et al*. 2009, 2011) etc. have been used.

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We have been increasingly interested to develop stable electrode materials, particularly by modification of soft metallic electrodes such as Ag and Au etc. with spontaneously chemisorbed anionic species, for electrochemical oxidation of HO_2^-. For examples, we reported that the Au (poly) electrode modified with sub-monolayer of iodine and bromine (Miah *et al.* 2006, 2009) formed by the spontaneous chemisorption of iodide and bromide possessed an excellent enhanced stable electrocatalytic activity towards oxidation of HO_2^-. Very recently we reported that $OH^-|$Au (poly) electrode *in situ* fabricated by the chemisorption of OH^- also shows a significant catalytic effect towards the oxidation of HO_2^- (Miah *et al.* 2016) in alkaline media. The peak current of HO_2^- oxidation was significantly enhanced as compared with the plateau current achieved at the bare Au (poly) electrode under the same experimental conditions. A mechanism of the observed enhanced catalytic activity was discussed based on the electrostatic attraction of the OH^- induced positively charged Au (poly) electrode surface and negatively charged HO_2^-.

In the present article, we have demonstrated the catalytic activity of the *in situ* fabricated $OH^-|$Au (poly) electrode towards oxidation of HO_2^-. The stability of the catalytic activity has been investigated. Poisoning of catalytic activity of $OH^-|$Au (poly) electrode by chloride (Cl^-), effect of pH of the electrolytic solution and electrode holding time in solution etc. have been described. A calibration curve for detection of HO_2^- has also been achieved.

EXPERIMENTAL

The working (Au (poly)), counter (Pt spiral wire), and reference (Ag / ACl / NaCl (sat.)) electrodes, electrochemical cell (two-compartment Pyrex glass), polishing and pretreatment techniques were as same as those described earlier (Miah *et al.* 2016). The polycrystalline nature of the Au (poly) electrode was identified by recording the characteristic cyclic voltammogram as reported elsewhere (Miah *et al.* 2016). The electrolytic solution was purged with N_2 gas for 10 min. During the measurements, N_2 gas was flashed over the cell solution to maintain N_2 saturation for avoiding interference of O_2. The necessary amount of HO_2^- was added into the solution whenever needed. The measurements were performed at temperature of 25 ± 1 ℃. The $OH^-|$Au (poly) electrodes were fabricated by stirring the KOH solution for 5 min if otherwise not mentioned. Necessary amount of Cl^- was added into the electrolytic solution to investigate its poisoning effect on the catalytic activity of the $OH^-|$Au (poly) electrodes. Effect of pH was investigated using KOH solution having its concentration in the range of 0.00625-1.0 M. The scan rate of the electrochemical measurements was 0.1 V s^{-1} if otherwise not mentioned. Electrochemical measurements were performed using a CHI 602D electrochemical analyzer.

RESULTS AND DISCUSSION

Effect of scan rate on the oxidation of HO_2^- at the $OH^-|Au$ (poly) electrode: It has been described in our recent article (Miah *et al.* 2016) that oxidation peak current of HO_2^- at the $OH^-|Au$ (poly) electrode is significantly higher as compared with that obtained at the bare Au (poly) electrode the same experimental conditions. The oxidation of HO_2^- at the $OH^-|Au$ (poly) electrode was investigated over a wide potential scan rates and the corresponding LSVs are presented in Fig. 1. It clearly shows that the responses are very stable all over the potential scan rates. The anodic peak currents for the catalytic oxidation of HO_2^- were derived from the obtained LSVs and the values were plotted against the square root of scan rates and the result is shown in Fig. 2 (a). The values nicely fall on a straight line passing through the origin suggesting that the oxidation of HO_2^- at the $OH^-|Au$ (poly) electrode is a diffusion controlled process (Miah *et al.* 2006, 2009).
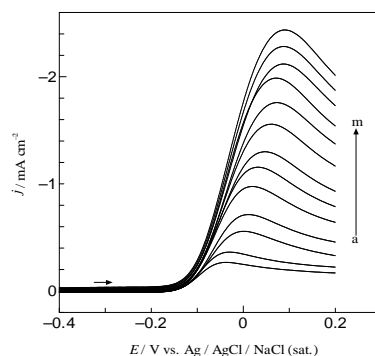

Fig. 1. LSVs obtained the $OH^-|Au$ (poly) electrode in 0.1 M KOH solution containing 1.0 mM HO_2^- at various scan rates of (a) 0.005, (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.10, (f) 0.15, (g) 0.20, (h) 0.30, (i) 0.40, (j) 0.50, (k) 0.60, (l) 0.70, (m) 0.80 V s^{-1} (form bottom to top).
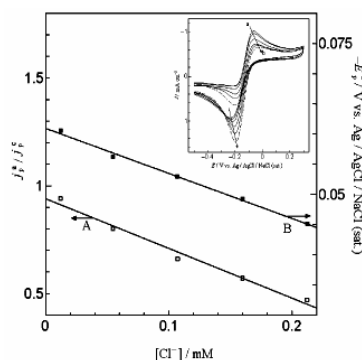

Fig. 2. Linear plots of (a) $-J_p$ vs. $v^{1/2}$ and (b) E_p vs. log v for the oxidation of HO_2^-. The data were derived from LSVs in Fig. 1.

The peak potentials were also derived and plotted against $\log(\nu / \text{V s}^{-1})$ and the result is presented in Fig. 2 (b). The slope of the straight line was obtained as 0.0631 V decade^{-1} from which the anodic transfer coefficient of oxidation HO_2^- was calculated as 0.47 (Laviron 1979) considering two electron oxidation of HO_2^-.

Competitive adsorption of Cl$^-$: Cl^- undergoes more efficient adsorption at the Au (poly) electrode surface (Marichev 1998) than OH^- and hence it can replace the adsorbed OH^-. Therefore, oxidation of HO_2^- was performed in the presence of Cl^- to further explore the catalytic activity of the chemisorbed OH^-. CVs were accordingly obtained at the $OH^-|Au$ (poly) electrode in 0.1 M KOH solution containing 1.0 mM HO_2^- in the presence of (a) 0.0125, (b) 0.055, (c) 0.1075, (d) 0.160 and (e) 0.2125 mM Cl^- and the results are shown in the inset of Fig. 3. The results show that the oxidation peak current of HO_2^- significantly decreased in the presence of Cl^-. The decrease of the anodic peak current is attributed to the efficient adsorption of Cl^- at the $OH^-|Au$ (poly) electrode surface by replacing OH^-.
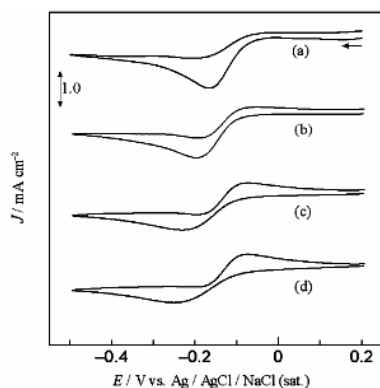

Fig. 3. Linear plots of (A) ratio of anodic to cathodic peak current $\left(j_p^a / j_p^c\right)$ vs. concentration of Cl^- and (B) anodic peak potential $\left(E_p^a\right)$ vs. concentration of Cl^-.
Inset shows the CVs obtained at the OH^- | Au (poly) electrode in 0.1 M KOH solution containing 1.0 mM HO_2^- in the presence of (a) 0.0125, (b) 0.055, (c) 0.1075, (d) 0.160 and (e) 0.2125 mM Cl^-.

The ratio of anodic to cathodic peak current was obtained (from the CVs shown in the inset of Fig. 3) and plotted against the concentration of Cl^- and the corresponding result is presented in Fig. 3(A). It shows a linear decrease of the values of the ratio suggesting the decrease of the catalytic activity due to the adsorption of Cl^-. Cl^- also has a significant effects on the oxidation peak potential. Fig. 3(B) shows that the oxidation peak potential shifts quickly to the direction of more positive potential with increasing $[Cl^-]$. F^- has very low affinity of chemisorption on metal surface compared to Cl^-.

Oxidation of HO_2^- at the $OH^-|Au$ (poly) electrode in presence of 0.2125 mM of F^- (maximum concentration used for Cl^-) was performed (data not shown). The oxidation peak current was found to remain almost unaltered in the F^- containing solution, while in Cl^- containing solution, the peak current decreased by ca. 50%. Adsorption of Cl^- decreased the value of Γ_{OH^-} and consequently resulted in a decrease of the catalytic activity of the electrode towards HO_2^- oxidation. Deactivation of the electrode material towards oxidation of HO_2^- by the adsorption of Cl^-, sulphate, nitrate, acetate was also described elsewhere (Lin *et al.* 2015).

Effect of electrode holding time: CVs in N_2-saturated 1.0 M KOH solution containing 1.0 mM HO_2^- were recorded after holding the clean Au (poly) electrode in the unstirred solution for different times of (a) 0, (b) 35, (c) 85 and (d) 110 min and the results are shown in Fig. 4.
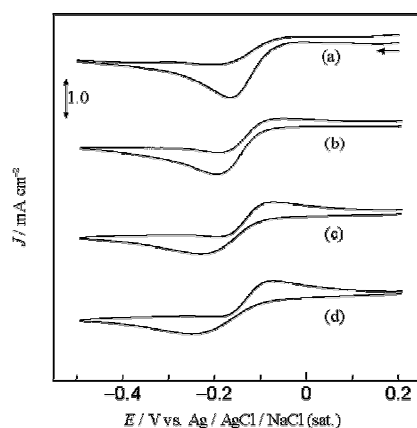

Fig. 4. CVs obtained at the initially clean Au (poly) electrode in 1.0 M KOH solutions containing 1.0 mM HO_2^- after holding the electrode in the unstirred solutions for (a) 0, (b) 35, (c) 85 and (d) 110 min.

The results show that the oxidation peak develops while the reduction peak diminishes with time. This is attributed to the gradual chemisorption of OH^- and increase of Γ_{OH^-}, suggesting that the chemisorbed OH^- plays a vital role towards the observed catalytic activity for the oxidation of HO_2^-.

Effects of KOH concentration on the HO_2^- oxidation: CVs were obtained at the $OH^-|Au$ (poly) electrode in N_2-saturated KOH solution having its concentrations in the range of 0.00625 to 1.0 M containing 1.0 mM HO_2^-. The values of anodic peak current were derived from the CVs and plotted against [KOH] and the result is shown in Fig. 5 (a). It shows that the anodic peak current passes through a maximum. Increase of [KOH] increases the value of Γ_{OH^-} at the $OH^-|Au$ (poly) electrode surface. The optimum concentration of KOH for the highest catalytic activity for the oxidation of HO_2^- was

found to be ca. 0.1 M. The oxidation peak current above 0.1 M of KOH decreased probably due to the increase of viscosity of the solution that led to lowering of the diffusion coefficient of HO_2^-.
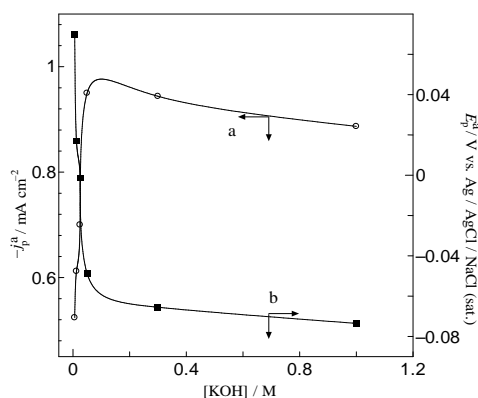

Fig. 5. Plots of (a) oxidation peak current and (b) peak potential vs. concentration of OH^-. The Data were derived from the LSVs obtained at the $OH^-|Au$ (poly) electrode in KOH solution having its concentration in the range of 0.00625–1.0 M in the presence of 1.0 HO_2^-.

Fig 5 (b) shows that the oxidation peak potential exponentially shifts to negative direction of potential when [KOH] ≤ 0.1 M. For [KOH]> 0.1 M the peak potential shows a level off trend. Being inner sphere reaction, oxidation of HO_2^- takes place at the bare portion of the electrode. Thus an optimized value of Γ_{OH^-} is essentially important for the catalytic oxidation.
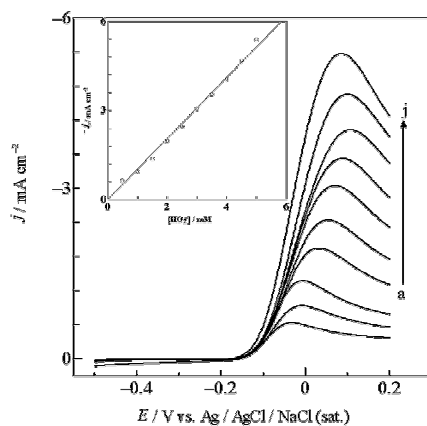

Fig. 6. LSVs obtained at the $OH^-|Au$ electrode in 0.1 M KOH solution in the presence of (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0, (g) 3.5, (h) 4.0, (i) 4.5 and (j) 5.0 mM HO_2^- (form bottom to top). Inset shows the linear plot of peak current vs. concentration of HO_2^-.

Determination of a calibration curve: LSVs were obtained at the OH⁻|Au (poly) electrode in N_2-saturated 0.1 M KOH solution containing HO_2^- in the rage of 0.5 to 5.0 mM and the results are presented in Fig. 6. The oxidation peak currents were derived from the LSVs and plotted as a function of $[HO_2^-]$ and the result has been shown in the inset of Fig. 6. The values nicely ($R^2 = 0.997$) fall on a straight line passing through the origin. The sensitivity of the electrode was obtained as 1.028 A cm^{-2} M^{-1}.

CONCLUSIONS

The *in situ* fabricated OH⁻|Au (poly) electrode showed an enhanced catalytic activity towards the oxidation of HO_2^-. The peak current of oxidation of HO_2^- significantly increased as compared with the bare clean Au (poly) electrode. The anodic response of HO_2^- oxidation was highly stable over a wide range of potential scan rates. The oxidation of HO_2^- was a diffusion controlled process. The anodic transfer coefficient of HO_2^- oxidation was estimated as 0.47. Competitive adsorption of Cl⁻ with OH⁻ severely poisoned the catalytic activity of the OH⁻|Au (poly) electrode towards the oxidation of HO_2^-. The optimum concentration of KOH for the maximum catalytic activity was obtained as ca. 0.1 M. A linear calibration curve was obtained in the concentration range of 0.5-5.0 mM of HO_2^- with a sensitivity equal to 1.028 A cm^{-2} M^{-1}. Thus the *in situ* fabricated OH⁻|Au (poly) electrode can advantageously be used for the detection of OH_2^- without the use of any additional reagent.

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