



Short communication

A study of the catalysis of cobalt hydroxide towards the oxygen reduction in alkaline media

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ABSTRACT

A cobalt hydroxide modified glassy carbon (Co(OH)₂/GC) electrode has been fabricated by a galvanostatic electrodeposition method. The catalytic activity for the oxygen (O₂) reduction reaction (ORR) of this electrode in alkaline media is studied by cyclic voltammetry, rotating disk electrode voltammetry, and rotating ring-disk electrode voltammetry. The O₂ reduction at the Co(OH)₂/GC disk electrode has been found to undergo an electrochemical process followed by sequential disproportionation of the electrochemical reduction intermediates, i.e., superoxide anion (O₂^{•-}) and hydrogen peroxide anion (HO₂⁻) in 0.1 M KOH solution. The Co(OH)₂ is first found to possess an excellent catalytic activity not only for the disproportionation of the O₂^{•-} produced into O₂ and HO₂⁻ but also for that of the HO₂⁻ produced, combined with electrochemical reduction of O₂ mediated by surface functional groups at the carbon electrode surface. The Co(OH)₂ is a potential electrode material for the ORR in alkaline fuel cells and metal–air batteries.

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1. Introduction

Fuel cells and metal–air batteries are expected to play significant roles as clean energy alternatives to ameliorate the worsening greenhouse effect [1,2]. For both systems, the oxygen reduction reaction (ORR) is the critical electrode chemical step responsible for the majority of electrode polarization loss [3]. To date, the noble metal platinum (Pt) is known to be the most effective electrocatalyst for the ORR in acid and alkaline low-temperature fuel cell [4–9]. However, Pt has the disadvantages of high cost and gradual degradation in catalytic activity, which limits its commercial applications. Therefore, the development of novel, low cost air electrodes in place of Pt is highly desirable. Recently, many non-Pt electrocatalyst materials including metals [10–14], metal oxides [15–18], perovskites [19–21], spinels [22,23], as well as metal macrocyclic complexes [24–28] have been investigated as an alternative catalyst to enhance the rate of the ORR.

As an important electrochemical functional material, cobalt hydroxide has been widely used as an additive to improve the electrochemical activity of alkaline secondary batteries [29,30] and as alternative electrode materials in place of noble metal oxides for supercapacitors [31–33]. In addition, cobalt hydroxide films can be

used as electrocatalytic materials for the oxidation of methanol, hydroquinone, and amino acids [34–36]. Meanwhile, little attention has been paid to the catalytic activity of cobalt hydroxide towards the ORR. Thus, the study on the catalysis of cobalt hydroxide towards the ORR is highly desirable.

In this work, we prepared cobalt hydroxide on a glassy carbon (GC) electrode by a galvanostatic electrodeposition method. The catalytic characterization and mechanism of cobalt hydroxide towards the ORR in alkaline media (0.1 M potassium hydroxide (KOH) solution) have been investigated using cyclic voltammetry, rotating disk electrode (RDE) voltammetry, and rotating ring-disk electrode (RRDE) voltammetry.

2. Experimental

2.1. Chemical and materials

Cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) was obtained from Tianjin BASF Chemical Reagent Co., Ltd., Tianjin, China. 0.1 M KOH (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) solution was prepared with Milli-Q water (MilliQ, Bedford, MA, USA) as the supporting electrolytes. Ultra-high purity nitrogen (N₂, 99.99%) and oxygen (O₂, 99.99%) gases were purchased from Qingdao Heli Gas Co., Qingdao, China and used for the deaeration of solution and the preparation of O₂-saturated solution, respectively. All reagents were of analytical grade.

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Table 1
Electrochemical parameters for ORR at the bare GC and Co(OH)₂/GC disk electrodes estimated from cyclic and RRDE voltammetry.

Electrodes	E_p^c (V) ^a	I_p^c (mA cm ⁻²) ^a	N^b	n^c	i_k (mA cm ⁻²) ^c
Bare GC disk electrode	-0.38	-0.38	0.26	2.0	1.3
Co(OH) ₂ /GC disk electrode	-0.37	-0.82	0.18	2.4	4.0

^a Obtained from Fig. 1.

^b Obtained from Fig. 5.

^c At -0.6 V (vs. Ag/AgCl, KCl-sat) and calculated from Fig. 3.

2.2. Preparation of cobalt hydroxide modified glassy carbon electrode

A rotating ring-disk electrode (RRDE, Pine Research Instrumentation, Grove City, PA, USA) with a GC disk (6 mm diameter) and a Pt ring (9 mm outer diameter and 7 mm inner diameter) was used in this study. The collection efficiency (N) of 0.37 calculated according to the geometry of the electrode is given by Pine Research Instrumentation. The disk electrode was polished firstly with #2000 emery paper, then two kinds of alumina powders with the particle size of 1 and 0.05 μm with the use of a polishing cloth, and were cleaned with Milli-Q water in an ultrasonic bath for 10 min. The cobalt hydroxide modified GC (abbreviated as Co(OH)₂/GC) disk electrode was prepared by a galvanostatic electrodeposition method. Briefly, an electrochemical cell was assembled in a three-electrode configuration in which the counter electrode was a Pt wire, the reference electrode was potassium chloride saturated silver/silver chloride (Ag/AgCl, KCl-sat), and the working electrode was a fresh GC disk electrode. An electrolyte solution of 0.1 M CoCl₂·6H₂O was used for the galvanostatic electrodeposition of cobalt hydroxide onto the GC disk electrode. The galvanostatic electrodeposition of cobalt hydroxide was carried out at a current of -2.5 mA cm⁻² for 5 s.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a conventional one-compartment, three-electrode cell with the bare GC disk electrode and Co(OH)₂/GC disk electrode as working electrodes, a Ag/AgCl (KCl-sat) electrode (+0.966 V vs. reversible hydrogen electrode (RHE)) as reference electrode, and a Pt wire as counter electrode. The electrolyte, 0.1 M KOH solution, was bubbled with pure O₂ or N₂ for at least 30 min to make a solution saturated with O₂ or N₂, respectively, and the corresponding experiments were carried out under O₂ or N₂ atmosphere. Cyclic voltammetry, RDE voltammetry, and RRDE voltammetry were conducted with a computer-controlled electrochemical system (CHI 760C, CH Instruments, Inc., Austin, TX, USA). RDE and RRDE measurements were conducted with a motor speed controller (Pine Research Instrumentation, Grove City, PA, USA). In RRDE measurement, a constant potential of +0.5 V (vs. Ag/AgCl, KCl-sat) was applied at the Pt ring electrode for the oxidation of HO₂⁻ produced at the disc electrode. All the experiments were conducted at room temperature of 25 ± 2 °C.

3. Results and discussion

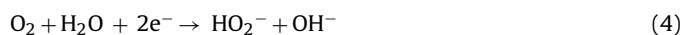
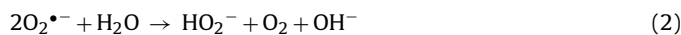
3.1. Cyclic voltammetric study on ORR catalyzed by cobalt hydroxide

Cyclic voltammograms for the ORR (curve a and curve a') obtained at the bare GC disk electrode and the Co(OH)₂/GC disk electrode (curve b and curve b') in 0.1 M KOH solution are shown in Fig. 1, and the first reduction peak potentials for the ORR at the individual electrodes are given in Table 1. As shown, the GC disk electrode exhibits an obvious reduction peak at ca. -0.38 V

(vs. Ag/AgCl, KCl-sat) (+0.59 V vs. RHE) in the potential window employed (curve a). This reduction process can be documented to be a 1-electron reduction of O₂ to O₂^{•-} (reaction (1)), which is electrochemically mediated by the quinone (Q)-like functional groups at the surface of the GC electrode [37–40]. The rate of reaction (1) is pH independent [41].



Once produced, the O₂^{•-} can disproportionate into O₂ and HO₂⁻ as given by reaction (2), or be reduced electrochemically to HO₂⁻ as given by reaction (3). Both of these processes are considered to be fast. The rate of reaction (2) is largely dependent on solution pH and electrolyte, and obviously decreases with increasing solution pH. This reveals that the O₂^{•-} produced can stably exist in a highly basic solution [42]. Moreover, an ill defined reduction peak at ca. -0.80 V (vs. Ag/AgCl, KCl-sat) (+0.17 V vs. RHE) can be observed in Fig. 1. This process can be attributed to be a direct 2-electron reduction of O₂ to HO₂⁻ (reaction (4)) at the bare GC electrode, which is not mediated by Q-like group at the surface of the GC electrode [37–40].



As shown in Fig. 1, in N₂-saturated KOH solution, the cyclic voltammetric response of the Co(OH)₂/GC disk electrode is featureless and the presence of Co(OH)₂ on the GC electrode does not yield any cyclic voltammetric waves (curve b'), which shows that the Co(OH)₂ used here is electro-inactive in the potential window employed and will not redox-mediate the ORR. However, as can be seen in Fig. 1 (curve b) and Table 1, the presence of Co(OH)₂ on the GC disk electrode greatly increased the first and second peak currents compared with the case when it is absent, indicating that the Co(OH)₂ has a high catalytic activity towards the ORR. However, it

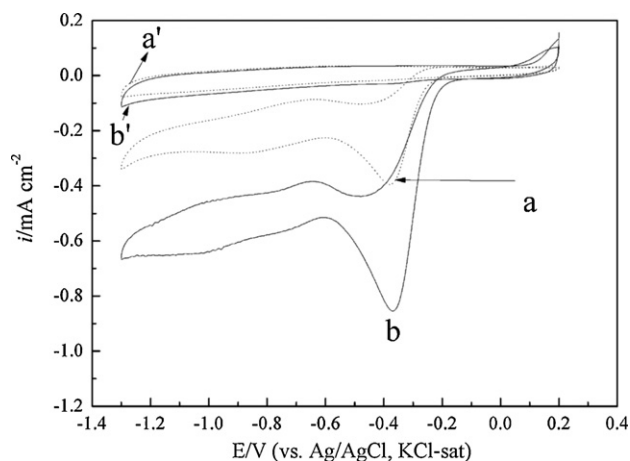


Fig. 1. Cyclic voltammograms with a scan rate of 100 mV s⁻¹ for the ORR at (a and a') a bare GC and (b and b') a Co(OH)₂/GC disk electrodes in O₂-saturated (a and b) and N₂-saturated (a' and b') 0.1 M KOH solutions.

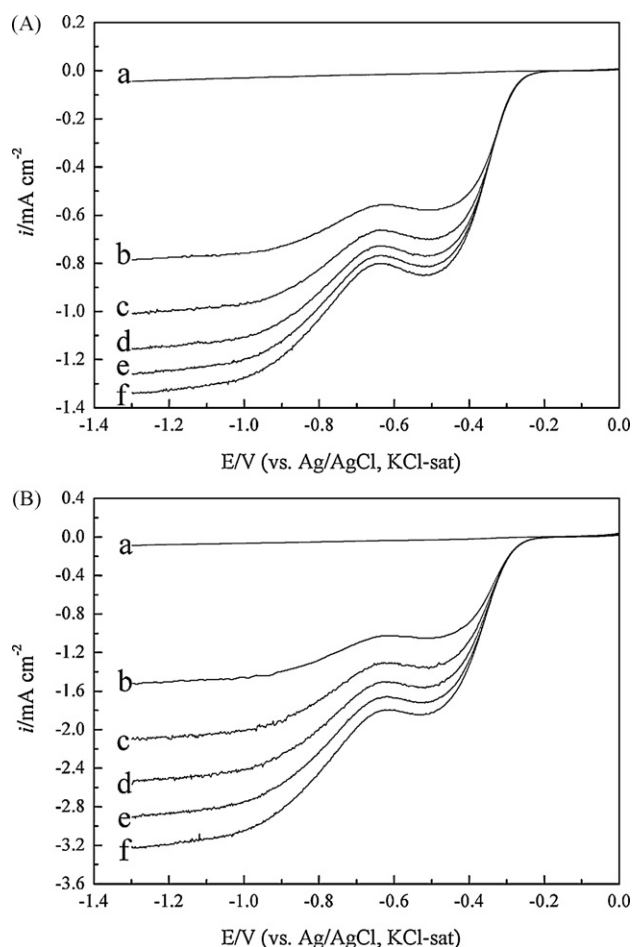


Fig. 2. RDE voltammograms with a scan rate of 10 mV s^{-1} for the ORR at (A) a bare GC disk electrode and (B) a $\text{Co(OH)}_2/\text{GC}$ disk electrode in (a) N_2 -saturated and (b–f) O_2 -saturated 0.1 M KOH solutions at a rotating rate of (b) 200 rpm , (a and c) 400 rpm , (d) 600 rpm , (e) 800 rpm , and (f) 1000 rpm .

can also be observed in Fig. 1 (curve b) and Table 1 that the first reduction potential towards the ORR shows almost no changes. As addressed above, the reduction of O_2 mediated by Q-like functional groups mainly produces $\text{O}_2^{\bullet-}$, which undergoes a slow disproportionation to produce HO_2^- and O_2 . However, in the 0.1 M KOH solution used in this case, the $\text{O}_2^{\bullet-}$ generated in the mediated reduction of O_2 is highly stable. Therefore, these results suggest that the Co(OH)_2 -catalyzed reaction (2) is an important factor for the observed increase in the peak current at the $\text{Co(OH)}_2/\text{GC}$ disk electrode and the re-reduction of the O_2 replenished from reaction (2) is responsible for the observed increase of peak current.

3.2. RDE voltammetry and transfer electron number for ORR

The RDE voltammograms obtained at the bare GC disk electrode and the $\text{Co(OH)}_2/\text{GC}$ disk electrode with various rotation rates of 200 , 400 , 600 , 800 , and 1000 rpm are shown in Fig. 2A and B, respectively. As shown in Fig. 2A, the ORR at the bare GC electrode certainly takes place under diffusion control with a half-wave potential at -0.35 V (vs. Ag/AgCl, KCl-sat) ($+0.62 \text{ V}$ vs. RHE), and the disk current passes through a maximum at -0.50 V (vs. Ag/AgCl, KCl-sat) ($+0.47 \text{ V}$ vs. RHE). Similar current maxima have been previously observed for GC electrodes in alkaline solution [18,39,40]. It can be observed in Fig. 2B that the presence of Co(OH)_2 only increases the disk current at the same rotation rate and does not change the half-wave potential of the first reduction process, which is consistent with the results of cyclic voltammetry.

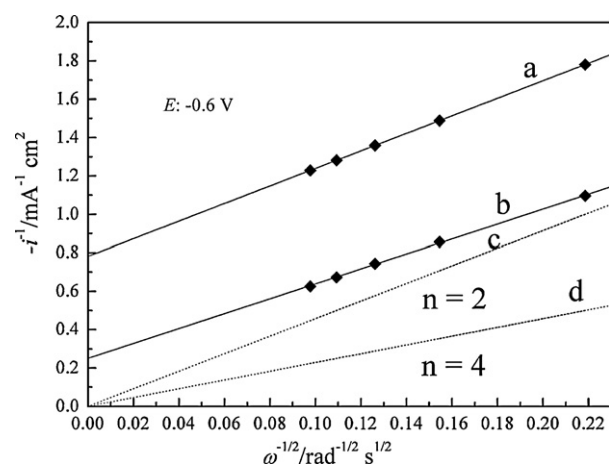


Fig. 3. Koutecký-Levich plots of the rotating disk current at -0.6 V (vs. Ag/AgCl, KCl-sat) obtained at (a) a bare GC disk electrode and (b) a $\text{Co(OH)}_2/\text{GC}$ disk electrode in O_2 -saturated 0.1 M KOH solution. The dotted lines of c and d correspond to the theoretical slopes calculated assuming the 2- and 4-electron processes for the ORR, respectively.

The number (n) of electrons transferred per O_2 molecule in the ORR can be estimated from Koutecký-Levich (K-L) plots using RDE voltammetry. The K-L plots, expressed as Eq. (5), obtained from RDE voltammograms (Fig. 2) are shown in Fig. 3 in which the limiting currents at -0.6 V (vs. Ag/AgCl, KCl-sat) are used.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62 n F C_0 D_0^{2/3} \nu^{-1/6} \omega^{1/2}} \quad (5)$$

where i is the disk current density, i_k is the kinetically current density, ω is the angular velocity of rotation, and F is the Faraday constant ($96,485 \text{ C mol}^{-1}$). The value of the concentration of O_2 (C_0), the diffusion coefficient of O_2 (D_0) in 0.1 M KOH solution, and the kinematic viscosity (ν) of 0.1 M KOH solution are cited as $1.15 \times 10^{-3} \text{ M}$, $1.95 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $0.008977 \text{ cm}^2 \text{ s}^{-1}$, respectively [43].

The lines c and d in Fig. 3 represent the theoretical slopes calculated by assuming the 2- and 4-electron reduction of O_2 with Eq. (5). The plots a and b obtained for the bare GC disk electrode and the $\text{Co(OH)}_2/\text{GC}$ disk electrode are almost parallel to the theoretical line for the 2-electron reduction of O_2 (line c in Fig. 3). From the slopes of the K-L plots shown in Fig. 3, the value of n for the ORR at a bare GC disk electrode was estimated to be 2.0, whereas the value of n for the ORR at a $\text{Co(OH)}_2/\text{GC}$ disk electrode was estimated to be 2.4, indicating that a small fraction of the HO_2^- produced can be further reduced by the presence of cobalt hydroxide.

The values of i_k for the ORR at -0.6 V (vs. Ag/AgCl, KCl-sat) on the individual electrodes were also calculated using Eq. (5) and the intercepts of the K-L plots. The results are listed in Table 1. For the 2-electron reduction of O_2 , the i_k value obtained at the $\text{Co(OH)}_2/\text{GC}$ disk electrode is ca. 3 times than that at the bare GC disk electrode, indicating that the Co(OH)_2 has a high catalytic activity towards the ORR.

3.3. RRDE voltammetry for ORR

The catalytic mechanism of cobalt hydroxide towards the ORR was further investigated by RRDE voltammetry. O_2 reduction occurs on a bare GC disk electrode and a $\text{Co(OH)}_2/\text{GC}$ disk electrode, and HO_2^- produced at the disk electrode, is oxidized at Pt ring electrode as shown in Fig. 4. At the bare GC disk electrode, two reduction steps (curve a in Fig. 4B) were obtained that essentially correspond to reactions (1) and (4) obtained with cyclic voltammetry (curve a in Fig. 1). The presence of cobalt hydroxide at the

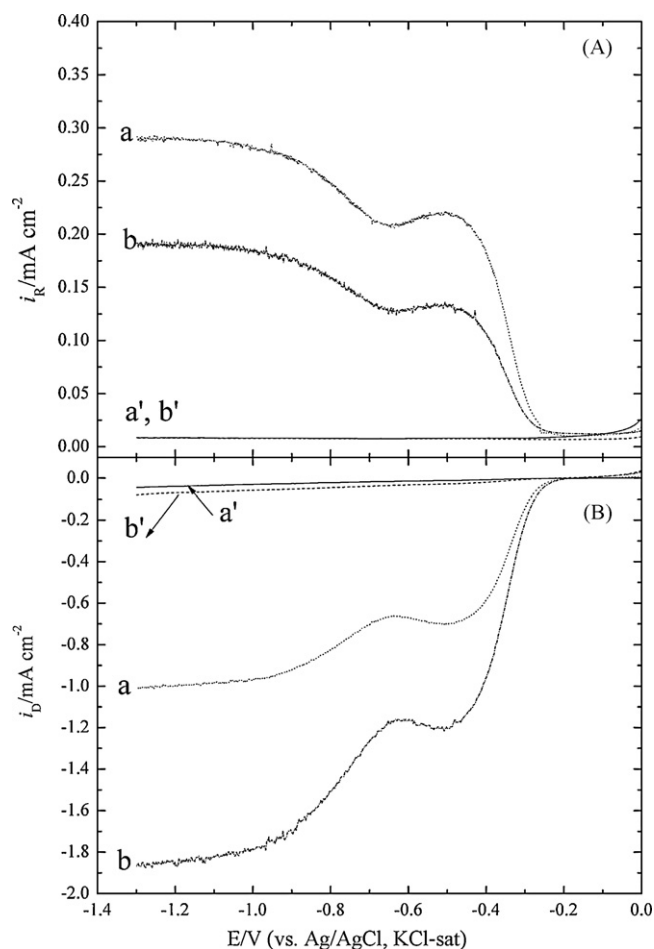


Fig. 4. RRDE voltammograms for ORR at (a and a') a bare GC disk electrode and (b and b') a $\text{Co}(\text{OH})_2/\text{GC}$ disk electrode and Pt ring electrodes in (a and b) O_2 -saturated and (a' and b') N_2 -saturated 0.1 M KOH solutions. Rotation rate: 400 rpm. Scan rate: 10 mV s^{-1} . The ring electrode was polarized at +0.5 V (vs. Ag/AgCl, KCl-sat). i_D and i_R show the current density at the disk and ring electrodes, respectively.

bare GC disk electrode clearly increases the disk current (curve b in Fig. 4B), whereas it decreases the ring current for the oxidation of HO_2^- (curve b in Fig. 4A). These results suggest that the presence of cobalt hydroxide has the properties of accelerating HO_2^- disproportionation (reaction (6)) [38].



This process can also replenish O_2 , which can result in the increase in the reduction peak currents of O_2 to $\text{O}_2^{\bullet-}$ (curve b in Fig. 1). As addressed above, the presence of cobalt hydroxide has a bifunctional catalytic activity for the change in the peak currents of the $\text{O}_2/\text{O}_2^{\bullet-}$ couple (reaction (1)) (curve b in Fig. 1). That is, $\text{O}_2^{\bullet-}$ and HO_2^- produced from the O_2 reduction is consumed by sequential cobalt hydroxide-catalyzed disproportionations, i.e., first through the disproportionation of $\text{O}_2^{\bullet-}$ (reaction (2)) and then through the disproportionation of HO_2^- to give the final product of OH^- (reaction (6)). The subsequent reduction of O_2 replenished from the sequential disproportionation reactions increases the reduction peak.

The collection efficiency (N) of the RRDE is defined by:

$$N = \frac{N_R}{N_D} \quad (7)$$

where N_D is the number of moles of a disk product produced in a given time and N_R is the number of moles of a disk product collected at the ring. The value of N can be determined according to Eq. (8)

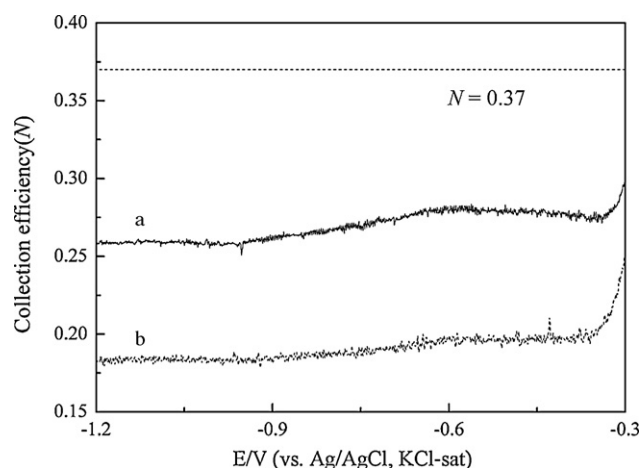


Fig. 5. The relationship between collection efficiency (N) and potential obtained at (a) a bare GC and (b) a $\text{Co}(\text{OH})_2/\text{GC}$ disk and Pt ring electrode.

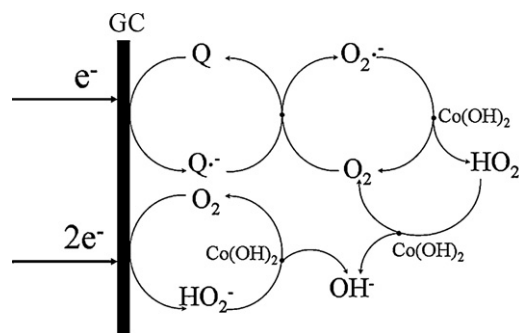


Fig. 6. Schematic illustration of the catalytic reduction pathway of O_2 with cobalt hydroxide ($\text{Co}(\text{OH})_2$) as the catalyst on a GC electrode in alkaline media. Q and $\text{Q}^{\bullet-}$ represent the redox couple of the quinone-like functional groups on the surface of the GC electrode.

[44].

$$N = \frac{I_R}{I_D} \quad (8)$$

where I_R and I_D are the respective ring and disc currents following at the same voltage. The electrocatalytic activity of the cobalt hydroxide towards the ORR may be further seen from the plots of N vs. electrode potential as shown in Fig. 5. The values of N at the $\text{Co}(\text{OH})_2/\text{GC}$ disk electrode in the potential range of -0.3 to -1.2 V (vs. Ag/AgCl, KCl-sat) are smaller than that obtained at the bare GC disk electrode, which further suggests higher catalytic activity of the present cobalt hydroxide for the disproportionation of HO_2^- .

In summary, the efficient coupling of the mediated reduction of O_2 with the sequent disproportionation reactions (2) and (6) substantially enables a quasi-4-electron reduction of O_2 at the cobalt hydroxide modified GC electrode as schematically depicted in Fig. 6, in which cobalt hydroxide shows good bifunctional catalytic behavior towards both reactions (2) and (6).

4. Conclusions

The present results demonstrate that the presence of cobalt hydroxide on the GC electrode has a high catalytic activity for the ORR in alkaline media. Cobalt hydroxide was first found to possess bifunctional catalytic activity for the sequential disproportionations of $\text{O}_2^{\bullet-}$ and HO_2^- in alkaline media. This finding not only demonstrates the catalytic mechanism of cobalt hydroxide towards the ORR in alkaline media, but also suggests a novel strategy for

developing new non-Pt based air electrodes with high performance for new metal–air batteries and advanced fuel cells.

Acknowledgments

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