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Recommended Citation
DOI: 10.61558/2993-074X.2616
Available at: https://jelectrochem.xmu.edu.cn/journal/vol18/iss5/8

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The Oxidation of Hydrogen Peroxide on Nanostructured Rhodium Microelectrodes

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Abstract: Mesoporous Rh films were deposited onto platinum microelectrodes from the H₂OT liquid crystalline phase of C₁₂EO₈ (octaethyleneglycol monododecylether). The electrodes show well defined voltammetry for the oxidation and the reduction of hydrogen peroxide at low concentrations (<10 mmol·L⁻¹) with excellent stability for operation at neutral pH. Based on the hysteresis in the current and the potential dependence the oxidation of hydrogen peroxide occurs through a CEE mechanism involving Rh(OH)₃ on the mesoporous Rh electrode surface. At higher hydrogen peroxide concentrations the current reaches a plateau that is due to either saturation of the binding sites for hydrogen peroxide or limitation of the reaction due to acidification of the solution within the pores. For the thin films (below 200 nm) the hydrogen peroxide calibration curves we fitted to a one dimensional model for diffusion and reaction within the pores.

Key words: hydrogen peroxide; rhodium; microelectrode; nanoporous; lyotropic liquid crystal; templated electrodeposition

CLC Number: O646

Document Code: A

1 Introduction

Mesoporous metal films with regular nanoporous architectures between about 2 and 10 nm can be electrodeposited from hexagonal lyotropic liquid crystalline phases. They represent an interesting type of high surface area metallic structure in which the surface is concave and strongly curved in contrast to the much more widely studied convex surfaces of nanoparticulate systems. One of the potential practical applications of mesoporous metal films is for the detection of hydrogen peroxide over a wide range of concentrations. Hydrogen peroxide is of interest in many fields, for example in the food industry, as well as in waste water treatment. In particular, many investigations have been undertaken of the amperometric detection of hydrogen peroxide for biosensing applications.

Concentrations range from micromolar for in vivo applications to millimolar for bleaching and even molar in the field of water treatment.

The accurate amperometric measurement of hydrogen peroxide has been a difficult task since the reactions at the electrode are irreversible and the voltammograms are often irreproducible. Different electrode materials have been used to monitor hydrogen peroxide, including carbon fibres, glassy carbon, and platinum. However, in many cases the electrodes show poor stability and the amperometric response becomes non-linear at high hydrogen peroxide concentrations.

Solutions have been put forward to overcome the irreproducibility and instability of the responses such as the modification of the electrode surface with enzymes (horseradish peroxidise and others) or Prussian Blue. Enzyme based biosensors...
have shown a high sensitivity \((1.5 \text{ A} \cdot \text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-2})\) and very low detection limits \((10 \text{ nmol} \cdot \text{L}^{-1})[15]\), however in this case the upper limit does not go beyond 12 mmol-L\(^{-1}\) [16]. Another disadvantage was that the stability of the Prussian-Blue based sensor decreased with repeated use[16].

The oxidation of hydrogen peroxide has been studied on platinum and platinum/iridium electrodes and a decrease in the response was observed above 1 mmol-L\(^{-1}\), this was attributed to the saturation of oxygen and hydrogen peroxide on the platinum catalytic sites[17]. Gorton came to the same conclusion in his study of the mechanism for hydrogen peroxide oxidation on high surface palladium electrodes[18].

Johnston et al. proposed a surface binding site model for hydrogen peroxide oxidation on palladium assuming that the reaction obeys a form of Michaelis-Menten kinetics[19]. An identical surface binding site model was then adapted by Hall et al. for hydrogen peroxide oxidation on Pt electrodes[20-24]. According to a series of papers from Hall et al.[20-24], the oxidation current for hydrogen peroxide oxidation is under mixed kinetic and diffusion control and occurs through a CEE mechanism (chemical reaction step by two sequential electrochemical steps) in which hydrogen peroxide is adsorbed and then oxidised at the oxide coated metal surface in a chemical step which is followed by the electrochemical reformation of the surface oxide. The availability of Pt oxide sites is then a limiting factor in the reaction at high hydrogen peroxide concentrations and this results in the saturation of the response. This mechanism also accounts for the ready poisoning of the reaction since the catalytic sites can be blocked by other species from solution.

Microdisc electrodes are attractive for amperometric analytical measurements because under mass transport limited conditions they attain a steady state in which the limiting current is proportional to concentration. However, this advantage is not readily realised in the case of hydrogen peroxide because of the CEE mechanism. A way to overcome this problem is to increase the electroactive surface area whilst maintaining the diffusion properties of the microelectrodes and this can be achieved by coating the microelectrode with a high surface area mesoporous metal film, for example of platinum, by deposition from the hexagonal lyotropic liquid crystalline phase as described by Elliott et al.[25]. Hydrogen peroxide electrochemistry has been investigated on H\(_2\)e mesoporous Pt films (where H\(_2\)e denotes the film electroplated from the H, lyotropic liquid crystalline phase) deposited on platinum microelectrodes[2] and the steady-state response was found to be stable over a wide linear range. In a separate paper, Han et al. used hydrogen peroxide detection on an H\(_2\)e mesoporous Pt film as part of a glutamate microsensor[26].

In the present work we have investigated the use of H\(_2\)e rhodium films for hydrogen peroxide oxidation. Rhodium has the advantage that the oxide is formed at lower potential than for platinum or palladium and this should allow the use of lower potentials for hydrogen peroxide detection. In turn this offers the potential advantage of reduced interferences from other species such as ascorbate, acetamidophenol or uric acid when using the electrode in biological samples at neutral pH. Rivas et al. have used rhodinized glassy carbon for hydrogen peroxide oxidation in glucose biosensors[27-28]. Here we present results for hydrogen peroxide oxidation at H\(_2\)e Rh coated microelectrodes as a function of film thickness in pH 7 phosphate buffer and we analyse the results in terms of a mechanism which combines mass transport in the mesoporous film with reaction at the surface of the nanopores through the CEE mechanism.

2 Experimental

Platinum microdiscs were made by sealing platinum wires of the appropriate diameter into glass and were polished with a slurry of 0.3 \(\mu\)m alumina (Buehler) to obtain a fine mirror finish on a Buehler microcloth. The microelectrodes were then cleaned by cycling in sulphuric acid. All solutions were prepared using water from a Whatman Still and RO 50 water purification system.
The polished platinum disc microelectrodes were modified by the electrodeposition of a mesoporous rhodium film using a plating mixture prepared from an aqueous solution containing 47 wt.% C₈EO₅ (octaethyleneglycol monododecylether, 98% purity, Fluka), 12 wt.% RhCl₃ (99.9% purity, Sigma-Aldrich), 39 wt.% deionised water and 2 wt.% n-heptane (99% purity, Sigma-Aldrich). Heptane was added to the composition to obtain the hexagonal phase as reported by Bartlett and Marwan in their work using C₈EO₅ as the surfactant²⁹. The metal film is obtained by the electroreduction of the metal from the hexagonal lyotropic liquid crystalline phase. The exact phase was identified by polarised optical microscopy (Olympus BH-2 polarized light microscope equipped with a Linkam TMS90 heating/cooling stage and a control unit). Electrodeposition of the H₂e rhodium film was carried out at -0.2 V vs. SCE (saturated calomel electrodes) until the required charge had been passed. The electrode was then soaked in iso-propanol (HPLC, Rathburn) and then in water overnight to remove the plating mixture from the electrode surface. The thickness of the film was estimated from the deposition charge assuming 100% Faradaic efficiency and taking the idealized hexagonal structure for the mesoporous film, assuming 4.5 nm pore diameter with 6.5 nm centre to centre spacing. This gives a value for the thickness per unit charge, σ, of 289 cm·C⁻¹ for deposition on a 25 μm diameter microdisc.

Cyclic voltammetry was performed to remove any residual plating mixture from the pores by cycling between -0.70 and 0.85 V vs. SMSE (saturated mercurous sulphate electrode) at 200 mV·s⁻¹ in 1 mol·L⁻¹ sulphuric acid until a stable cyclic voltammogram was obtained (after 20 and 30 cycles). The electrodes were kept in deionised water at room temperature when not in use.

Cyclic voltammetry and electrochemical depositions were performed using an EG&G model 263A potentiostat/galvanostat. Electrochemical impedance spectroscopy was performed using an Autolab PGSTAT30. SEM images of the microelectrodes were obtained with a Philips XL30 ESEM. Transmission electron microscopy of the H₂e Rh was obtained using a JOEL 3010 TEM. The samples were prepared by scraping particles of the electrodeposition from the surface of an evaporated gold electrode onto a 300 mesh carbon TEM grid (Agar) using a scalpel blade. Small angle XRD was performed using a Bruker D5000 using 0.154 nm Cu-Kα radiation, scanning from 0.5° to 6° at 12°·min⁻¹.

Hydrogen peroxide solutions were standardised by iodometric titration according to the method of Vogel³⁰ and solutions were diluted as required in 0.1 mol·L⁻¹ pH 7 sodium phosphate buffer or water. Calibration curves for hydrogen peroxide were obtained in a water jacketed cell thermostated at 25 °C with a platinum gauze counter electrode. The potential at the working electrode (5, 10, 25 and 50 μm in diameter for microelectrodes and 0.5 cm for the RDE) was held at 0 V vs. SMSE in 0.1 mol·L⁻¹ pH 7 sodium phosphate buffer. The background current was recorded 20 min before adding 20 aliquots of H₂O₂. The solution was stirred during addition using a magnetic stirrer. After addition of H₂O₂ and stirring for 1 min, the stirring was stopped and measurement was made for 2 ~ 3 min (when the current became stable) before the next addition of H₂O₂. Rotating disc electrode measurements were carried out using an H₂e Rh coated Pt RDE (Pine Research Instrumentation AFE3T-50PT electrode and AF CPRB E rotator).

3 Results and Discussion

3.1 Characterisation of Mesoporous Rhodium Films

The mesoporous rhodium films were characterised by voltammetry, TEM and small angle X-ray diffraction. Fig. 1 shows the cyclic voltammogram of a H₂e mesoporous Rh coated microelectrode in 1 mol·L⁻¹ sulphuric acid.

The characteristics of the cyclic voltammogram for H₂e mesoporous Rh in sulphuric acid are the same as those of polycrystalline rhodium³¹. According to Jerkiewicz et al.³¹-³², different oxide films on Rh
grow with increasing potential on the anodic sweep. The first oxide formation on Rh starts at -0.2 V vs. SMSE and involves the electrochemisorption of one monolayer of OH resulting in the formation of Rh(OH) species (crosshatched area in Fig. 1). At about 0.3 V vs. SMSE further oxidation and the formation of Rh(OH)$_2$ species (shaded area in Fig. 1) occurs. These oxide species were identified for Rh electrodes in a study by Peuckert using combined X-ray Photoelectron Spectroscopy (XPS) measurements and voltammetry[33]. Simultaneously with the electroosorption of OH on the rhodium surface, a place exchange occurs between rhodium atoms and the adsorbed OH species leading to a reorganisation of the rhodium superficial layer[39]. At higher anodic potentials RhO(OH) can form but under the present conditions we believe we only form Rh(OH)$_2$ because there is only one stripping oxide peak in the cyclic voltammogram[31-32].

The hydrogen peaks for the H$_x$e mesoporous Rh film in the potential range -0.4 to -0.7 V are similar to those reported for polycrystalline Rh electrodes, with a peak for hydrogen adsorption (red hatching in Fig. 1) at -0.62 V on the cathodic sweep and for hydrogen desorption at -0.6 V vs. SMSE on the anodic sweep (blue hatching in Fig. 1). The surface area of rhodium electrodes can be calculated from the area of the oxide formation peaks by using a conversion factor of 660 $\mu$C $\cdot$ cm$^{-2}$ or from the area under the hydrogen desorption peak using a conversion factor of 221 $\mu$C $\cdot$ cm$^{-2}$[31]. The conversion factor of 660 $\mu$C $\cdot$ cm$^{-2}$ corresponds to the experimental conditions in which the scan rate was 50 mV $\cdot$ s$^{-1}$, the electrolyte was 0.5 mol $\cdot$ L$^{-1}$ H$_2$SO$_4$ and the anodic
potential limit was 1.3 V vs. NHE. Using either the hydrogen adsorption peak or the oxide stripping peak to determine the surface area is problematic because the peaks overlap. For this reason, the surface area was calculated from the hydrogen desorption peak (after subtracting the contribution from double layer charging). The resulting calculated surface area is 380 ± 50 times the geometric area of the electrode, consistent with the regular, highly porous structure expected for the HCe film.

TEM, Fig. 2, confirms the regular nanoporous structure of the HCe Rh films. Pores can be observed on the thinnest edges of the particle with rows of pores running through the metal arranged in a hexagonal array. Based on the TEM, the pore size was estimated to be 4.5 ± 0.2 nm with a wall thickness of ~ 2.0 nm. These values are similar to those reported in earlier studies of mesoporous Rh and also in studies of other mesoporous metals electrodeposited from the hexagonal lyotropic liquid crystalline phase using C_{12}EO_{8} and heptane. Small angle XRD (supplementary information) of the material shows a well resolved peak at 2θ of 2.24° corresponding to a (100) lattice spacing with a pore size of 4±1 nm.

The results of the voltammetry in acid, TEM and small angle XRD all confirm the successful electrodeposition of the nanostructured HCe Rhodium films.

![TEM image](image)

**Fig. 2** TEM image of an HCe Rh sample electrodeposited on a gold coated glass slide from a mixture of 12 wt% RhC_{13}, 47 wt% C_{12}EO_{8}, 39 wt% water and 2 wt% heptane at -0.2 V vs. SCE.

### 3.2 Voltammetry of Mesoporous Rhodium in Phosphate Buffer

Fig. 3 shows a cyclic voltammogram for an HCe Rh coated microelectrode in pH 7 phosphate buffer. The voltammetry is very similar to that in sulphuric acid (compared to Fig. 1) with the same surface processes occurring. The major difference is that the potentials are all shifted cathodically by 300 mV, there is also some broadening of the peaks. This shift is somewhat less than the predicted shift of 413 mV calculated on the basis of a shift of 59 mV per pH unit for processes involving equal numbers of protons and electrons and assuming a pH of 0 for 1 mol·L^{-1} sulphuric acid. This probably reflects a local pH change within the pores during cycling, which is consistent with observation that the peaks are somewhat broader even though the scan rate is much slower. The similarity in voltammetry confirms that the same surface oxides are involved in neutral and acid solution.

### 3.3 Voltammetry of Hydrogen Peroxide on HCe Rh at Neutral pH

Fig. 4 shows a cyclic voltammogram for an HCe Rh coated microelectrode with 5 mmol·L^{-1} hydrogen peroxide in 0.1 mol·L^{-1} pH 7 sodium phosphate buffer.
It is notable that hydrogen peroxide oxidation occurs at the same potential as the oxidation of the Rh surface to Rh(OH)$_3$ in pH 7 phosphate buffer (compared Figs. 3 and 4) and the hysteresis in the hydrogen peroxide voltammetry corresponds to the hysteresis in the formation of Rh(OH)$_3$ from Rh(OH) and the oxide stripping. The oxidation and reduction of hydrogen peroxide depend on the rhodium surface state: if the rhodium surface is in the oxidised Rh(OH)$_3$ state it can catalyse hydrogen peroxide oxidation; on the other hand, the oxide free rhodium surface catalyses the hydrogen peroxide reduction as shown by the limiting reduction current at cathodic potential. It is interesting to note that the potential of zero current in Fig. 4 corresponds to the mass transported disproportionation of hydrogen peroxide at the Rh surface:

$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$  \hspace{1cm} (1)

This same behaviour is seen on platinum but occurs around 0.2 to 0.3 V more cathodic. For a recent discussion of this reaction on Pt in the context of the oxygen reduction reaction see the recent work of Katsounaros et al.[35].

For potentials negative of -0.6 V, three peaks are observed when H$_2$O$_2$ reduction occurs: one on the anodic sweep (I) and two on the cathodic sweep (II and III). These peaks can be identified by reference to the voltammetry in phosphate buffer shown in Fig. 3; the two peaks (I) and (II) at $\sim -0.9$ V correspond to hydrogen desorption/adsorption, the cathodic peak (III) at $\sim 0.7$ V corresponds to the oxide stripping peak. The charge under peak (I) corresponds to 60 % of the charge measured for hydrogen desorption in sulphuric acid.

Using the microdisc equation

$$i_l = 4nFD[H_2O_2]_{\text{bulk}}$$  \hspace{1cm} (2)

where $n$ is the number of electrons transferred, $F$ is the Faraday, $[H_2O_2]_{\text{bulk}}$ is the concentration of the hydrogen peroxide, $D$ its diffusion coefficient and $a$ the radius of the microdisc, we can determine the diffusion coefficient for hydrogen peroxide. The limiting current was recorded for 5 mmol·L$^{-1}$ H$_2$O$_2$ in 0.1 mol·L$^{-1}$ pH 7 phosphate buffer H.e Rh coated microelectrodes with diameters of 5, 10, 25 and 50 μm, Fig. 5. In each case the diameter of the microelectrode was verified by SEM before and after deposition in case of any overgrowth of the film. From the slope (assuming $n = 2$) we obtain a value for $D$ of $1.48 \times 10^{-5} \pm 0.08 \text{ cm}^2\cdot\text{s}^{-1}$. This is in good agreement with the values reported by other authors under similar conditions: $1.43 \times 10^{-5} \pm 0.08 \text{ cm}^2\cdot\text{s}^{-1}$ van Stroe-Biezen et al.[36] in 0.1 mol·L$^{-1}$ pH 6.7 sodi-

---

**Fig. 4** Cyclic voltammogram of an H.e Rh film on a platinum disc microelectrode (25 μm diameter, 8.68 μC deposition charge) in 5 mmol·L$^{-1}$ H$_2$O$_2$, 0.1 mol·L$^{-1}$ pH 7 phosphate buffer recorded at 2 mV·s$^{-1}$. The solution was de aerated by purging with argon for at least 20 min prior to the measurements. The arrows indicate the direction of the cycle.

**Fig. 5** Limiting currents of hydrogen peroxide oxidation (corrected for double layer charging) recorded for different radii of microdisc electrodes for 5 mmol·L$^{-1}$ H$_2$O$_2$ in 0.1 mol·L$^{-1}$ pH 7 sodium phosphate buffer. The solid line represents a linear fit of the data points. The error bars correspond to measurements from three different voltammograms.
3.4 The Mechanism for Hydrogen Peroxide Oxidation

Hall et al. in a series of papers describe a CEE mechanism for the oxidation of hydrogen peroxide on Pt based on rotating disc measurements\[^{20-24}\]. The results in Figs. 4 and 6 are consistent with a similar mechanism, involving the surface Rh(OH)\(_3\) oxide species, for the reaction on rhodium.

\[
\text{H}_2\text{O}_2 + \text{Rh(OH)}_3 \rightleftharpoons \text{Rh(OH)}_2 \cdot \text{H}_2\text{O} \quad (3)
\]

\[
\text{Rh(OH)}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{Rh(OH)} + 2\text{H}_2\text{O} + \text{O}_2 \quad (4)
\]

\[
\text{Rh(OH)} + 2\text{H}_2\text{O} \rightleftharpoons \text{Rh(OH)}_2 + 2\text{H}^+ + 2\text{e} \quad (5)
\]

where \(K_M\) is the equilibrium constant for \(\text{H}_2\text{O}_2\) adsorption and \(K_w\) the rate constant for the oxidation of the adsorbed \(\text{H}_2\text{O}_2\). The \(\text{H}_2\text{O}\) Rh film comprises an hexagonal array of \(~4\) nm diameter high aspect ratio cylindrical pores separated by walls \(~2\) nm thick. For this geometry we can treat the diffusion reaction problem within the porous structure as a one dimensional problem. A similar situation for diffusion and adsorption in nanoporous silica particles has been discussed by Amatore\[^{37-38}\]. The appropriate model for one dimensional diffusion in a film coupled to complex formation and reaction has been described by Albery et al.\[^{39-41}\] and was previously used in our group to describe the oxidation of NADH at polymer modified electrodes\[^{42-44}\].

According to this model the current is given by

\[
i = nF A K_{sl} D_{sl} / L \quad (6)
\]

and

\[
y = \left[ \frac{2\alpha - \alpha \ln(1 + \alpha)}{(1 + \alpha)^2} \right] \tanh \left[ \frac{\varepsilon \ell^2 a}{2(\alpha - \alpha \ln(1 + \alpha))^2} \right] \quad (7)
\]

where \(L\) is the thickness of the film, \(D\) is the diffusion coefficient of \(\text{H}_2\text{O}_2\) in the film (assumed to be equal to the diffusion coefficient of \(\text{H}_2\text{O}_2\) in the bulk) and

\[
\varepsilon = \frac{L^2 \Gamma_{sl} k_{sl}}{DK_M} \quad (8)
\]

and

\[
\alpha = [\text{H}_2\text{O}_2]/K_M \quad (9)
\]

where \([\text{H}_2\text{O}_2]\) is the concentration at the surface of the Rh film. The film thickness was estimated...
from the deposition charge, $Q$,

$$L = \alpha Q$$  \hspace{0.5cm} (10)

where $\alpha$ was taken as 289 cm$\cdot$C$^{-1}$ for the 25 $\mu$m diameter electrodes.

The concentration of hydrogen peroxide at the electrode surface was calculated using

$$[\text{H}_2\text{O}_2]_0 = [\text{H}_2\text{O}_2]_{\text{bulk}} - \nu/nFAK'_{0b}$$  \hspace{0.5cm} (11)

where, in the case of the microdisc electrode,

$$K'_{0b} = 4D/\pi\alpha$$  \hspace{0.5cm} (12)

and we use the diffusion coefficient for hydrogen peroxide, $1.48 \times 10^{-5}$ cm$^2$ s$^{-1}$, obtained above.

Eqs. (6) to (12) define four different limiting cases for the behaviour of the system. The interrelation between the four cases together with the limiting expressions for the current in each case and expressions for the current across the boundaries of the different cases are given in Fig. 7.

The four possible cases correspond to different physical situations. In Case I the film is thin ($\varepsilon < 1$) and the concentration of H$_2$O$_2$ is insufficient to saturate the reaction sites ($\alpha < 1$). As a result the reaction occurs throughout the film and the current is first order in H$_2$O$_2$ and depends on film thickness. In Case II the film is thick ($\varepsilon > 1$) but the concentration of H$_2$O$_2$ is insufficient to saturate the reaction sites ($\alpha < 1$). Under these conditions the H$_2$O$_2$ is consumed in a first order reaction layer at the outside of the film and the current is first order in H$_2$O$_2$ but independent of the film thickness. In Case III the concentration of H$_2$O$_2$ is now sufficient to saturate the sites ($\alpha > 1$) and the film is sufficiently thin ($\varepsilon < 2\alpha$) so that the reaction of H$_2$O$_2$ occurs with zero order kinetics throughout the whole film. As a result the current is independent of H$_2$O$_2$ but increases with film thickness. In Case IV the concentration of H$_2$O$_2$ is sufficient to saturate the sites at the upper part of the pore ($\alpha > 1$) but falls as it is consumed within the film ($\varepsilon > 2\alpha$) so that the kinetics become unsaturated further into the film. Under these conditions the current is half order in H$_2$O$_2$ but independent of film thickness.

### 3.5 Analysis of Microelectrode Results

The effect of the H$_{1.4}$ Rh film thickness on the hydrogen peroxide oxidation current was investigated to test the model described above. Fig. 8 shows the calibration data for eight different thicknesses between 45 nm and 3.56 $\mu$m over the range of 0 to 75 mmol$\cdot$L$^{-1}$ of hydrogen peroxide.

At low concentrations the current increases
with increasing \( \text{H}_2\text{O}_2 \) and then becomes independent of \( \text{H}_2\text{O}_2 \) at high concentration (above 40 mmol·L\(^{-1}\)). According to our model, if the current is independent of \( \text{H}_2\text{O}_2 \) we should be in Case III but if this were correct the current should be proportional to the film thickness and this is clearly not the case.

There are several obvious possibilities to account for this discrepancy including possible inhibition by the product or physical blocking of the pores by oxygen gas generated in the reaction. We now consider these in turn. To test for product inhibition we investigated the current for hydrogen peroxide oxidation at an \( \text{H}_2\text{e} \) \( \text{Rh} \) coated rotating disc electrode in the presence, and in the absence, of oxygen in solution (data not shown) but found no evidence for inhibition by oxygen. To test for the possibility of blocking of the pores by oxygen gas bubbles generated by hydrogen peroxide oxidation we carried impedance measurement at 0 V vs. SMSE over the range 0.1 Hz to 100 kHz in the absence of hydrogen peroxide and whilst oxidising hydrogen peroxide at the porous electrode (data not shown). If oxygen gas is formed and blocks the pores there should be a significant change in the double layer capacitance of the electrode because of the decrease in electrochemical accessible surface area. Again we found no effect. We therefore consider next the possible effects of local changes in pH.

### 3.6 Effect of the Phosphate Buffer Concentration

The oxidation of hydrogen peroxide liberates protons, see Eqs. (3) to (5). In a nanoporous solid this can lead to local changes in pH if the concentration of the buffer is insufficient. This effect has been reported by Kicela and Daniele for hydrogen peroxide oxidation at platinum black electrodes\(^{[45]}\). If the solution at the bottom of the pores becomes acidic because of insufficient buffering, Fig. 9, this will shift the voltammetry of the \( \text{Rh} \) oxide so that the surface is no longer covered by \( \text{Rh(OH)}_3 \) at 0 V (see schematic voltammograms in Fig. 9) and switch off hydrogen peroxide in the bottom of the pore.

Increasing the buffer capacity will, in general, also change the ionic strength of the solution. Therefore to first test whether the current was altered by increasing the ionic strength we investigated the effect of adding \( \text{K}_2\text{SO}_4 \) while maintaining the concentration of the phosphate buffer constant. For a 'thick' mesoporous \( \text{Rh} \) film (34.72 \( \mu \text{C} \) deposition charge, \( \sim \) 3.6 \( \mu \text{m} \) thick) we observed a slight decrease (\( \sim \) 10%) in the oxidation current for hydrogen peroxide going from 0.1 mol·L\(^{-1}\) phosphate buffer to 0.1 mol·L\(^{-1}\) phosphate buffer with 0.2 mol·L\(^{-1}\) \( \text{K}_2\text{SO}_4 \) (results not shown). This can be accounted for in the slight change in the pH of the buffer solution from 7.00 to 6.83 on addition of \( \text{K}_2\text{SO}_4 \).

The effect of the buffer capacity was then investigated by changing the concentration of the phosphate buffer, Fig. 10. At low buffer capacity the current reaches a plateau at the lowest hydrogen peroxide concentration and, on increasing the buffer capacity, the response to hydrogen peroxide continues to higher concentrations. These results are consistent with hydrogen peroxide oxidation occurring further into the pore at high concentrations for higher-
Fig. 9 Schematic representation of reaction within the pore. The dashed line represents the demarcation between the phosphate buffer (pH = 7) (A) and a more acidic solution down the pore (B). The two voltammograms on the right show the Rh electrochemistry in neutral and acidic solution and the vertical solid line marks the applied potential (0 V vs. SMSE).

Fig. 10 Calibration curves at 0 V vs. SMSE for the oxidation of hydrogen peroxide at an H.e Rh coated platinum microelectrode (25 μm diameter, 34.72 μC deposition charge) for different concentrations of the phosphate buffer, pH = 7, T = 25 °C: (●) 0.2 mol·L⁻¹, (○) 0.1 mol·L⁻¹, and (▼) 0.05 mol·L⁻¹. The electrode was held at 0 V vs. SMSE for 20 min before the addition of aliquots of hydrogen peroxide. The drawings on the right indicate the approximate depth to which the hydrogen peroxide oxidation penetrates within the pore.
buffer capacity.

From Fig. 9 we can see that increasing the electrode potential should also increase the current at high concentrations of hydrogen peroxide since this will allow the \( \text{Rh(OH)}_n \) to be formed at the Rh pore surface under more acidic conditions. Fig. 11 shows a set of calibration curves recorded at different potentials.

At concentrations of hydrogen peroxide up to 25 mmol·L\(^{-1}\) the currents are linear and independent of potential. At higher concentrations, when acidification within the pores starts, the oxidation currents are higher at higher potential as expected from the model.

The calibration curve obtained at 0.2 V vs. SMSE is consistent with that of Evans et al.\(^{[10]}\) obtained at 0.6 V vs. Ag/AgCl (~ 0.2 V vs. SMSE) for an H\(_e\) Pt coated microelectrode. The values and the trend of the calibration curve in their study are similar to our present work.

Fig. 12 shows the calibration curves and the best fits for the ‘thin’ H\(_e\) Rh films to Eqs. (6) to (12) for the diffusion reaction model. The corresponding fitting parameters are given in Tab. 1. From Fig. 11 we can see that the fit to the model is good for the individual thin films and we obtain a value of ~ 20 mmol·L\(^{-1}\) for \( K_a \) with a value for \( k_{\text{cat}} \) of ~ 4 mol·cm\(^{-2}\)·C\(^{-1}\)·s\(^{-1}\) under these conditions. In this analysis we have made the simplification that the diffusion coefficient for hydrogen peroxide within the pores has the same value as the bulk. For very small pores there may be significant effects on the rate of diffusion within the pore as discussed by Amatore\(^{[37]}\). In the present case this would not have an effect on the analysis because we consider only the thin layer cases I and III where the diffusion coefficient within the pore does not occur in the expressions for the current.

4 Conclusions

Mesoporous Rh films were deposited onto platinum microelectrodes from the H\(_e\) lyotropic liquid crystalline phase. These electrodes show well defined voltammetry for the oxidation and the reduction of hydrogen peroxide at low (~10 mmol·L\(^{-1}\)) concentrations with excellent stability for operation at neutral pH. From the mass transport limited current at low concentration we obtain a diffusion coef-
Tab. 1 Fitting parameters for the best fits of the experimental results for thin H_e Rh films to the expression for the case I-III boundary. The film thicknesses were estimated from Eq. (10).

<table>
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<th>Deposition charge/μC</th>
<th>Estimated film thickness/nm</th>
<th>$k_{cat}Γ_{ads}$/(mol·cm$^{-2}$·C$^{-1}$·s$^{-1}$)</th>
<th>$K_{cat}$/mmol·L$^{-1}$</th>
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</table>

Acknowledgments

This work was supported by the EPSRC Grant EP/E0473X/1.

Supporting Information Available:

The supporting information is available free of charge via the internet at http://electrochem.xmu.edu.cn

References:


Jerkiewicz G, Borodzinski J J. Relation between the sur-


H₂O₂ 在具有纳米结构的 Rh 微电极上的电催化氧化

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摘要: 在含有 C₁₂EO₈(Octaethyleneglycol Monododecyl Ether)的 H₂O₂溶致液晶相中 Pt 微电极上电沉积 Rh 介孔膜。该电极在中性、低浓度 (H₂O₂ < 10 mmol·L⁻¹) 条件下, 对 H₂O₂有较好的氧化还原响应及稳定性。由于电流磁滞效应, H₂O₂ 在 Rh 介孔膜微电极上的氧化与电位相关, 且遵循与 Rh(OH)₃ 有关的 CEE (Chemical reaction step by two sequential electrochemical steps) 反应机制。H₂O₂ 浓度较大时, 由于孔电极表面其结合点位趋于饱和或孔内溶液酸化的反应限制, 电流呈现一平台。Rh 介孔膜厚度小于 200 nm 的电极, H₂O₂ 浓度校正曲线符合膜孔反应—维扩散模型。

关键词: H₂O₂; Rh; 微电极; 纳米孔; 溶致液晶; 模板电沉积