

ENHANCED ELECTROCHEMICAL OXIDATION OF HYDROGEN PEROXIDE AT HYDROXYL ION-MODIFIED GOLD ELECTRODE IN ALKALINE MEDIA

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ABSTRACT

Chemisorption of hydroxyl ion (OH^-) from aqueous solution of KOH at the polycrystalline gold (Au (poly)) electrode under stirring condition was studied. A pre-wave at ca. 0.19 V was observed due to partial discharging of the chemisorbed OH^- . The linear plot of the pre-wave current vs. scan rate passed through the origin suggesting that it was associated with a surface confined process. An extraordinary enhanced electrocatalytic oxidation of hydrogen peroxide (HO_2^-) at the *in situ* fabricated OH^- -modified Au (poly) ($\text{OH}^- | \text{Au (poly)}$) electrode was achieved. A mechanism of the observed catalytic activity was proposed on the basis of electrostatic attraction between the chemisorbed OH^- and partial positively charged hydrogen ($\text{H}^{\delta+}$) of HO_2^- molecules.

Key words: Linear sweep voltammetry, Polycrystalline Au electrode, Chemisorption of OH^- , Surface coverage, Hydrogen peroxide oxidation, Electrocatalysis

INTRODUCTION

Hydrogen peroxide (HO_2^-) is an important intermediate in many environmental, biological and fuel cell reactions and is widely used in industrial processes as a universal oxidant and hence its monitoring is greatly significant in many fields, such as food, clinical, pharmaceutical, industrial and environmental analysis. Electrochemical oxidation of HO_2^- has received considerable scientific interests for its proper monitoring. For examples, electrochemical oxidation of HO_2^- at different electrodes modified with numerous materials, such as iodine and bromine adatoms (Miah *et al.* 2006, 2009), MnO_2 (Feng *et al.* 2016, Zhang *et al.* 2009) and Pt nanoparticles (Zhang *et al.* 2016) was extensively investigated.

The adsorption of anions, particularly hydroxide ion (OH^-), on metallic electrode surface is of considerable interest in many fundamental sciences and technologies, e.g. electrochemistry, electrocatalysis, corrosion and protection of metals (Tymosiak-Zielinska *et al.* 2000, Marichev 1998). Extensive studies on the chemisorption of OH^- at the Au (poly) and different single crystalline gold electrodes were performed (Marichev

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1998, Tymosiak-Zielinska *et al.* 2001, Zhen *et al.* 2004, Hamelin *et al.* 1990, Huong *et al.* 1980, Chen *et al.* 1999, Chen *et al.* 1999, Zhang *et al.* 1993). Numerous techniques, such as cyclic voltammetry (Marichev 1998, Tymosiak-Zielinska *et al.* 2001, Zhen *et al.* 2004, Hamelin *et al.* 1990), electroreflectance spectroscopy (ERS) (Huong *et al.* 1980, Strbac *et al.* 1996), electrochemical quartz crystal microbalance (EQCM) and Fourier transform infrared spectroscopy (FTIRS) (Zhen *et al.* 2004, Chen *et al.* 1999), surface enhanced Raman spectroscopy (SERS) (Strbac *et al.* 1996, Zhang *et al.* 1993) and contact electroresistance (CER) technique (Marichev 1998), were employed to study the chemisorption of OH^- at metallic electrodes. The formation of a sub-monolayer of OH^- at the gold electrode surface was postulated on the basis of the cyclic voltammetric studies in acidic solution (Angerstein-kozłowska *et al.* 1979, Angerstein-kozłowska *et al.* 1990). ERS was used to give the direct evidence of the chemisorption of OH^- (Huong *et al.* 1980). The energetics of adsorption of OH^- at the Au(111) single crystalline electrode was investigated quantitatively by using chronocoulometry and subtractive normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) (Chen *et al.* 1999). Sorption valence (electron exchange to electrode surface for sorption) of OH^- at the gold electrode depends on the different single crystalline domains. It was estimated 0.3 for the Au (poly) electrode (Angerstein-kozłowska *et al.* 1979, Angerstein-kozłowska *et al.* 1990), while the value was determined as 1 for the Au(100) single crystalline electrode (Strbac *et al.* 1996, Paliteiro 1994). The electron exchanged for the chemisorption of OH^- is the highest for Au(100) domain, while it is the lowest for the Au(111) domain (Strbac *et al.* 1996).

The chemisorbed OH^- at the gold electrode plays a key role in determining the catalytic activity towards many electrochemical reactions, such as the reduction of O_2 (Strbac *et al.* 1996, Sun *et al.* 1994) and oxidations of glycine (Zhen *et al.* 2004), organic compounds (Sun *et al.* 1994, Cordova *et al.* 1979), methanol (Borkowska *et al.* 2004) and HO_2^- (Garlache *et al.* 1997, 1998, Prabhu *et al.* 1981). It was reported that the roughened and activated Au (poly) electrode with chemisorbed OH^- showed enhanced catalytic activity towards the oxidation of methanol in alkaline media (Borkowska *et al.* 2004). In addition, it was described that the chemisorbed OH^- at the Au(100) domain catalyzed the direct 4-electron reduction of O_2 in alkaline media, while the Au(110) and Au(111) domains supported only a 2-electron reduction of O_2 under the same experimental conditions (Strbac *et al.* 1996). The chemisorbed OH^- at the gold electrode has a significant role in oxidation of HO_2^- in alkaline media (Garlache *et al.* 1998, Marichev 1998). For example, two oxidation peaks for oxidation of HO_2^- were observed depending on polishing of the electrode surface (Garlache *et al.* 1998). The first peak current increased significantly when the Au electrode was polished with Al_2O_3 . The adhered hydrophilic Al_2O_3 on the surface enhanced the chemisorption of HO^- and thus increased

HO_2^- oxidation current. On the other hand, polishing the electrode with oily materials diminished the first peak, while the second one increased due to the loss of hydrophilicity of the surface by adsorption of organic species rather than OH^- (Garlache *et al.* 1998, Marichev 1998).

The authors report on the chemisorption of OH^- at the electrochemically pre-treated clean Au (poly) electrode under stirring condition in aqueous alkaline solution using cyclic voltammetric technique. The catalytic activity of this *in situ* fabricated $\text{OH}^-|\text{Au}$ (poly) electrode towards the oxidation of HO_2^- in alkaline solution has been described for the first time. A mechanism of the observed catalytic oxidation of HO_2^- has been developed based on the coulombic attraction between chemisorbed OH^- and partial positively charged hydrogen ($\text{H}^{\delta+}$) of HO_2^- molecules.

EXPERIMENTAL

The Au (poly) working electrode (sealed in a Taflon jacketed) had a diameter equal to 1.6 mm. Pt wire was used as counter electrode, while Ag/AgCl/NaCl (sat.) was used as reference electrode. Pyrex glass cell was used as reaction vessel. N_2 -saturated 0.1 M KOH solution was used as electrolyte. Electrochemical oxidation of HO_2^- was carried out in presence of its necessary amount in the N_2 -saturated 0.1 M KOH solution. The experimental temperature was $25 \pm 1^\circ\text{C}$. Polishing and electrochemical pre-treatment of the Au (poly) electrode were done according to the reported procedure (Miah *et al.* 2006). Roughness factor of the Au (poly) electrode was calculated as 1.3 from the charge consumed (obtained by cutting-weighing technique) for the formation of Au oxide monolayer (Germain *et al.* 2004). The $\text{OH}^-|\text{Au}$ (poly) electrodes were fabricated by stirring the 0.1 M KOH solution by N_2 gas bubbling for 5 min if otherwise not mentioned. Electrochemical measurements were performed using a CHI 602D electrochemical analyzer.

RESULTS AND DISCUSSION

Chemisorption of OH^- at the Au (poly) electrode: Fig.1 shows the linear sweep voltammograms (LSVs) obtained at the (a) Au (poly) and (b) $\text{OH}^-|\text{Au}$ (poly) electrodes in N_2 -saturated 0.1 M KOH solution at a scan rate of 0.1 V s^{-1} . The current in the double layer region has non-zero value which is attributed to the chemisorption of OH^- . The curve (b) shows more current than (a) in the double layer region indicating that more OH^- have undergone chemisorption at the electrode surface due to the stirring of the solution. The charge in the potential range of -0.5 to 0.4 V associated with the LSVs obtained at the $\text{OH}^-|\text{Au}$ (poly) electrodes in (a) 0.01, (b) 0.05 and (c) 0.1 M KOH solutions was estimated, plotted against potential and the results are shown in Fig. 2. The charge consumed is higher than the typical charging current. This is due to the partial oxidation

of chemisorbed OH^- . The sudden increase of charge appeared at the potentials higher than 0.3 V is attributed to the Au (poly) electrode surface oxidation. Similar results were also reported previously (Chen *et al.* 1999).

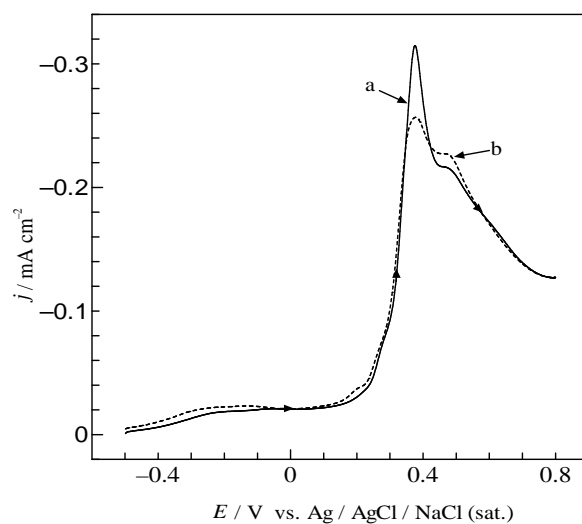


Fig. 1. LSVs obtained at the (a) Au (poly) and (b) $\text{OH}^-|\text{Au}$ (poly) electrodes in N_2 -saturated 0.1 M KOH solution. The $\text{OH}^-|\text{Au}$ (poly) electrode was fabricated by stirring the same 0.1 M KOH solution for 5 min keeping the Au (poly) electrode in the solution. Potential scan rate: 0.1 V s^{-1} .

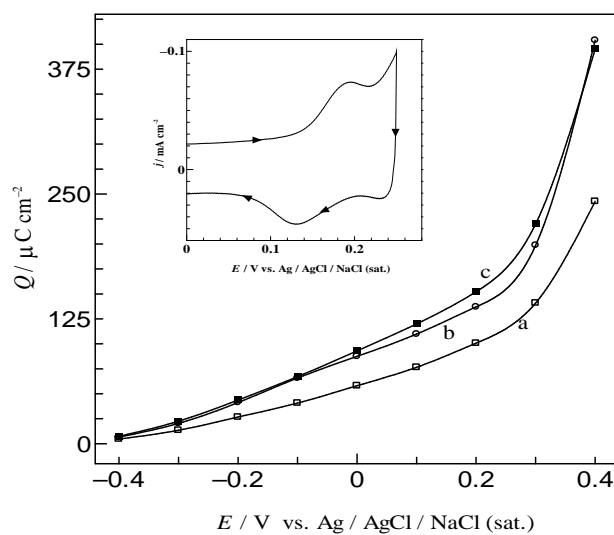


Fig. 2. Plots of charge ($Q/\mu\text{C cm}^{-2}$) vs. potential (E/V) for the partial oxidation of chemisorbed OH^- at the $\text{OH}^-|\text{Au}$ (poly) electrodes. The charge was estimated from LSVs obtained in N_2 -saturated (a) 0.01, (b) 0.05 and (c) 0.1 M KOH solutions. Inset shows the extended view of the pre-wave for the partial discharging of the chemisorbed OH^- .

Gold surface oxidation in different media as a probe of OH⁻ chemisorption: Oxidation of Au (poly) electrode surface strongly depends on the media and its pH (Tymosiak-Zielinska *et al.* 2000, Tymosiak-Zielinska *et al.* 2001, Richard *et al.* 1997, Blizanac *et al.* 2004, Jurczakowski *et al.* 2004). In acidic solution, gold surface oxidation occurs at much positive potential than that in neutral media. In alkaline media, oxidation occurs at a much negative potential as compared with either of the acidic or neutral media. pH-dependent oxidation of gold surface can be explained by chemisorption of OH⁻. The adsorption of OH⁻ constitutes the first step of surface oxidation (Borkowska *et al.* 2004). The specifically adsorbed OH⁻ is then oxidized to AuOH and consecutively to AuO at positive potential. In acidic, neutral and alkaline media the concentrations of OH⁻ are the lowest, medium and highest, respectively. A large number of OH⁻ in alkaline media facilitate the specific adsorption of OH⁻ and catalyze the surface oxidation at much negative potential than either of the acidic or neutral media. It is shown in the Fig. 3 that the gold surface oxidation potential in 0.1 M KOH solution is 0.8 V more negative than that in 0.1 M H₂SO₄ solution. A pre-wave due to the partial discharging of chemisorbed OH⁻ is observed prior to the sharp rise of current for gold surface oxidation in alkaline media (Marichev 1998, Hamelin *et al.* 1990, Borkowska *et al.* 2004, Strbac *et al.* 1992, Hamelin *et al.* 1990, Strbac *et al.* 1992, Anastasijevic *et al.* 1988). Inset of the Fig. 2

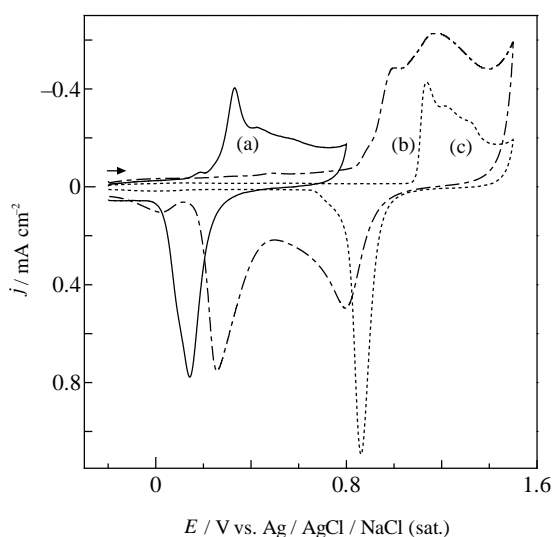


Fig. 3. CVs obtained at the Au (poly) electrode in N₂-saturated 0.1 M (a) KOH, (b) NaClO₄ and (c) H₂SO₄ solutions. Potential scan rate was 0.1 V s⁻¹.

shows an extended view of the pre-wave around 0.19 V obtained at anodic sweep. The pre-wave was recorded over scan rates ranging from 0.01 to 0.5 V s⁻¹ and the corresponding LSVs are presented in Fig. 4. The peak currents were derived from the LSVs and plotted against the scan rates (inset (a) in Fig 4). The values nicely fall on a

straight line passing through the origin indicating that the pre-wave is associated with a surface-confined process (Tymosiak-Zielinska *et al.* 2000, Paliteiro 1994, Matsumoto *et al.* 2003).

The peak currents of Au surface oxidation were also derived from the LSVs and plotted against the scan rate (inset (b) in Fig. 4). The values also fall on a straight line passing through the origin suggesting that the latter one is also a surface-confined process. The surface coverage of OH^- ($\Gamma(\text{OH}^-)$) was calculated as 2.3×10^{-11} mole cm^{-2} using Eq. (1) (Salami *et al.* 2001) considering the value of n (number of electron of partial discharging of OH^- at Au (poly) electrode) as 0.3 (Tymosiak-Zielinska *et al.* 2001).

$$\Gamma(\text{OH}^-) = Q / nF \quad (1)$$

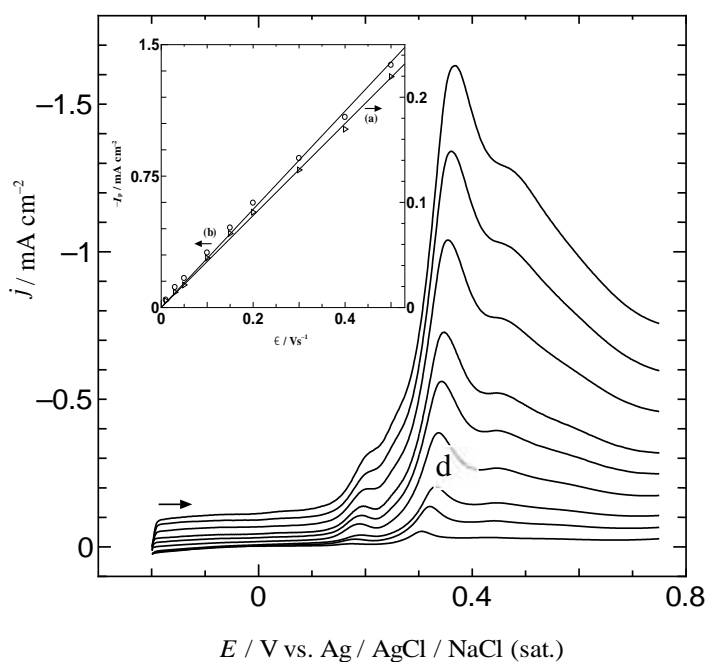


Fig. 4. LSVs obtained at the $\text{OH}^-|\text{Au}$ (poly) electrode in N_2 -saturated 0.1 M KOH solution at various scan rates of (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.10, (e) 0.15, (f) 0.20, (g) 0.30, (h) 0.40 and (i) 0.50 V s^{-1} (form bottom to top). Inset shows the linear plots of the peak current associated with the (a) pre-wave and (b) surface oxidation vs. scan rate.

Catalytic oxidation of HO_2^- at the $\text{OH}^-|\text{Au}$ electrode: Fig. 5 shows the LSVs obtained at the (a, b, e) $\text{OH}^-|\text{Au}$ (poly) and (c, d) Au (poly) electrodes in N_2 -saturated 0.1 M KOH solution containing (e) 0, (b, d) 1.0 and (a, c) 10.0 mM HO_2^- at a scan rate of 0.1 V s^{-1} . The values of current in the potential range of -0.5 to -0.16 V was similar to the background current (curve (e)) in case of the $\text{OH}^-|\text{Au}$ (poly) electrode, suggesting

that the reduction and catalytic decomposition of HO_2^- are absolutely hindered due to the adsorbed OH^- . On the contrary, HO_2^- undergoes catalytic decomposition at the bare Au (poly) electrode to O_2 which consequently undergoes reduction to produce HO_2^- (wave I and II in curve (c)) (Prabhu *et al.* 1981). Unlike the bare Au (poly) electrode, HO_2^- undergoes enhanced oxidation at the $\text{OH}^-|\text{Au}$ (poly) electrode. The onset potential of electrocatalytic oxidation of HO_2^- at the $\text{OH}^-|\text{Au}$ (poly) electrode is -0.160 V, which is about 60 mV more negative compared with the bare Au (poly) electrode (curves (a) and (c)). No well-defined peak for the oxidation of HO_2^- at the bare Au (poly) electrode was observed, while a well-shaped and intense catalytic oxidation peak was achieved at the $\text{OH}^-|\text{Au}$ (poly) electrode. Similar electrocatalytic oxidation of HO_2^- was also reported elsewhere (Evans *et al.* 2002, Limoges *et al.* 1997, Miah *et al.* 2006, 2009, Shankaran *et al.* 2003, Taniguchi *et al.* 1900). The ratio of the oxidation peak current obtained at the $\text{OH}^-|\text{Au}$ (poly) electrode to the plateau current obtained at the bare Au (poly) electrode at the same potential is ca. 4.6 in case of 10.0 mM HO_2^- .

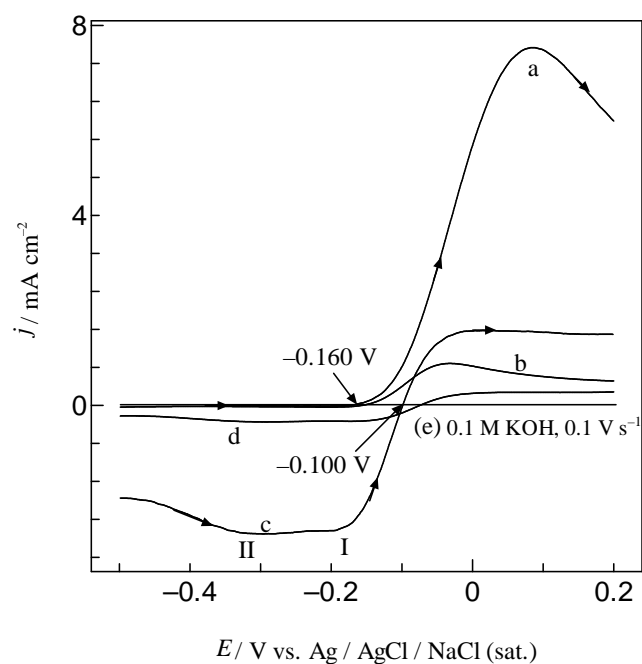


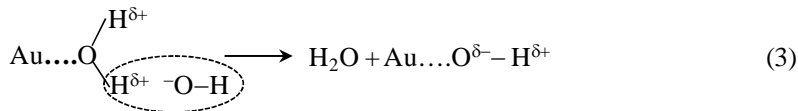
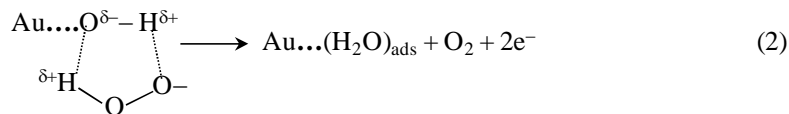
Fig. 5. LSVs obtained at the (a, b, e) $\text{OH}^-|\text{Au}$ (poly) and (c, d) Au (poly) electrodes in N_2 -saturated 0.1 M KOH solution containing (e) 0.0, (b, d) 1.0 and (a, c) 10.0 mM HO_2^- . Potential scan rate 0.1 V s^{-1} .

The result therefore, suggests the strong catalytic activity of the *in situ* fabricated $\text{OH}^-|\text{Au}$ (poly) electrode towards the oxidation of HO_2^- in alkaline solution. The clean Au (poly) electrode surface has very strong catalytic activity towards the chemical decomposition of HO_2^- (Miah *et al.* 2006, 2009). The *in situ* generated O_2 consequently

undergoes electrochemical reduction and thus the shape of the LSV becomes complex. The catalytic chemical decomposition also reduces the surface concentration of HO_2^- that lowers the current for the oxidation of HO_2^- at the bare Au (poly) electrode. On the other hand, the chemisorbed OH^- at the $\text{OH}^-|\text{Au}$ (poly) electrode surface very effectively deactivates the catalytic effect of the electrode towards the decomposition of HO_2^- and thus no cathodic current corresponding to the reduction of O_2 is observed in the potential zone of -0.5 to -0.16 V. The enhanced catalytic activity of the $\text{OH}^-|\text{Au}$ (poly) electrode is partially attributed to the (i) higher HO_2^- surface concentration because of inhibition of its catalytic decomposition and (ii) coulombic force of attraction between adsorbed OH^- and $\text{H}^{\delta+}$ of HO_2^- (discussed later).

Mechanism of electrocatalytic oxidation of HO_2^- at the $\text{OH}^-|\text{Au}$ (poly) electrode:

H_2O_2 in alkaline solution exists as HO_2^- in equilibrium with undissociated H_2O_2 and the degree of dissociation depends on pH of solution (Taniguchi *et al.* 1900, Jose *et al.* 1984). $\text{H}^{\delta+}$ of HO_2^- molecules is electrostatically attracted by the negatively charged $\text{O}^{\delta-}$ end, while O^- of HO_2^- to the positively charged $\text{H}^{\delta+}$ of the chemisorbed OH^- at the Au electrode surface as shown by the dotted lines in Eq. 2. Being strongly attracted, HO_2^- undergoes enhanced oxidation producing O_2 and H_2O .



Produced H_2O remains adsorbed at the Au electrode surface. The $\text{H}^{\delta+}$ of $\text{H}_2\text{O}_{(\text{ads})}$ immediately combines with solution OH^- in alkaline media and produces free H_2O and $\text{Au}\dots\text{O}^{\delta-}-\text{H}^{\delta+}$ (Eq. 3) that again recycles in the catalytic oxidation process of HO_2^- .

CONCLUSIONS

Chemisorption of OH^- at Au (poly) electrode was performed by holding the Au (poly) electrode in KOH solution under stirring with N_2 bubbling. Chemisorbed OH^- at the $\text{OH}^-|\text{Au}$ (poly) electrode was detected by cyclic voltammetric measurements. A pre-wave at potential of 0.19 V, prior to the Au surface oxidation appeared due to the partial discharging of the chemisorbed OH^- . The line obtained by plotting pre-wave current against the scan rate was linear and passed through the origin suggesting that the pre-wave is associated with the chemisorbed OH^- . The *in situ* fabricated $\text{OH}^-|\text{Au}$ (poly) electrode was used for the oxidation of HO_2^- . The peak current of HO_2^- oxidation was ca.

4.5 times higher than the plateau current at the bare Au (poly) electrode under the same experimental condition. The reagent less *in situ* modification of the Au (poly) electrode thus showed an extraordinary catalytic activity towards the oxidation of HO_2^- and hence it can be used as HO_2^- sensor replacing many expensive techniques. A mechanism of the enhanced oxidation of HO_2^- was also proposed.

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