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 \textit{in situ} fabricated OH\(^{-}\)-modified Au (poly) (OH\(^{-}\)\lceil Au (poly)\rceil) 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 (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 \textit{et al.} 2006, 2009), MnO\(_{2}\) (Feng \textit{et al.} 2016, Zhang \textit{et al.} 2009) and Pt nanoparticles (Zhang \textit{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 \textit{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-kozlowska et al.1979, Angerstein-kozlowska 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-kozlowska et al. 1979, Angerstein-kozlowska 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$_2$O$_3$. The adhered hydrophilic Al$_2$O$_3$ 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 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 (H$^+$) of HO$_2^-$ molecules.

EXPERIMENTAL

The Au (poly) working electrode (sealed in a Taflon jacket) 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 ± 1°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 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) 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 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).

![Figure 1](image1.png)

**Fig. 1.** LSVs obtained at the (a) Au (poly) and (b) OH\(^-\)/Au (poly) electrodes in N\(_2\)-saturated 0.1 M KOH solution. The OH\(^-\)/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\(^{-1}\).

![Figure 2](image2.png)

**Fig. 2.** Plots of charge (Q/\(\mu\)C cm\(^{-2}\)) vs. potential (E/V) for the partial oxidation of chemisorbed OH\(^-\) at the OH\(^-\)/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, Jurczakowsk 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 H\(_2\)SO\(_4\) 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 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 \( \text{OH}^- \) was calculated as \( 2.3 \times 10^{-11} \) mole cm\(^{-2}\) using Eq. (1) (Salami et al. 2001) considering the value of \( n \) (number of electron of partial discharging of \( \text{OH}^- \) at Au (poly) electrode) as 0.3 (Tymosiak-Zielinska et al. 2001).

\[
(Q / nF) = (Q / nF) \times (C / (OH^-))
\]

(1)

**Catalytic oxidation of \( \text{HO}_2^- \) at the \( \text{OH}^- | \text{Au} \) electrode:** Fig. 5 shows the LSVs obtained at the \( \text{OH}^- | \text{Au} \) (poly) electrode in \( \text{N}_2 \)-saturated 0.1 M KOH solution at a scan rate of 0.01 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 \( \text{HO}_2^- \) are absolutely hindered due to the adsorbed \( \text{OH}^- \). On the contrary, \( \text{HO}_2^- \) undergoes catalytic decomposition at the bare Au (poly) electrode to \( \text{O}_2 \) which consequently undergoes reduction to produce \( \text{HO}_2^- \) (wave I and II in curve (c)) (Prabhu et al. 1981). Unlike the bare Au (poly) electrode, \( \text{HO}_2^- \) undergoes enhanced oxidation at the \( \text{OH}^- | \text{Au} \) (poly) electrode. The onset potential of electrocatalytic oxidation of \( \text{HO}_2^- \) at the \( \text{OH}^- | \text{Au} \) (poly) electrode is \(-0.160 \text{ V}\), 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 \( \text{HO}_2^- \) 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 \( \text{HO}_2^- \) 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 \( \text{HO}_2^- \).

![Graph](image_url)

**Fig. 5.** LSVs obtained at the (a, b, e) \( \text{OH}^- | \text{Au} \) (poly) and (c, d) Au (poly) electrodes in \( \text{N}_2\)-saturated 0.1 M KOH solution containing (e) 0.0, (b, d) 1.0 and (a, c) 10.0 mM \( \text{HO}_2^- \). 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 \( \text{HO}_2^- \) in alkaline solution. The clean Au (poly) electrode surface has very strong catalytic activity towards the chemical decomposition of \( \text{HO}_2^- \) (Miah et al. 2006, 2009). The *in situ* generated \( \text{O}_2 \) consequently
undergoes electrochemical reduction and thus the shape of the LSV becomes complex. The catalytic chemical decomposition also reduces the surface concentration of \( \text{HO}_2^- \) that lowers the current for the oxidation of \( \text{HO}_2^- \) at the bare Au (poly) electrode. On the other hand, the chemisorbed OH\(^-\) at the OH\(^-\) | Au (poly) electrode surface very effectively deactivates the catalytic effect of the electrode towards the decomposition of \( \text{HO}_2^- \) 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 OH\(^-\) | Au (poly) electrode is partially attributed to the (i) higher \( \text{HO}_2^- \) surface concentration because of inhibition of its catalytic decomposition and (ii) coulombic force of attraction between adsorbed OH\(^-\) and H\(^{\delta^+}\) of \( \text{HO}_2^- \) (discussed later).

\textit{Mechanism of electrocatalytic oxidation of HO}_2^- \textit{at the OH}/Au (poly) electrode:} 
H\(_2\)O\(_2\) in alkaline solution exists as \( \text{HO}_2^- \) in equilibrium with undissociated H\(_2\)O\(_2\) and the degree of dissociation depends on pH of solution (Taniguchi et al. 1900, Jose et al. 1984). H\(^{\delta^+}\) of \( \text{HO}_2^- \) molecules is electrostatistically attracted by the negatively charged O\(^{\delta^-}\) end, while O\(^-\) of \( \text{HO}_2^- \) to the positively charged H\(^{\delta^+}\) of the chemisorbed OH\(^-\) at the Au electrode surface as shown by the dotted lines in Eq. 2. Being strongly attracted, \( \text{HO}_2^- \) undergoes enhanced oxidation producing O\(_2\) and H\(_2\)O.

\[
\text{Au}...\text{O}^{\delta^-}\text{H}^{\delta^+} \rightarrow \text{Au}...(\text{H}_2\text{O})_{\text{ads}} + \text{O}_2 + 2\text{e}^- \quad (2)
\]

\[
\text{Au}...\text{O}^{\delta^-}\text{H}^{\delta^+} \rightarrow \text{H}_2\text{O} + \text{Au}...\text{O}^{\delta^-}\text{H}^{\delta^+} \quad (3)
\]

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

\text{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 OH\(^-\) | 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 \textit{in situ} fabricated OH \textit{|} Au (poly) electrode was used for the oxidation of \( \text{HO}_2^- \). The peak current of \( \text{HO}_2^- \) 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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