

Electrocatalytic Oxidation of Hydrogen Peroxide Anions by Chemisorbed Hydroxyl Species in Alkaline Media: Role of Interfacial Hydroxyl Concentration

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ABSTRACT

The interfacial role of chemisorbed hydroxyl species in the electrocatalytic oxidation of hydrogen peroxide anions was investigated at a clean polycrystalline gold electrode under alkaline conditions. Surface modification through in situ hydroxyl chemisorption substantially enhanced the electrochemical oxidation response of hydrogen peroxide anions, indicating that interfacial hydroxyl coverage plays a critical role in controlling the electrode–electrolyte reaction environment. Electrochemical analysis showed that the oxidation process was predominantly diffusion-controlled, with an estimated anodic transfer coefficient of 0.47. The stability and catalytic contribution of the interfacial hydroxyl layer were further examined using chloride ions as competitive adsorbates. The introduction of Cl^- displaced chemisorbed hydroxyl species from the gold surface and consequently suppressed the electrocatalytic response, providing evidence for the direct involvement of surface-bound hydroxyl species in the oxidation process. The hydroxide concentration also exerted a pronounced influence on the catalytic behavior, with an optimum KOH concentration of approximately 0.1 M producing the highest oxidation activity. Under these optimized conditions, a linear analytical response was obtained for hydrogen peroxide anion concentrations between 0.5 and 5 mM, with a sensitivity of $1.028 \text{ A cm}^{-2} \text{ M}^{-1}$. Overall, the findings demonstrate that controlling the interfacial hydroxyl environment provides an effective means of modulating hydrogen peroxide anion oxidation at polycrystalline gold electrodes.

INTRODUCTION

Hydrogen peroxide and its conjugate anion, hydroperoxide (HO_2^-), are chemically important peroxide species with broad relevance to food processing, clinical diagnostics, pharmaceutical applications, industrial operations, and environmental monitoring. Reliable determination of their concentration is therefore essential in both analytical and technological contexts. Among the available analytical

approaches, electrochemical methods have attracted considerable attention because they provide direct detection, relatively simple instrumentation, rapid response, and the possibility of controlling the interfacial reaction through the applied electrode potential and surface composition.

Electrochemical detection of HO_2^- can proceed through either oxidation or reduction pathways. However, the oxidation route has received particular interest because the electrochemical behavior of peroxide species is strongly influenced by the nature and stability of the electrode surface. Under anodic conditions, HO_2^- can interact strongly with electrode materials and may contribute to surface degradation or modification, making the selection and preparation of a suitable electrode interface an important consideration. Consequently, considerable efforts have been directed toward developing electrode materials and surface architectures capable of promoting HO_2^- oxidation while maintaining adequate electrochemical stability.

A variety of electrode materials and surface modifications have previously been investigated for the electrochemical oxidation of peroxide species. These include platinized platinum electrodes (Pt-black) [1] platinum electrodes [2], gold nanoparticles [3], MnO_2 microsphere/Nafion composite films deposited on glassy carbon electrodes, and flower-like copper oxide structures [4]. Although these systems demonstrate the feasibility of electrochemical peroxide detection, their catalytic behavior is closely associated with the physicochemical properties of the electrode–solution interface. This highlights the importance of understanding not only the bulk electrode material but also the chemical species that are present at, and interact directly with, the electrode surface.

Surface chemisorption provides an effective strategy for modifying the interfacial properties of metallic electrodes without necessarily requiring the formation of a thick coating or complex composite structure. In particular, soft metallic substrates such as silver and gold can undergo spontaneous chemisorption of suitable anionic species, producing modified interfaces with electrochemical characteristics that differ substantially from those of the unmodified metal. Our previous studies demonstrated that polycrystalline gold electrodes modified with sub-monolayer quantities of iodine and bromine through spontaneous chemisorption exhibited enhanced and stable electrocatalytic activity toward HO_2^- oxidation [5].

More recently, attention has been directed toward hydroxyl species as an interfacial modifier for gold electrodes. An OH^- -modified polycrystalline gold electrode, denoted as $\text{OH}^-|\text{Au}(\text{poly})$, can be generated *in situ* through chemisorption of hydroxyl ions from an alkaline electrolyte. This surface modification was shown to produce a pronounced enhancement in the electrochemical oxidation response of HO_2^- compared with the response obtained at the bare $\text{Au}(\text{poly})$ electrode under otherwise comparable conditions [6]. The enhanced activity was initially interpreted in terms of electrostatic interactions at the electrode–electrolyte interface, where chemisorbed hydroxyl species modify the interfacial charge environment and facilitate interaction with the negatively charged HO_2^- species.

The present study extends this concept by considering the **interfacial hydroxyl concentration** as a central factor governing the electrocatalytic response. In an alkaline electrolyte, the concentration of OH^- is not merely a bulk solution parameter; it can influence the availability of hydroxyl species for surface chemisorption and, consequently, the chemical characteristics and coverage of the electrode interface. Changes in the hydroxide concentration may therefore alter the population of chemisorbed hydroxyl species and modify the electrostatic and chemical environment in which HO_2^- oxidation takes place. Establishing this relationship is important for understanding how the catalytic response of the modified gold surface can be controlled through the composition of the surrounding electrolyte.

The interfacial nature of the hydroxyl-mediated catalytic effect can be further examined through competitive adsorption. Chloride ions provide an appropriate probe for this purpose because their

interaction with the gold surface can compete with surface-bound hydroxyl species. Displacement of chemisorbed OH^- by Cl^- and the subsequent decrease in the oxidation response would provide evidence that the enhanced catalytic behavior is associated with the presence and surface contribution of chemisorbed hydroxyl species rather than solely with the underlying gold substrate. Such competitive adsorption therefore offers a means of evaluating the relationship between surface hydroxyl coverage and electrocatalytic activity.

In addition to surface modification, the electrochemical response of HO_2^- depends on the transport of reactant species to the electrode interface and on the kinetics of electron transfer. Characterizing these parameters is essential for distinguishing the contribution of interfacial hydroxyl species from diffusion-related effects. The dependence of the oxidation response on hydroxide concentration, together with the influence of chloride-induced surface displacement, provides a framework for examining the interaction between electrolyte composition, interfacial hydroxyl concentration, and catalytic performance.

Accordingly, the objective of the present work is to systematically investigate the electrocatalytic oxidation of HO_2^- at an *in situ* hydroxyl-modified polycrystalline gold electrode in alkaline media, with particular emphasis on the role of the **interfacial hydroxyl environment**. The study evaluates the catalytic response as a function of alkaline electrolyte conditions, examines the influence of hydroxyl availability on the electrode interface, investigates the effect of chloride as a competitive adsorbate, and characterizes the electrochemical behavior of HO_2^- oxidation. The analytical response toward different HO_2^- concentrations is also evaluated to establish the applicability of the modified interface for quantitative peroxide detection. Through this approach, the study seeks to clarify how controlling the hydroxyl-rich electrode–electrolyte interface can regulate peroxide oxidation and enhance the electrocatalytic performance of polycrystalline gold.

2. Experimental

2.1. Electrochemical cell and electrode configuration

Electrochemical experiments were conducted using a polycrystalline gold electrode, Au(poly), as the working electrode, a platinum spiral wire as the counter electrode, and a saturated Ag/AgCl/NaCl reference electrode. Measurements were performed in a two-compartment Pyrex glass electrochemical cell. The preparation, polishing, cleaning, and electrochemical pretreatment of the Au(poly) electrode followed the procedures previously established for this electrode system [6]. The polycrystalline character and electrochemical cleanliness of the gold surface were verified by recording its characteristic cyclic voltammetric response prior to the experiments.

2.2. Preparation of the hydroxyl-modified gold interface

The hydroxyl-modified gold electrode, denoted as $\text{OH}^-|\text{Au}(\text{poly})$, was prepared *in situ* in alkaline electrolyte through interaction of hydroxyl ions with the clean polycrystalline gold surface. Unless otherwise stated, the KOH electrolyte was stirred for 5 min before electrochemical measurements to establish the hydroxyl-modified interfacial condition. Because the concentration of OH^- in the electrolyte directly determines the availability of hydroxyl species for interfacial chemisorption, KOH concentration was treated as an important experimental parameter in evaluating the relationship between the alkaline environment and electrocatalytic activity.

To examine the influence of the interfacial hydroxyl environment, KOH concentrations ranging from 0.00625 to 1.0 M were investigated. This concentration range allowed the electrochemical response of HO_2^- to be evaluated under progressively different hydroxide conditions and provided a basis for identifying the alkaline concentration associated with the maximum catalytic response.

2.3. Preparation and electrochemical measurement of HO_2^-

The required amount of HO_2^- was introduced into the electrolyte immediately before the corresponding electrochemical measurement. Unless otherwise indicated, electrochemical measurements were conducted at a potential scan rate of 0.1 V s^{-1} . Linear sweep voltammetry (LSV) was employed to characterize the anodic oxidation response of HO_2^- at the hydroxyl-modified Au(poly) interface.

The effect of scan rate was investigated over a range of potential scan rates to determine the dominant transport characteristics of the oxidation process. The resulting anodic peak currents were correlated with the square root of the scan rate to assess whether the reaction was controlled primarily by diffusion.

2.4. Competitive adsorption experiments

The contribution of surface-bound hydroxyl species to the catalytic response was further examined using chloride ions as competitive adsorbates. Appropriate amounts of Cl^- were introduced into the alkaline electrolyte to evaluate their influence on the oxidation response of HO_2^- at the $\text{OH}^-/\text{Au}(\text{poly})$ electrode. Suppression of the catalytic current following chloride addition was considered in relation to the displacement of chemisorbed hydroxyl species from the gold surface.

This approach provided an indirect assessment of the relationship between surface hydroxyl coverage and catalytic activity and allowed the interfacial contribution of chemisorbed OH^- to be distinguished from the intrinsic electrochemical response of the bare gold electrode.

2.5. Experimental conditions and instrumentation

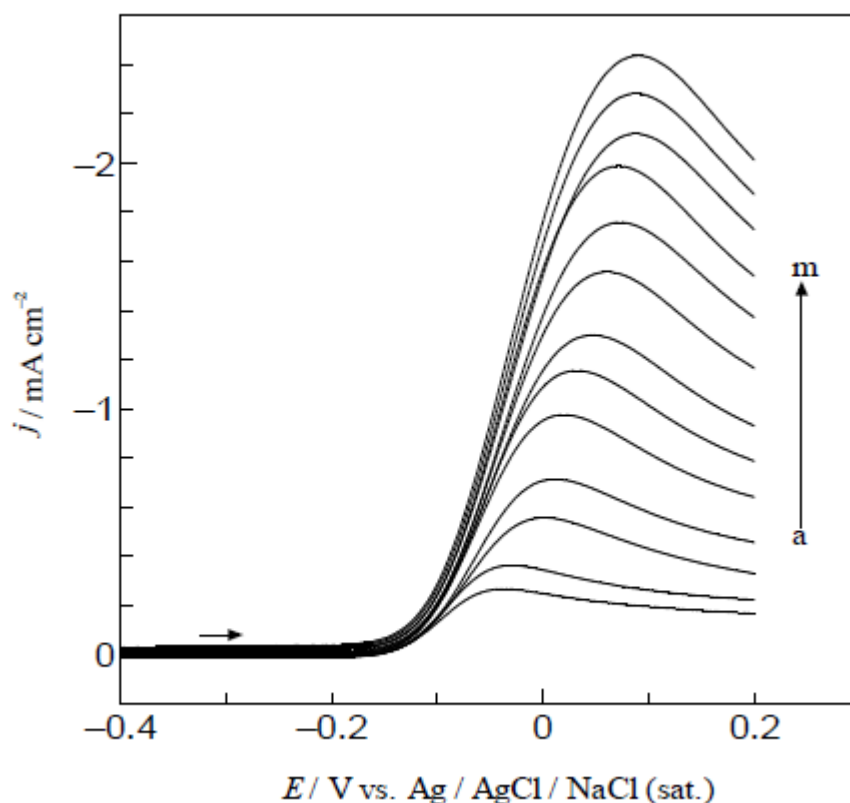
All electrochemical measurements were performed at $25 \pm 1 \text{ }^\circ\text{C}$. Prior to each measurement, the electrolyte solution was purged with nitrogen for 10 min to remove dissolved oxygen. During the electrochemical experiments, nitrogen was continuously passed over the solution surface to maintain an oxygen-free environment and minimize interference from dissolved O_2 .

Electrochemical measurements were carried out using a **CHI 602D electrochemical analyzer**. Unless otherwise specified, experimental parameters were maintained constant while individual variables, including hydroxide concentration, scan rate, chloride concentration, and HO_2^- concentration, were varied systematically.

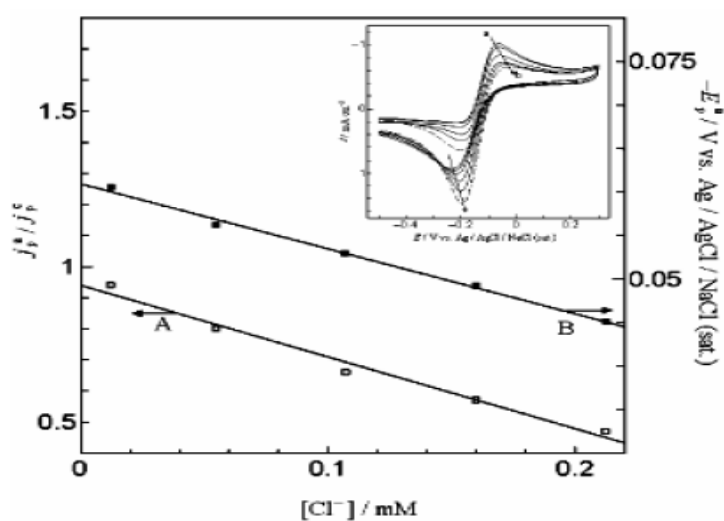
3. Results and Discussion

3.1. Influence of scan rate on HO_2^- oxidation at the hydroxyl-modified Au(poly) interface

The electrochemical response of HO_2^- at the hydroxyl-modified polycrystalline gold electrode was initially examined as a function of potential scan rate. Previous observations demonstrated that incorporation of chemisorbed hydroxyl species substantially increases the oxidation response of HO_2^- compared with the response obtained at the unmodified Au(poly) surface under otherwise identical conditions (Miah et al., 2016). The present investigation further examines this response in the context of the interfacial hydroxyl environment.



Linear sweep voltammograms recorded over a broad range of potential scan rates showed well-defined and reproducible anodic responses for HO_2^- oxidation at the $\text{OH}^-|\text{Au}(\text{poly})$ electrode (Fig. 1). The persistence of the catalytic response over the investigated scan-rate range indicates that the hydroxyl-modified interface remains electrochemically active under the applied experimental conditions.



To determine the dominant mass-transport characteristics of the oxidation process, the anodic peak current was plotted against the square root of the potential scan rate (Fig. 2a). A linear relationship was obtained, with the experimental points closely following a straight line passing through the origin. This dependence indicates that the oxidation current is primarily governed by diffusion of HO_2^- toward the electrode interface.

The diffusion-controlled behavior is consistent with the electrochemical characteristics previously reported for HO_2^- oxidation at chemically modified gold surfaces (Miah et al., 2006, 2009). Importantly, the presence of a diffusion-controlled response does not diminish the role of the hydroxyl-modified interface. Rather, the chemisorbed hydroxyl layer appears to establish an interfacial environment that promotes the electrochemical oxidation of HO_2^- , while the subsequent magnitude of the observed current remains dependent on the transport of HO_2^- from the bulk electrolyte to the electrode surface.

From the perspective of the present study, this distinction is important because the catalytic enhancement should be considered as an interfacial phenomenon superimposed on a diffusion-controlled reactant transport process. Accordingly, changes in hydroxide concentration are expected to influence the response not simply through changes in bulk alkalinity, but also through their potential effect on the availability and interfacial concentration of chemisorbed hydroxyl species.

The observed linear dependence of peak current on the square root of scan rate therefore establishes a suitable electrochemical basis for subsequently examining the effect of hydroxide concentration on the catalytic response. In the following experiments, the KOH concentration was systematically varied to determine whether changes in the hydroxyl-rich interfacial environment are accompanied by corresponding changes in the electrocatalytic oxidation of HO_2^- .

3.2. Potential dependence and electron-transfer kinetics

In addition to the dependence of the oxidation current on the potential scan rate, the variation of the anodic peak potential with scan rate was examined to further characterize the kinetics of HO_2^- oxidation at the hydroxyl-modified Au(poly) interface. The peak potentials obtained from the corresponding voltammograms were plotted as a function of $\log(v/V \text{ s}^{-1})$, as shown in Fig. 2b.

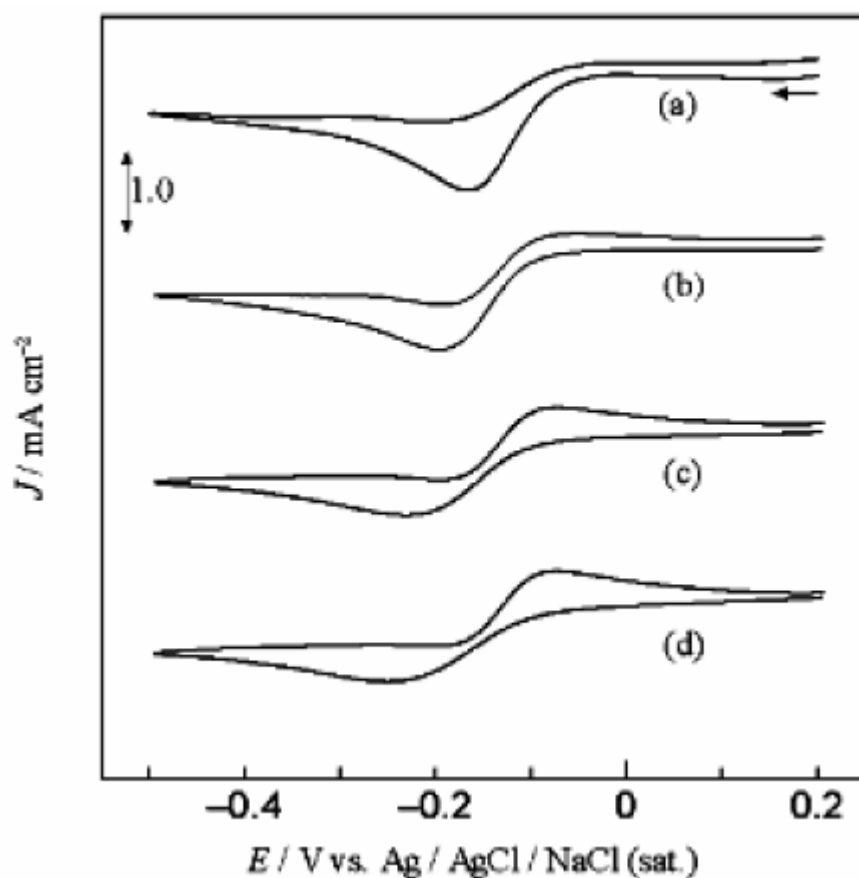
A linear dependence was observed between the anodic peak potential and the logarithm of the scan rate. The slope of the resulting relationship was $0.0631 \text{ V decade}^{-1}$. Using the Laviron formalism [7] and considering the two-electron oxidation pathway of HO_2^- , the anodic transfer coefficient was estimated to be 0.47.

The obtained transfer coefficient indicates that electron-transfer kinetics contribute measurably to the observed anodic response, although the linear relationship between the peak current and the square root of scan rate demonstrates that mass transport remains an important limiting factor under the investigated conditions. These observations collectively indicate that the electrochemical oxidation of HO_2^- at the $\text{OH}^-/\text{Au}(\text{poly})$ interface involves an interplay between interfacial electron transfer and diffusion of the reactive species toward the electrode surface.

More importantly, the electrochemical response is strongly dependent on the chemical state of the electrode-electrolyte interface. The presence of chemisorbed hydroxyl species modifies the local interfacial environment and provides the surface configuration responsible for the enhanced catalytic response. Consequently, subsequent experiments were designed to establish whether changes in the amount of interfacial hydroxyl species are directly reflected in the catalytic activity.

3.3. Competitive adsorption of chloride and suppression of the hydroxyl-mediated catalytic response

The contribution of chemisorbed hydroxyl species to the oxidation of HO_2^- was further investigated through competitive adsorption experiments. Chloride ions exhibit a strong affinity for gold surfaces and can compete effectively with hydroxyl species for surface adsorption sites [8]. Therefore, chloride was employed as an interfacial probe to examine the relationship between hydroxyl surface coverage and electrocatalytic activity.



Cyclic voltammograms were recorded at the $\text{OH}^-|\text{Au}(\text{poly})$ electrode in N_2 -saturated 0.1 M KOH containing 1.0 mM HO_2^- and different concentrations of Cl^- : 0.0125, 0.055, 0.1075, 0.160, and 0.2125 mM. The corresponding voltammograms are presented in the inset of Fig. 3.

A progressive decrease in the anodic peak current was observed with increasing chloride concentration. The systematic suppression of the oxidation response indicates that chloride adsorption disrupts the hydroxyl-rich interfacial environment responsible for the enhanced catalytic activity. In this context, the decrease in current can be interpreted as a reduction in the effective interfacial hydroxyl population, Γ_{OH^-} , caused by competitive occupation of gold surface sites by Cl^- .

To quantify this effect, the ratio of the anodic to cathodic peak currents was determined from the corresponding voltammograms and plotted against chloride concentration (Fig. 3a). The resulting approximately linear decrease demonstrates that the catalytic response progressively deteriorates as the concentration of the competing adsorbate increases.

A simultaneous change in the anodic peak potential was also observed. As shown in Fig. 3b, increasing Cl^- concentration caused the oxidation peak to shift toward more positive potentials. This positive displacement is consistent with modification of the interfacial reaction environment following chloride adsorption and the associated reduction in hydroxyl-mediated catalytic sites.

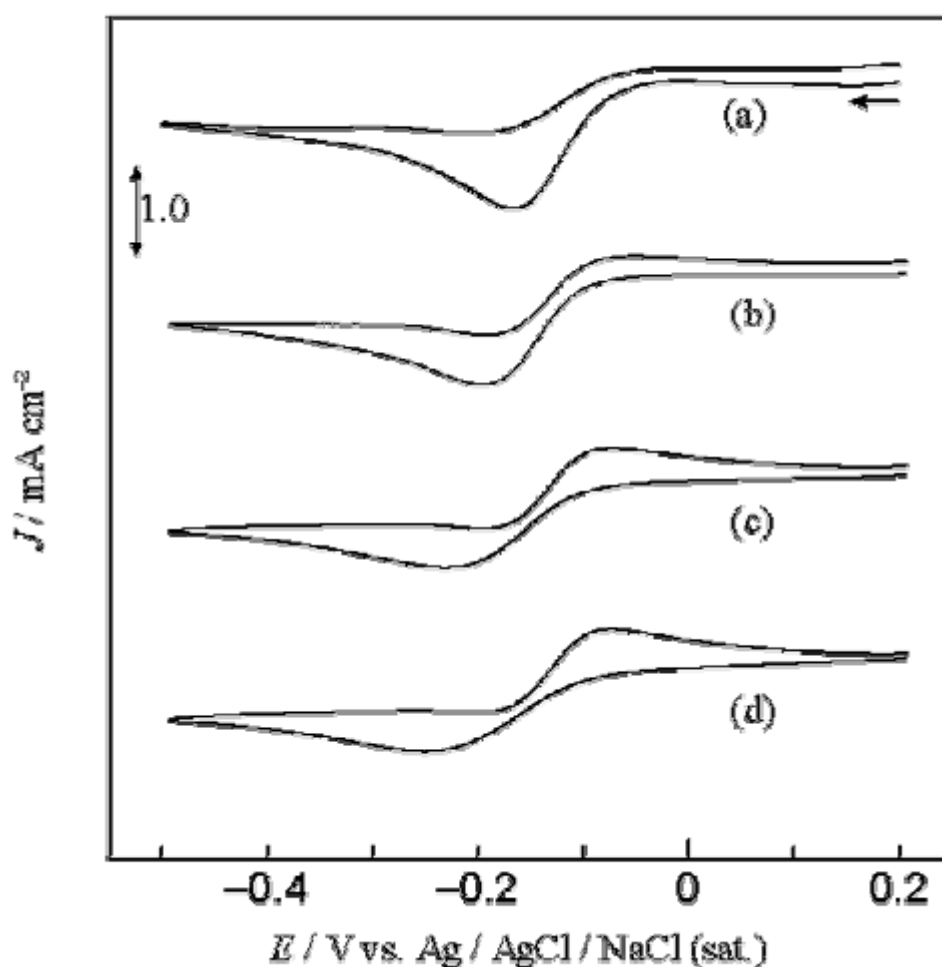
The selectivity of this competitive-adsorption effect was further examined using fluoride ions. Unlike chloride, fluoride exhibits a substantially lower tendency to chemisorb strongly on metallic surfaces under comparable conditions. When HO_2^- oxidation was examined in the presence of 0.2125 mM F^- , the maximum concentration used in the chloride experiments, the oxidation current remained nearly unchanged. In contrast, the same concentration of Cl^- resulted in an approximately 50% decrease in the oxidation peak current.

This comparison provides additional evidence that the suppression of catalytic activity is associated primarily with competitive surface adsorption rather than simply with the presence of an additional anion in the electrolyte. The results therefore support a direct relationship between the population of surface-bound hydroxyl species and the catalytic oxidation of HO_2^- .

The observed decrease in Γ_{OH^-} following chloride adsorption provides a mechanistic explanation for the loss of catalytic activity. Similar deactivation effects associated with adsorption of chloride, sulfate, nitrate, and acetate species on catalytic electrode surfaces have previously been reported [3]. In the present system, however, the competitive adsorption experiment specifically demonstrates the importance of maintaining an appropriate hydroxyl population at the Au(poly) interface.

3.4. Time-dependent development of the hydroxyl-modified interface

The temporal development of the hydroxyl-modified electrode surface was investigated by monitoring the electrochemical response of a clean Au(poly) electrode after immersion in an unstirred alkaline solution. Cyclic voltammograms were recorded in N_2 -saturated 1.0 M KOH containing 1.0 mM HO_2^- after holding the electrode in the solution for 0, 35, 85, and 110 min.



The resulting voltammograms are presented in Fig. 4. A progressive development of the anodic oxidation peak was observed with increasing electrode holding time, accompanied by a corresponding diminution of the reduction response.

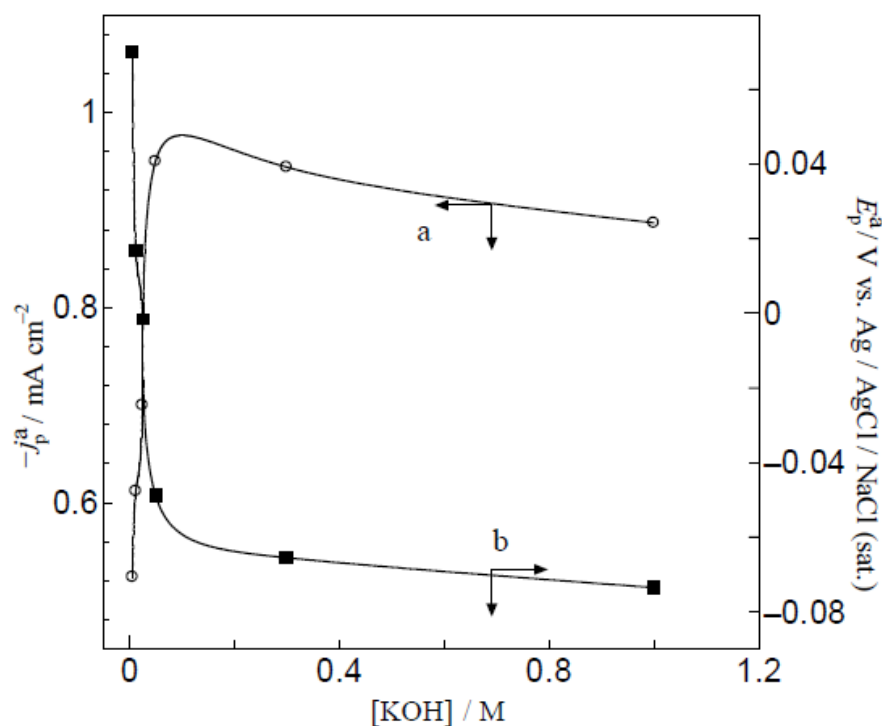
The time-dependent evolution of the voltammetric response indicates that the electrode surface does not attain its catalytically active state instantaneously. Instead, the interfacial hydroxyl population develops progressively during exposure of the gold surface to the alkaline electrolyte. The increase in oxidation activity with holding time can therefore be associated with the gradual formation and accumulation of chemisorbed hydroxyl species at the electrode interface.

These observations provide direct support for the central role of interfacial hydroxyl concentration in determining the catalytic response. In particular, the increase in the oxidation signal with increasing exposure time suggests that the electrochemical behavior of the electrode is governed not only by the bulk concentration of OH^- but also by the extent to which hydroxyl species are established at the gold surface.

The time-dependent behavior also provides an important distinction between bulk alkalinity and surface hydroxyl concentration. Although the electrolyte concentration remains constant during each experiment, the electrochemical response changes with the duration of electrode exposure. This behavior is consistent with progressive modification of the electrode–electrolyte interface through hydroxyl chemisorption.

3.5. Effect of hydroxide concentration on HO_2^- oxidation

The influence of the alkaline environment on HO_2^- oxidation was investigated systematically by varying the KOH concentration from 0.00625 to 1.0 M while maintaining the HO_2^- concentration at 1.0 mM. Cyclic voltammograms obtained under these conditions are summarized in Fig. 5.



The anodic peak current initially increased with increasing KOH concentration and subsequently passed through a maximum. The maximum catalytic response was obtained at approximately 0.1 M KOH. This non-monotonic behavior demonstrates that the relationship between bulk hydroxide concentration and electrocatalytic activity is not simply proportional.

At relatively low KOH concentrations, increasing hydroxide availability promotes the formation of chemisorbed hydroxyl species at the Au(poly) surface. The resulting increase in the effective interfacial hydroxyl concentration, Γ_{OH^-} , enhances the catalytic response toward HO_2^- oxidation. Thus, the initial increase in current can be attributed to progressive development of the hydroxyl-mediated catalytic interface.

When the KOH concentration exceeded approximately 0.1 M, however, the anodic current decreased. One possible contribution to this decline is the increase in electrolyte viscosity at higher KOH concentrations, which can reduce the diffusion coefficient of HO_2^- and consequently decrease the diffusion-controlled oxidation current.

The results therefore indicate the existence of an optimum interfacial condition rather than a simple concentration-dependent increase in catalytic activity. At approximately 0.1 M KOH, the electrode appears to possess a favorable balance between hydroxyl-mediated surface modification and efficient transport of HO_2^- through the electrolyte.

The dependence of the anodic peak potential on KOH concentration provides additional evidence for the influence of the interfacial environment. As shown in Fig. 5b, the oxidation peak potential shifted progressively toward more negative values as the KOH concentration increased up to approximately 0.1 M. Above this concentration, the peak potential exhibited a relatively weak dependence on KOH concentration.

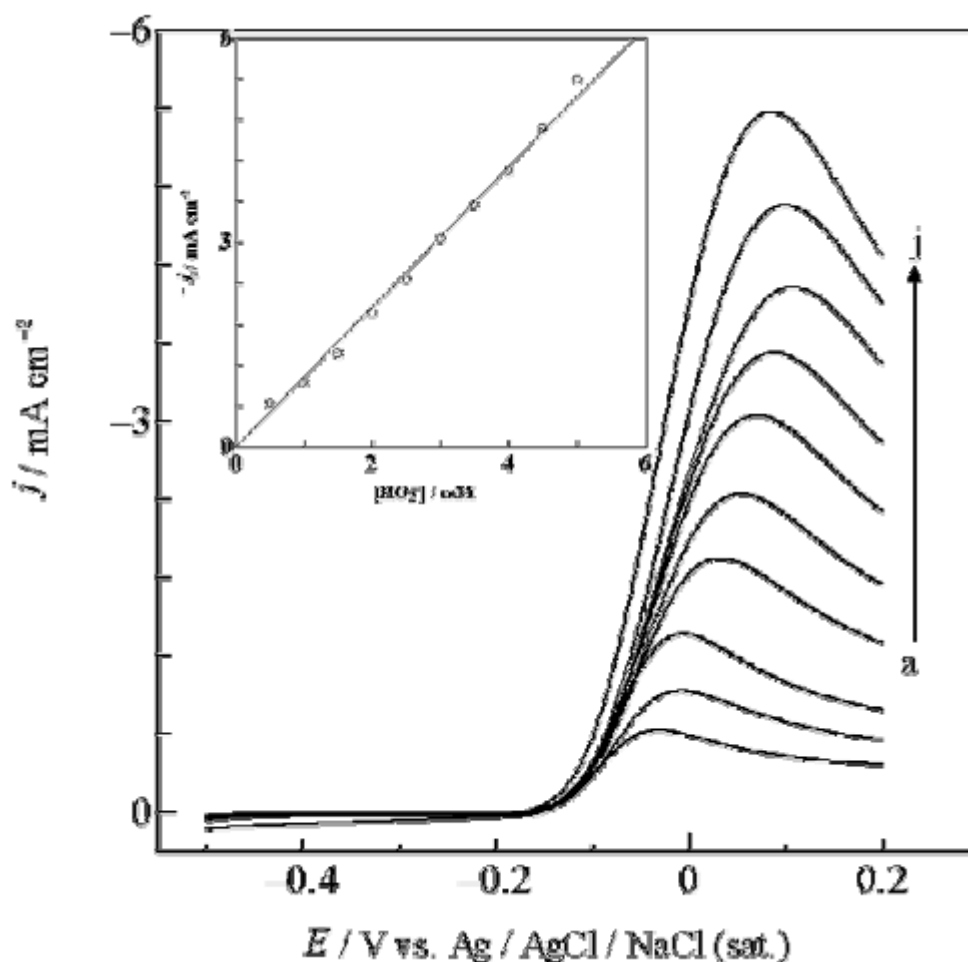
This behavior suggests that increasing hydroxide availability progressively modifies the electrochemical environment until an approximately stable interfacial condition is reached. The observation is consistent with the formation of a hydroxyl-rich surface at higher alkaline concentrations.

Because HO_2^- oxidation involves an inner-sphere contribution, the reaction occurs at electrochemically accessible regions of the electrode surface. Complete occupation of the surface by hydroxyl species is therefore not necessarily expected to produce the highest catalytic response. Rather, an appropriate hydroxyl surface population is required to establish a favorable catalytic environment while preserving sufficient accessible surface sites for interaction with HO_2^- .

Accordingly, the maximum observed activity at approximately 0.1 M KOH can be interpreted as an **optimum interfacial hydroxyl condition**, rather than simply an optimum bulk hydroxide concentration. This distinction is central to understanding the catalytic behavior of the $\text{OH}^-/\text{Au}(\text{poly})$ electrode.

3.6. Analytical response toward HO_2^-

The analytical applicability of the hydroxyl-modified $\text{Au}(\text{poly})$ electrode was evaluated under the optimized alkaline condition of 0.1 M KOH. Linear sweep voltammograms were recorded in N_2 -saturated electrolyte containing HO_2^- concentrations ranging from 0.5 to 5.0 mM (Fig. 6).



A progressive increase in the anodic oxidation current was observed with increasing HO_2^- concentration. The corresponding peak currents were plotted against HO_2^- concentration, as shown in the inset of Fig. 6. The experimental points exhibited an excellent linear relationship, with a coefficient of determination of $R^2 = 0.997$.

The resulting calibration behavior demonstrates that the $\text{OH}^-|\text{Au}(\text{poly})$ interface provides a reproducible electrochemical response over the investigated HO_2^- concentration range. The slope of the calibration relationship corresponds to a sensitivity of $1.028 \text{ A cm}^{-2} \text{ M}^{-1}$.

The high linearity of the response is consistent with the diffusion-controlled behavior established from the scan-rate experiments. Under the optimized interfacial condition, changes in the concentration of HO_2^- are directly reflected in the measured oxidation current, providing a basis for quantitative electrochemical detection.

Taken together, the calibration results demonstrate that controlling the hydroxyl-modified interface can provide both catalytic enhancement and a useful analytical response without requiring an additional catalytic reagent in solution.

3.7. Mechanistic interpretation of the interfacial hydroxyl effect

The collective electrochemical observations provide a consistent picture of the role played by interfacial hydroxyl species in HO_2^- oxidation. Three experimental observations are particularly important: the development of catalytic activity with electrode holding time, the suppression of the response by chloride adsorption, and the existence of an optimum KOH concentration.

The increase in oxidation activity during electrode exposure to alkaline solution indicates progressive formation of chemisorbed hydroxyl species. Conversely, the addition of chloride causes a substantial decrease in catalytic activity, consistent with displacement of hydroxyl species from the gold surface. Finally, the maximum oxidation current at approximately 0.1 M KOH demonstrates that the catalytic response depends on establishing an appropriate interfacial hydroxyl population.

These observations collectively suggest that the electrocatalytic behavior can be described in terms of an interfacial hydroxyl-dependent process:

Bulk OH^- concentration $\rightarrow$ hydroxyl chemisorption $\rightarrow$ interfacial hydroxyl population (Γ_{OH^-}) $\rightarrow$ modification of the electrode/electrolyte interface $\rightarrow$ enhanced HO_2^- oxidation.

The catalytic effect should therefore not be attributed exclusively to the bulk alkalinity of the electrolyte. Instead, the results indicate that the chemical composition and effective hydroxyl population of the gold surface are critical determinants of the observed electrocatalytic response.

The competitive adsorption experiments further demonstrate that the interfacial hydroxyl population can be disrupted by strongly adsorbing species. This provides an experimental basis for treating Γ_{OH^-} as a meaningful descriptor of catalytic activity at the modified gold interface.

3.8. Proposed interfacial model

Based on the experimental findings, a conceptual model can be proposed in which hydroxyl ions from the alkaline electrolyte interact with the Au(poly) surface and generate a hydroxyl-modified interfacial layer. This layer alters the local electrostatic and chemical environment and facilitates the oxidation of the negatively charged HO_2^- species.

At insufficient hydroxide concentration, the surface hydroxyl population is relatively limited, resulting in a weaker catalytic effect. Increasing the KOH concentration increases the availability of hydroxyl species and promotes formation of the active interfacial environment. At the optimum condition, approximately 0.1 M KOH, the surface possesses a favorable hydroxyl population while adequate electrochemically accessible sites remain available for HO_2^- oxidation.

At still higher KOH concentrations, the catalytic current decreases, most likely because transport limitations associated with the increasingly viscous electrolyte become more significant. Similarly, adsorption of Cl^- reduces the effective hydroxyl population and suppresses the catalytic response.

Thus, the electrocatalytic activity of the $\text{OH}^-|\text{Au}(\text{poly})$ electrode can be viewed as the result of a balance between **hydroxyl surface modification, accessibility of reactive electrode sites, and mass transport of HO_2^- .**

Ethical Considerations

Not applicable. This study did not require ethical approval because it does not include human or animal subjects and does not involve any personal or sensitive data.

List of Abbreviations:

Linear sweep voltammetry (LSV); MnO_2 : Manganese dioxide; HO_2^- = Hydroperoxyl anion; OH^- : Hydroxide ion; KOH: Potassium hydroxide; CHI: Chloriodomethane;

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Author Contribution:

All authors contributed equally to the main contributor to this paper. All authors read and approved the final paper.

Declaration of generative AI and AI-assisted technologies in the writing process

The authors hereby declare that no generative artificial intelligence or AI-assisted technologies were used at any stage during the preparation of this manuscript, including language editing, proofreading, or content development. The authors take full responsibility for the originality and integrity of the work presented in this publication.

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Conflicts of Interest:

“The authors declare no conflict of interest.”

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