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Nanoparticles of Fe₂O₃ and Co₃O₄ as Efficient Electrocatalysts for Oxygen Reduction Reaction in Acid Medium

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This paper presents a comparative study about the oxygen reduction reaction (ORR) catalyzed by nanoparticles of Fe₂O₃ and Co₃O₄ applied on the surface of glassy carbon electrodes (GCE). The nanoparticles were synthesized using the modified polymeric precursor method (Pechini). These two nanomaterials were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. The estimated average particle sizes were 21 and 31 nm for Fe₂O₃ and Co₃O₄, respectively. Electrochemical impedance spectroscopy (EIS) showed that Fe₂O₃/GCE has lower charge transfer resistance than Co₃O₄/GCE. The surface electrochemistry of both Fe₂O₃/GCE and Co₃O₄/GCE was studied in the solution free of O₂, and their corresponding reaction mechanisms were analyzed. The electrocatalytic ORR activities of these two catalysts were studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) in acidic solution. The results obtained by RDE indicated that both Fe₂O₃/GCE and Co₃O₄/GCE can catalyze the ORR with a dominating 2-electron transfer process to produce H₂O₂, using a potential of -0.8 V. These kinetic results indicate that Fe₂O₃/GCE is more efficient than Co₃O₄/GCE in terms of ORR. Considering the low cost of these two non-noble metal catalysts, they may be used as viable alternatives for ORR electrocatalysts.

Keywords: electrocatalysis, metallic nanoparticles, iron oxide, cobalt oxide, oxygen reduction

Introduction

In electrochemical energy storage and conversion devices such as fuel cell and metal-air batteries, the applications of electrocatalysts for cathode oxygen reduction reaction (ORR) are of paramount importance.^{1,2} As recognized, ORR in aqueous solutions occurs mainly through two pathways: one is the direct 4-electron reduction from O₂ to water (H₂O), and the other is the 2-electron reduction from O₂ to hydrogen peroxide (H₂O₂). In general, the ORR kinetics on electrodes is sluggish. To speed up

this reaction for a practical operation, electrocatalysts are necessary. Normally, platinum (Pt) and its alloys are used as electrocatalysts for ORR. However, Pt is expensive hindering its large-scale commercialization in electrochemical conversion technologies such as fuel cells and metal-air batteries.³ Thus, researchers have made great efforts to replace Pt-based catalysts with non-precious metal ones for enabling the practical application of the technologies, and these metals have been considered for both, cathode⁴⁻⁶ and anode of fuel cells.⁷⁻⁹ Regarding non-precious metal electrocatalysts, many types have been explored, including metal oxides, organometallic complexes, and so on.¹⁰

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Among non-precious metal oxide materials, iron (Fe) and cobalt (Co) oxides have been extensively investigated as electrocatalysts for ORR. For example, Wu *et al.*¹¹ synthesized iron oxide (Fe₃O₄) nanoparticles supported on nitrogen-doped graphene airgel (Fe₃O₄/N-GAs), and found its high catalytic activity towards ORR, and claimed that their catalyst had an even higher durability than the commercial Pt/C. Chen *et al.*¹² reported that a nanostructured cobalt oxide (Co₃O₄) supported on hollow carbon spheres (Co₃O₄/HCS) was an efficient catalyst for ORR in basic media. Recently, iron oxide nanoparticles in different phases (Fe₃O₄, γ -Fe₂O₃, α -Fe₂O₃ and α -FeOOH) forming a composite with reduced graphene oxide aerogels,¹³ and cobalt oxide with nitrogen-doped graphene (Co-N/G),¹⁴ were used as electrocatalysts, showing good catalytic ORR performance.

The synthesis method can significantly influence the sizes of nanoparticles, and this is a determinant factor in the electrocatalytic ORR performance. The existing methods, such as sol-gel,¹⁵ liquid combustion,¹⁶ spraydrying,^{17,18} hydrothermal^{19,20} and the polymeric precursor are proved to be efficient. Among them, the polymeric precursor method, also called Pechini,²¹⁻²³ stands out as a promising technique for the preparation of crystalline and nanometric metal oxides with controlled particle sizes. Actually, to our best knowledge, there is no work yet found for using this polymeric precursor method to synthesize ORR electrocatalysts, which is why we have chosen this method to synthesize the catalysts in this paper.

In this paper, we have synthesized nanoparticles of iron and cobalt oxides (Fe₂O₃ and Co₃O₄) using the polymeric precursors method and explored their catalytic ORR performance in acidic medium. The synthesized catalysts were characterized using the techniques of Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The electrocatalytic ORR activity of the catalyst-modified electrodes was evaluated by cyclic voltammetry (CV), linear scanning voltammetry (LSV), and rotational disk electrode (RDE). The electrochemical impedance spectroscopy (EIS) was also used to analyze the electron/mass transfer resistances related to the catalytic ORR process.

Experimental

Reagents

All reagents used in this work were analytical grade and used without further purification. Cobalt(II) chloride hexahydrate, iron(II) chloride tetrahydrate, citric acid, ethylene glycol, boric acid, sodium perchlorate monohydrate, and sodium hydroxide were all purchased from Merck (Darmstadt, Germany). Sulfuric acid and

Nafion[®] were purchased from Sigma-Aldrich (Saint Louis, USA), acetic acid and phosphoric acid were purchased from Vetec (Saint Louis, USA). The study of pH influence on the electrochemical response was performed using the Britton-Robson (BR) buffer prepared in the usual way, i.e., by mixing solutions of phosphoric acid, acetic acid and boric acid, all 0.04 mol L⁻¹, whose solution had a pH close to 1.8. An appropriate amount of 2 mol L⁻¹ sodium hydroxide solution was added dropwise to the solution to adjust the pH as desired. All solutions were prepared using deionized water (18 M Ω cm resistance), purified by a Milli-Q system (Millipore Inc., USA).

Synthesis of nanoparticles of iron and cobalt oxides

The nanoparticles of the metal oxides (Fe₂O₃ and Co₃O₄) were synthesized by the polymeric precursor method. First, 7.0 g of the metal precursor (cobalt(II) chloride hexahydrate or iron(II) chloride tetrahydrate) were added to 50 mL of water under constant stirring at 80 °C until the complete dissolution of the salt. Then citric acid (20.29 g for cobalt(II) chloride hexahydrate solution, or 16.96 g for iron(II) tetrahydrate chloride solution) was added with a mole ratio of metal to acid of 1:3 for the formation of metal citrate solution. The temperature was then raised to 120 °C, and ethylene glycol (12.18 g for cobalt(II) chloride hexahydrate solution, or 10.18 mL for iron(II) chloride tetrahydrate solution) was added in a ratio of the ethylene glycol to metal of 60:40 (%m/m) for polymerization to occur. The obtained gel was dried in an oven (ca. 100 °C) for 24 h to remove excess water. After the procedure above, the obtained material was subjected to a calcination process at a temperature of 300 °C for 2 h to form the puff, which was ground, and again calcined at 500 °C for 2 h for obtaining the metal oxides.²¹⁻²³

Modification of working electrode and electrochemical measurements

For the modification of the glassy carbon electrode (GCE) with the catalysts, a suspension at the concentration of 3.0×10^{-3} mol L⁻¹ of catalyst nanoparticles (Fe₂O₃ or Co₃O₄) in deionized water with 1% of Nafion[®] was prepared under ultrasonication for 5 min at room temperature. Prior to modification, the GCE surface was buffed with alumina and rinsed with deionized water. After cleaning, a 15 μ L aliquot of the catalyst suspension was deposited onto the GCE surface, and then the modified electrode was taken to the desiccator for vacuum drying. The catalyst loadings for both Fe₂O₃ or Co₃O₄ were approximately 6.43×10^{-4} mmol cm⁻².

The electrochemical experiments were performed using a potentiostat model PGSTAT 302 from Metrohm-Autolab. A conventional three-electrode cell containing the catalyst-modified disk GCE with a geometric surface (A_{geom}) of 0.07 cm^2 as the working electrode was employed for both the cyclic voltammetry and rotating disk electrode experiments. $\text{Ag}_{(\text{s})}|\text{Cl}_{(\text{s})}|\text{Cl}^- (\text{KCl}_{\text{sat}})$ was used as the reference electrode and a platinum wire as the counter electrode. For the measurements with rotating disk electrode, a controller of rotation from Autolab (motor controller) was used.

The O_2 -saturated standard solution was produced by bubbling double distilled water with pure O_2 at room temperature for 1 h. The O_2 content in the O_2 saturated water was taken as $1.21 \times 10^{-3} \text{ mol L}^{-1}$, calculated as recommended by the literature.²⁴⁻²⁶ The electrochemical measurements were carried out in a 25 mL cell with 10 mL solutions which were purged with pure nitrogen and kept under nitrogen atmosphere at room temperature.

Results and Discussion

Physical-chemical characterization of the catalysts

Infrared spectra (FTIR) of the synthesized catalyst materials (Fe_2O_3 and Co_3O_4) were recorded on a Shimadzu IR Prestige-21 spectrometer in the wavenumber region of 400 to 4000 cm^{-1} . The test samples were prepared in KBr pellets (1%). The XRD analysis was performed using a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ angle range between 10 and 80° .

Figure 1 shows the infrared spectra obtained in the region of 400 to 4000 cm^{-1} for Fe_2O_3 and Co_3O_4 samples, respectively. The spectrum obtained for Fe_2O_3 shows intense bands at 452 and 551 cm^{-1} , which are related to the transverse stretching vibrations of $\text{Fe}-\text{O}$.^{27,28} The weak band at 1050 cm^{-1} can be attributed to hematite,²⁹ and the one at 2345 cm^{-1} can be attributed to air CO_2 . Similar behavior was observed by Eigler *et al.*³⁰ For Co_3O_4 , the bands at 567 and 665 cm^{-1} are related to the $\text{Co}-\text{O}$ stretching vibrations. The presence of these bands supports the formation of the Co_3O_4 spinel network. The band at 567 cm^{-1} corresponds to the stretching of the $\text{Co}^{3+}-\text{O}$ bond, while the band at 665 cm^{-1} can be attributed to the $\text{Co}^{2+}-\text{O}$ stretching vibration. These assignments are in accordance with the literature,^{31,32} thus confirming the formation of metallic spinel structure.

XRD analysis was performed to investigate the phase and structure of the synthesized catalyst materials. The diffractogram obtained for iron oxide (Figure 2) shows the diffraction peaks at 2θ of 24.2° , 30.2° , 35.6° , 41° , 49.5° , 54.1° , 57.5° , 62.4° , and 64.1° , corresponding to

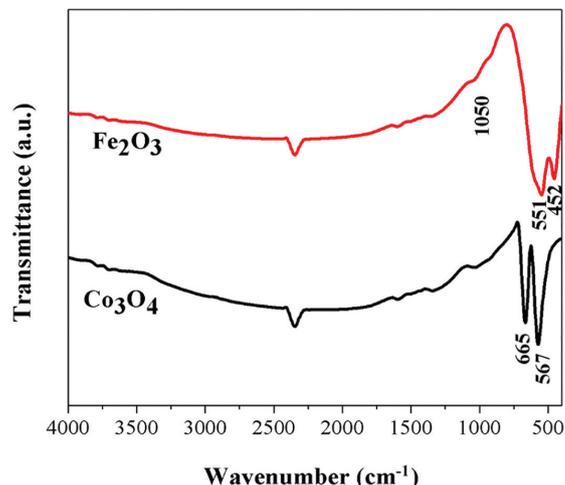


Figure 1. FTIR spectra (KBr) of the Fe_2O_3 and Co_3O_4 samples.

the planes 012, 104, 110, 113, 024, 116, 018, 214, and 300, respectively, for $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, which can be easily indexed to their hexagonal phase, as reported by Mirzaei *et al.*²¹ The peak at 2θ of 43° is assigned to plane 400 of magnetite (Fe_3O_4).³³⁻³⁵ Cobalt oxide (Figure 2) exhibits peaks at 2θ 19.1° ; 31.3° ; 36.8° ; 38.5° ; 44.9° ; 55.7° ; 59.4° ; 65.2° ; referring to planes 111, 220, 311, 222, 400, 422, 511, and 440, respectively.^{36,37} The positions of these peaks can be indexed to Co_3O_4 structure in cubic spinel. This phase is characteristic of the cubic face centered structure, which coincides with that presented by Gunnewiek *et al.*²² The format of the diffractogram coincides with those reported in previous works.^{37,38}

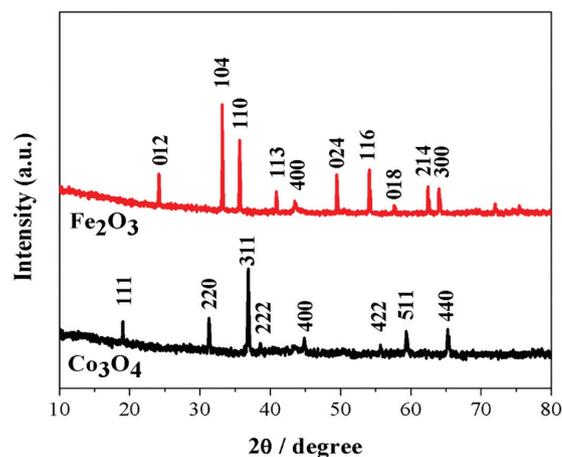


Figure 2. Diffractograms of Fe_2O_3 and Co_3O_4 catalyst samples.

The crystallite dimensions were estimated by applying the Scherrer method³⁹ (equation 1) to the diffractograms shown in Figure 2.

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where d is the size of the crystallites (nm), λ is the wavelength of the Cu K α radiation (0.154 nm), β is the width at half height in radians, and θ is the Bragg angle in the plane relative to the peak. The average sizes of the calculated crystallites are approximately 21 and 31 nm for the nanoparticles of Fe₂O₃ and Co₃O₄, respectively. These results show the efficiency of the method in synthesizing the nanoparticles of the catalysts. Compared with those reported in literature, the catalyst nanoparticle sizes are smaller: Gunnewiek *et al.*²² obtained Co₃O₄ nanoparticles with a mean diameter of 36 nm, and Mirzaei *et al.*²¹ obtained an approximate value of 70 nm for α -Fe₂O₃. Compared with the sample obtained by hydrothermal method, the nanoparticle sizes of α -Fe₂O₃ crystallites were 45–65 nm, which are larger than ours. Sahoo and Satpati³¹ also used the hydrothermal method and obtained Co₃O₄ nanoparticles with a mean size of 50 nm. All these results above show that the polymeric precursor method is more efficient in obtaining nanoparticles with smaller sizes.

Electrochemical behavior of GCE modified with Fe₂O₃ and Co₃O₄

Figure 3a shows the cyclic voltammograms of GCEs modified with Fe₂O₃ and Co₃O₄, respectively, recorded between –0.8 and 0.9 V vs. Ag_(s)|Cl_(s)|Cl[–] (KCl_{sat}), in BR buffer pH 1.8, saturated with N₂. For comparison, those results with bare GCE are also displayed in the figure.

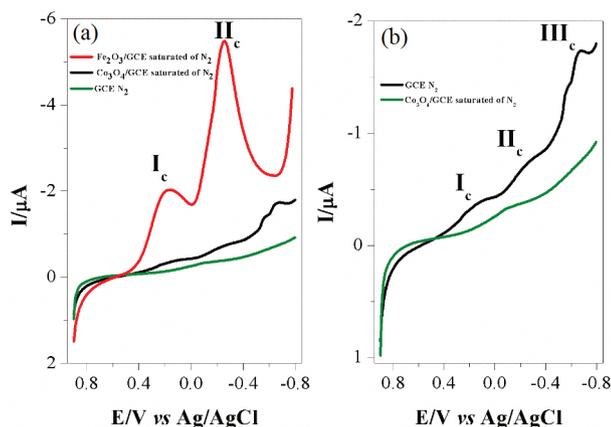


Figure 3. (a) Linear scanning voltammograms (LSV) obtained in 0.1 mol L^{–1} BR buffer (pH 1.8) saturated with N₂ at GCE (olive-green line), Fe₂O₃/GCE (red line) and Co₃O₄/GCE (black line) with a catalyst loading of 0.643 mg cm^{–2}; (b) GCE (olive-green line) and Co₃O₄/GCE (black line). Potential scan rate: 20 mV s^{–1}. The scan directions for all curves are from left to right.

In Figure 3a, there is no significant redox process observed on the unmodified GCE electrode. Note that there is a small reduction wave around –0.1 V, which comes from the C=O group on the carbon surface. For Fe₂O₃/GCE, two

cathodic peaks can be observed, which are marked as: I_c and II_c, located at 0.21 and –0.255 V vs. Ag/AgCl, respectively. By referring to literature^{40,41} these peaks can be proposed to the following two reactions:

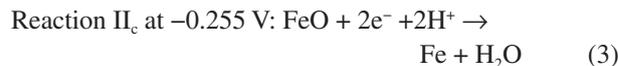
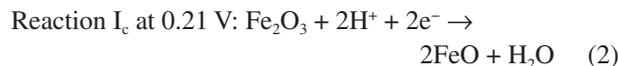
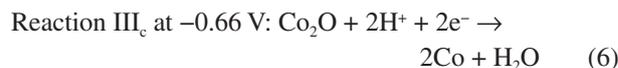
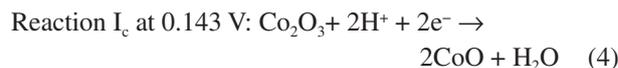


Figure 3b shows the enlarged voltammogram of only Co₃O₄/GCE from Figure 3a, in which three processes marked as I_c, II_c and III_c can be clearly observed. These three redox processes may be assigned to equations 4, 5 and 6, respectively, by referring to the literature^{42,43} for acidic redox processes of Co₃O₄. Actually, Co₃O₄ is a mixed oxide containing CoO and Co₂O₃, which can be expressed as CoO.Co₂O₃. The process I_c at 0.143 V may be assigned to Co³⁺/Co²⁺ according to equation 4. The process II_c at –0.261 V refers to Co²⁺/Co⁺ redox reaction expressed by equation 5. The process III_c at –0.66 V may be assigned to the redox reaction of Co⁺/Co⁰.



Electrocatalytic ORR performance of both Fe₂O₃/GCE and Co₃O₄/GCE

Figure 4 shows the cyclic voltammograms (CVs) of GCE, Fe₂O₃/GCE and Co₃O₄/GCE in BR buffer pH 1.8 saturated by oxygen (1.3 × 10^{–3} mol L^{–1}). For comparison, cyclic voltammograms in the absence of oxygen were also recorded. It can be seen that, although the unmodified GCE shows an insignificant ORR activity in the presence of oxygen, the electrode modified with Fe₂O₃ or Co₃O₄ gives significantly enhanced ORR current, demonstrating that both Fe₂O₃ and Co₃O₄ have strong catalytic ORR activities. The current densities obtained in this experiment for ORR by Fe₂O₃/GCE and Co₃O₄/GCE were 40 and 30 μA, respectively, showing that the modification with iron oxide presents a significant increase in current densities. For Fe₂O₃/GCE, the electrocatalytic process occurs close to the redox response of Fe³⁺ (peak II_c), indicating that the

Fe^{2+} metal center is responsible for the electrocatalytic process of ORR. Wu *et al.*¹¹ obtained similar behavior using Fe oxide nanoparticles supported on graphene. For the $\text{Co}_3\text{O}_4/\text{GCE}$, the process occurs near the peak III_c , which corresponds to $\text{Co}^{3+}/\text{Co}^{2+}$, indicating that this Co^{2+} metal center is responsible for the electrocatalytic ORR activity. This result is similar to that reported by Chen *et al.*¹²

From Figure 4, it can also be observed that, under the same conditions, $\text{Fe}_2\text{O}_3/\text{GCE}$ can give higher ORR than $\text{Co}_3\text{O}_4/\text{GCE}$. For this phenomenon may have contributed two factors, one is the higher intrinsic catalytic ORR activity of the former than the latter, and the second is the size effect of the catalyst nanoparticles. The average size of Fe_2O_3 particles is smaller than that of Co_3O_4 , as analyzed by diffractograms in Figure 2. The small-sized Fe_2O_3 can have a larger contact surface, therefore, a higher catalytic current can be expected.^{44,45}

Effect of potential scanning rate on ORR activity

Figure 5 shows the linear sweep voltammograms obtained at different potential rates from 5 to 500 mV s^{-1}

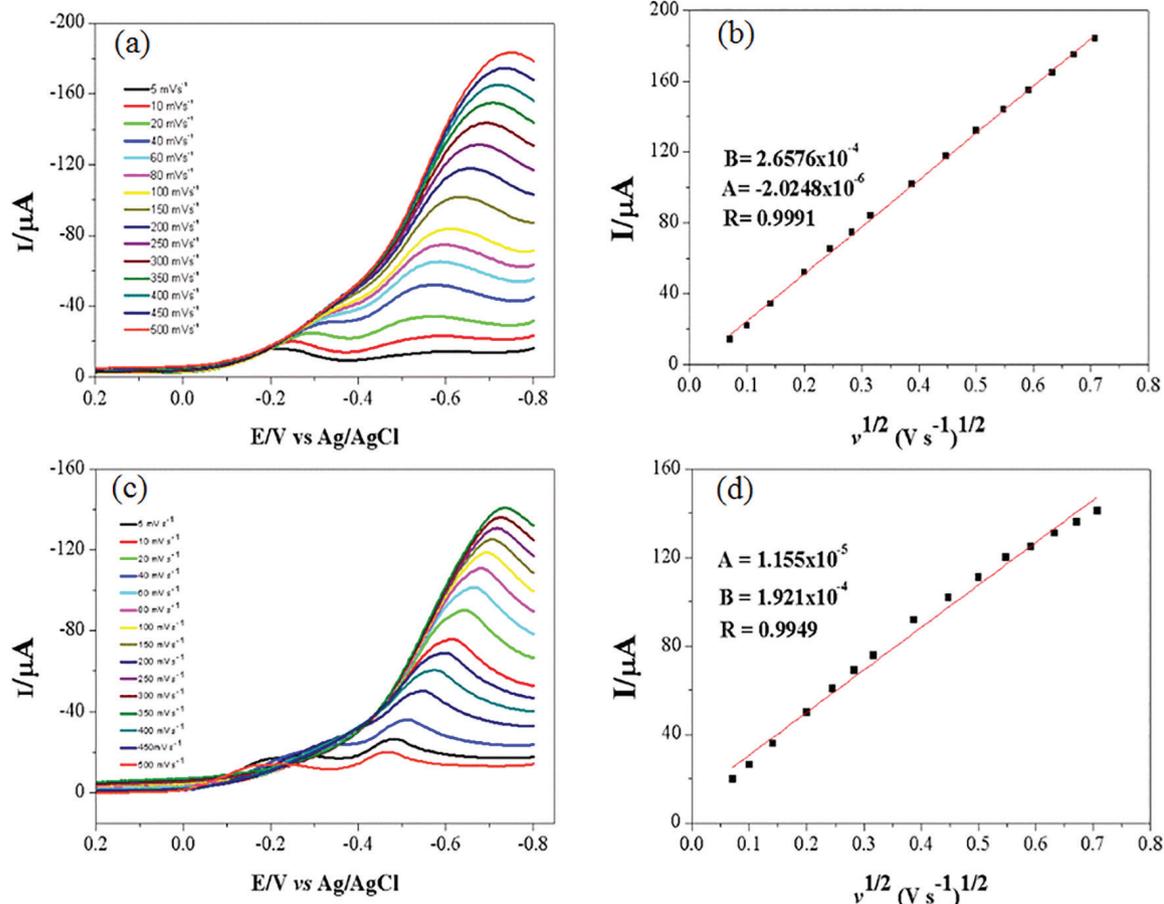


Figure 5. (a) Linear sweep voltammetry (LSV) curves of ORR on $\text{Fe}_2\text{O}_3/\text{GCE}$ obtained in 0.1 mol L^{-1} BR buffer pH 1.8 saturated with O_2 at different potential scan rates (5 to 500 mV s^{-1}); (b) I_p versus $v^{1/2}$ for $\text{Fe}_2\text{O}_3/\text{GCE}$; (c) ORR LSV on $\text{Co}_3\text{O}_4/\text{GCE}$ at different scan rates; (d) I_p versus $v^{1/2}$ for $\text{Co}_3\text{O}_4/\text{GCE}$.

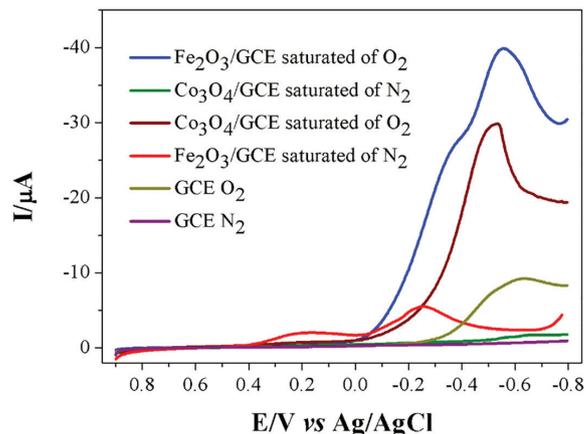


Figure 4. Cyclic voltammograms of GCE, $\text{Fe}_2\text{O}_3/\text{GCE}$ and $\text{Co}_3\text{O}_4/\text{GCE}$ in the presence of N_2 and O_2 . Purple curve: GCE N_2 ; dark yellow curve: GCE O_2 ; red curve: $\text{Fe}_2\text{O}_3/\text{GCE}$ in 0.1 mol L^{-1} BR buffer pH 1.8 saturated with N_2 ; blue curve: $\text{Fe}_2\text{O}_3/\text{GCE}$ in O_2 -saturated solution; green curve: $\text{Co}_3\text{O}_4/\text{GCE}$ in N_2 -saturated solution; brown curve: $\text{Co}_3\text{O}_4/\text{GCE}$ in O_2 -saturated solution. Potential scan rate: 20 mV s^{-1} .

in O_2 -saturated solution for oxygen reduction with individually Fe_2O_3 and Co_3O_4 modified GCE in BR buffer solution (pH 1.8). The voltammetric peak currents corresponding to the irreversible ORR process vary

linearly with the square root of the potential scan rate (Figures 5b and 5d) for both Fe₂O₃/GCE and Co₃O₄/GCE. This behavior suggests that the ORR catalyzed by these two catalysts is controlled by diffusion of the solution oxygen to the electrode surface.⁴⁶

Electrochemical impedance spectroscopy

Figure 6 shows the Nyquist plots obtained by electrochemical impedance spectroscopy for Fe₂O₃/GCE (Figure 6a) and Co₃O₄/GCE (Figure 6b) in oxygen-saturated BR buffer solution (pH 1.8), respectively. The cell potential was controlled at -0.5 V vs. Ag|AgCl in the frequency range of 100 mHz to 100 kHz.

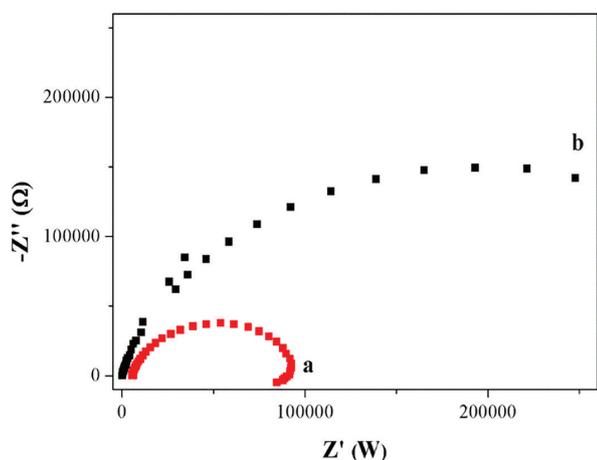


Figure 6. Nyquist plots for Fe₂O₃/GCE (a) and Co₃O₄/GCE (b) in the presence of saturating O₂ at a controlled potential of -0.5 V vs. Ag/AgCl in the frequency range of 100 mHz to 100 kHz with an amplitude of 0.005 rms.

The plots shown in Figure 6 consist of typical semicircles,⁴⁷ which represent the ORR charge transfer resistances. The smaller the size of the semicircle, the faster the charge transfer kinetics of the catalyzed ORR.⁴⁸⁻⁵⁰ Therefore, the catalytic ORR activity of Fe₂O₃/GCE is higher than that of Co₃O₄/GCE. This result is in consistence with those observed in Figures 4 and 5. Further quantitative measurements will be presented in the following sections.

Measurements on Fe₂O₃ and Co₃O₄ modified rotating disc electrodes

The steady-state LSV curves were recorded at different rotational rates (rpm) of Fe₂O₃ and Co₃O₄ modified rotating disc electrodes (RDEs); the results are shown in Figure 7a for Fe₂O₃/GCE and Figure 7b for Co₃O₄/GCE, respectively. It can be observed that, with increasing rotation rate, the ORR currents are increased. The ORR current density (I)

on the RDE can be expressed as equation 7 according to Koutecky-Levich.⁵¹

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} \quad (7)$$

where I is the measured current density, I_k represents the kinetic current density (absence of any mass transport effect) and I_d is the limit diffusional current density, defined by the following equation 8:

$$I_d = B \omega^{1/2} = (0.201 n F A D_o^{2/3} C_o v^{-1/6}) \omega^{1/2} \quad (8)$$

where n is the number of electrons involved in the ORR per O₂, F is the Faraday constant (96487 C mol⁻¹), A is the electrode area (0.07 cm²), D_o is the diffusion coefficient (1.93 × 10⁻⁵ cm² s⁻¹), C_o is the solubility of O₂ in the solution (1.21 × 10⁻⁶ mol cm⁻³ taken from literature), v is the kinematic viscosity of the solution (1.01 × 10⁻² cm² s⁻¹), and ω is the rotation rate of the electrode in rpm.

The graph of I_d⁻¹ versus ω^{-1/2}, according to equation 8, allows to estimate the apparent number of electrons transferred (n) for the electrocatalytic ORR. Figures 7b and 7d show the Koutecky-Levich plots at the -0.8 V potential for Fe₂O₃/GCE and Co₃O₄/GCE, respectively, and the theoretical plots for 2- and 4-electron processes in the ORR process are also shown for comparison. According to the slopes obtained, the average ORR electron number calculated for Fe₂O₃/GCE is n = 1.8, and for Co₃O₄/GCE is n = 1.7, respectively. These results suggest that the electrocatalysis of ORR by both Fe₂O₃/GCE and Co₃O₄/GCE is dominated by a 2-electrons transfer process to produce H₂O₂. In literature,^{11,52,53} there is some difference in ORR electron transfer numbers, either 2-electron or 4-electron transfer processes.

To further investigate the ORR kinetics, the Tafel slopes of the steady-state polarization curves for Fe₂O₃/GCE and Co₃O₄/GCE (Figure 8) at the rotation rate of 300 rpm were obtained, and also corrected for ORR mass transport. According to equation 7, the term “[I_d × I] / (I_d - I)” refers to the kinetic current density I_k of the ORR process. This current density is a result of the charge transfer process occurring between the surface of the catalyzed electrode and the solution oxygen, free of any mass transport effect. For Fe₂O₃/GCE, the Tafel slope obtained was 0.175 V dec⁻¹, while for Co₃O₄/GCE, the slope was 0.275 V dec⁻¹. These results indicate that Fe₂O₃/GCE is more favored than GCE/Co₃O₄ in terms of their catalytic ORR activities. The other possible reason may be the larger surface area of Fe₂O₃/GCE compared to that of Co₃O₄. Regarding Fe₂O₃/GCE ORR catalysis, Fu *et al.*⁴⁹ carried out a study

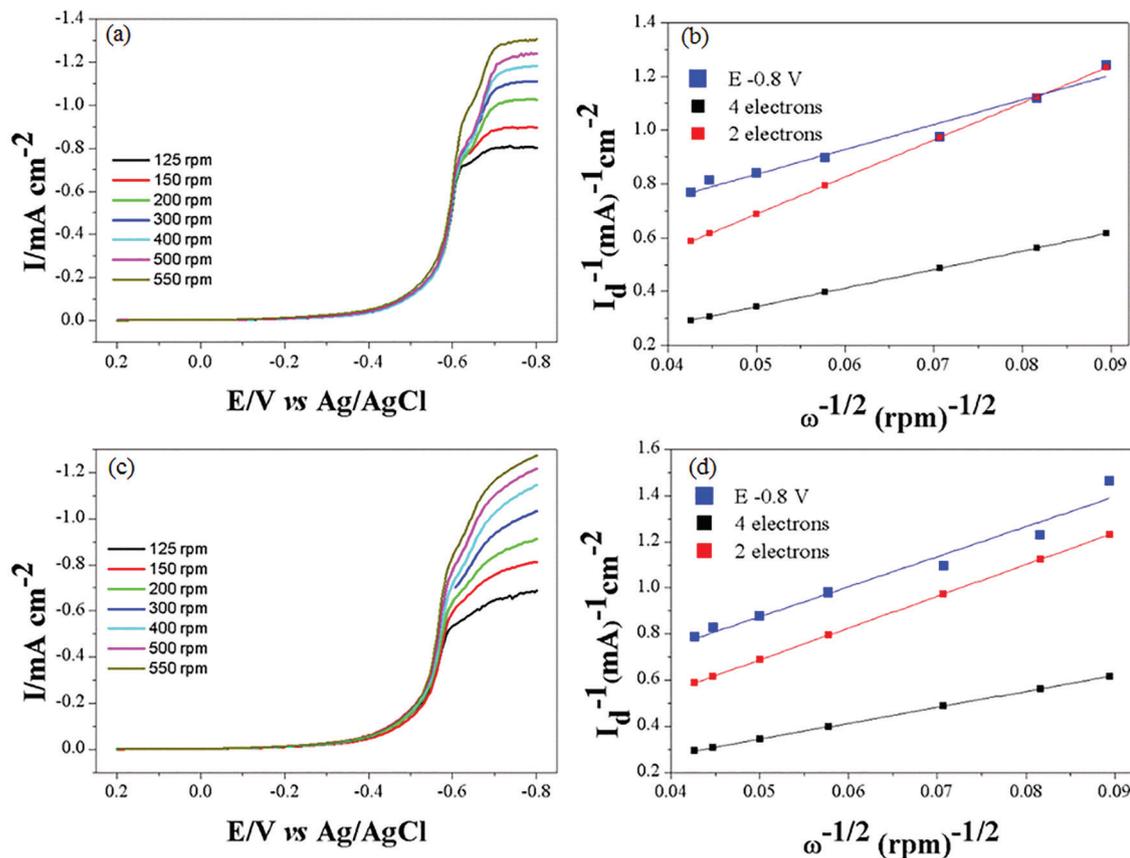


Figure 7. (a) ORR LSV curves recorded on $\text{Fe}_2\text{O}_3/\text{GCE}$ in O_2 -saturated BR buffer (pH = 1.8) at different electrode rotation rates from 125 to 550 rpm; (b) Koutecky-Levich (K-L) plots for $\text{Fe}_2\text{O}_3/\text{GCE}$ based on the data of (a); (c) ORR LSV curves for $\text{Co}_3\text{O}_4/\text{GCE}$ under the same conditions as (a); (d) K-L plots based on the data of (c). Potential scan rate: 5 mV s^{-1} .

with different forms of nanoparticle iron oxides ($\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{-PPy}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-C-N}$), and their Tafel slopes are similar to our results. Regarding $\text{Co}_3\text{O}_4/\text{GCE}$ ORR catalysis, Liang *et al.*⁵⁴ compared two electrodes ($\text{Co}_3\text{O}_4/\text{N-rmGO}$ and $\text{Co}_3\text{O}_4/\text{rmGO}$), showing that the $\text{Co}_3\text{O}_4/\text{N-rmGO}$ electrode presented a lower Tafel slope, resulting in a higher catalytic activity.

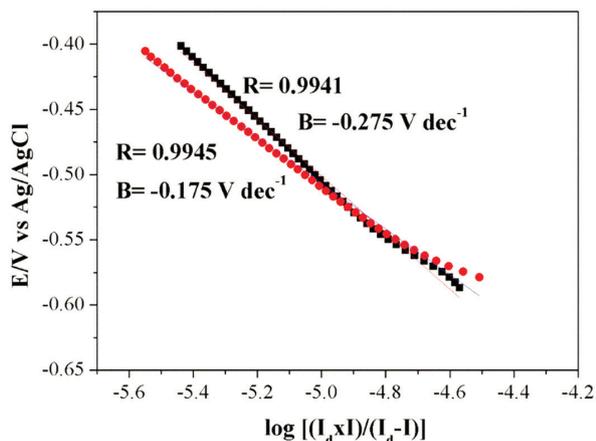


Figure 8. Tafel diagrams of ORR catalyzed by $\text{Fe}_2\text{O}_3/\text{GCE}$ (red circle line) and $\text{Co}_3\text{O}_4/\text{GCE}$ (black square line). Data extracted from the curve at 300 rpm of Figure 7.

Catalytic ORR current as a function of oxygen concentration

Figure 9 shows the linear sweep voltammograms (LSVs) of $\text{Fe}_2\text{O}_3/\text{GCE}$ and $\text{Co}_3\text{O}_4/\text{GCE}$ in the presence of different oxygen concentrations. It can be observed that for both electrodes the electrocatalytic currents increased with increasing oxygen concentration in the test cell. From the CVs, plots of $\log(I_p)$ vs. $\log[\text{O}_2]$ (Figures 9b and 9d) were obtained, which showed linear dependencies in the O_2 concentration range of 2.7×10^{-4} to $1.21 \times 10^{-3} \text{ mol L}^{-1}$. This result suggests that Fe_2O_3 or Co_3O_4 modified GCE electrodes can be used for analysis of O_2 concentration in aqueous solution.

Conclusions

The electrochemically catalyzed oxygen reaction (ORR) is one of the most important reactions in many applications, particularly in fuel cells² and metal-air batteries.¹ However, the currently practical electrocatalysts are mainly based on precious metals (Pt, Pd, Ir, etc.), which are high cost. The development of highly active, stable and efficient, and cost effective

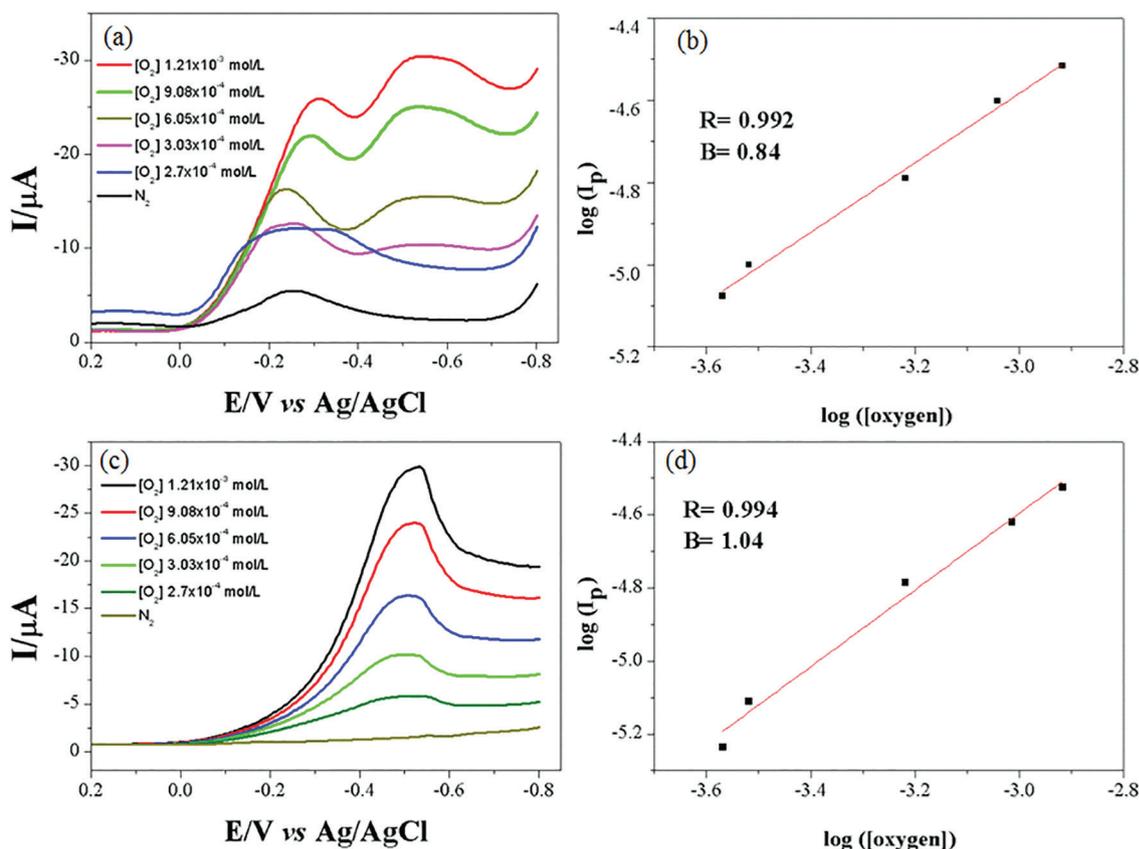


Figure 9. (a) LSVs at different oxygen concentrations for Fe₂O₃/GCE; (b) dependency of the logarithm I_p vs. the logarithm O₂ concentration [O₂] for Fe₂O₃/GCE; (c) Co₃O₄/GCE LSVs under the same conditions as (a); (d) dependency of the logarithm I_p vs. the logarithm [O₂] for Fe₂O₃/GCE.

non-precious metal electrocatalysts is therefore needed. In this paper, two non-noble metal catalysts, Fe₂O₃ and Co₃O₄ nanoparticles, were synthesized using the modified polymeric precursor method (Pechini). These two nanomaterials were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques for their compositions and crystal structures. The estimated average particle sizes were 21 and 31 nm for Fe₂O₃ and Co₃O₄, respectively. For characterizing the electrochemical activities, these two catalysts were individually employed to coat glass carbon electrodes for catalytic oxygen reduction reaction (ORR). Both cyclic voltammetry and rotating disc electrode (RDE) methods were employed to test the ORR activities of these catalysts. In particular, using RDE data and Koutecky-Levich theory, the results obtained indicate that both Fe₂O₃/GCE and Co₃O₄/GCE can catalyze ORR with a dominating 2-electron transfer process to produce H₂O₂. The electrochemical impedance spectroscopy was also used to obtain the charge transfer resistances of the ORR catalyzed by these two catalysts. In addition, the ORR Tafel slope for Fe₂O₃/GCE is lower than that of Co₃O₄/GCE, indicating that the former is more active than

the latter. For fundamental understanding, the surface reaction processes on the electrode as well as their catalyzed ORR mechanisms are explored based on the experimental data and literature.

The result also shows a linear behavior between the catalytic current and the oxygen concentration, which suggests that these Fe₂O₃/GCE and Co₃O₄/GCE can be used as modified electrodes for analysis of O₂ concentration.

Overall, the results show that the nanoparticles of both Fe₂O₃ and Co₃O₄ have good catalytic activities toward ORR, but the former is more efficient than that the latter. Considering the low cost of these two non-noble metal catalysts, they may be used as viable alternatives for ORR electrocatalysts.

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References

1. Wang, Y. J.; Fang, B.; Zhang, D.; Li, A.; Wilkinson, D. P.; Ignaszak, A.; Zhang, L.; Zhang, J.; *Electrochem. Energy Rev.* **2018**, *1*, 1.
2. Wang, R.; Wang, H.; Luo, F.; Liao, S.; *Electrochem. Energy Rev.* **2018**, *1*, 324.
3. Zhang, L.; Niu, J.; Dai, L.; Xia, Z.; *Langmuir* **2012**, *28*, 7542.
4. Ren, C.; Li, H.; Li, R.; Xu, S.; Wei, D.; Kang, W.; Wang, L.; Jia, L.; Yang, B.; Liu, J.; *RSC Adv.* **2016**, *6*, 33302.
5. Bezerra, C.; Zhang, L.; Lee, K.; Liu, H.; Marques, A.; Marques, E.; Wang, H.; Zhang, J.; Marques, A. L. B.; *Electrochim. Acta* **2008**, *53*, 4937.
6. Dias, V.; Fernandes, E.; da Silva, L.; Marques, E.; Zhang, J.; Marques, A.; Marques, A. L. B.; *J. Power Sources* **2005**, *142*, 10.
7. Costa, W. M.; Cardoso, W. S.; Marques, E. P.; Bezerra, C. W.; Ferreira, A. A. P.; Song, C.; Zhang, J.; Marques, A. L.; *J. Braz. Chem. Soc.* **2013**, *24*, 651.
8. Tian, N.; Lu, B. A.; Yang, X. D.; Huang, Y. H.; Huang, R.; Jiang, Y. X.; Zhou, Z. Y.; Sun, S. G.; *Electrochem. Energy Rev.* **2018**, *1*, 54.
9. Cardoso, W. S.; Dias, V. L.; Costa, W. M.; Rodrigues, I. A.; Marques, E. P.; Sousa, A. G.; Boaventura, J.; Bezerra, C. W. B.; Song, C.; Liu, H.; Zhang, J.; Marques, A. L. B.; *J. Appl. Electrochem.* **2009**, *39*, 55.
10. Higgins, D.; Zamani, P.; Yu, A.; Chen, Z.; *Energy Environ. Sci.* **2016**, *9*, 357.
11. Wu, Z. S.; Yang, S.; Sun, Y.; Parvez, K.; Feng, X.; Müllen, K.; *J. Am. Chem. Soc.* **2012**, *134*, 9082.
12. Chen, Z.; He, D.; Xu, X.; Liu, Z.; Huang, M.; Wang, X.; Jiang, H.; *RSC Adv.* **2016**, *6*, 34159.
13. Karunakaran, R.; Coghlan, C.; Tung, T. T.; Kabiri, S.; Tran, D. N.; Doonan, C. J.; Losic, D.; *New J. Chem.* **2017**, *41*, 15180.
14. Wang, Q.; Hu, W.; Huang, Y.; *Int. J. Hydrogen Energy* **2017**, *42*, 5899.
15. Xu, J.; Yang, H.; Fu, W.; Du, K.; Sui, Y.; Chen, J.; Li, M.; Zou, G.; *J. Magn. Magn. Mater.* **2007**, *309*, 307.
16. Epherre, R.; Duguet, E.; Mornet, S.; Pollert, E.; Louguet, S.; Lecommandoux, S.; Schatz, C.; Goglio, G.; *J. Mater. Chem.* **2011**, *21*, 4393.
17. Lima, S. A. M.; Sigoli, F. A.; Davolos, M. R.; Jafellicci, M. J.; *J. Alloys Compd.* **2002**, *344*, 280.
18. Silva, R. F.; Zaniquelli, M. E. D.; *Thin Solid Films* **2004**, *449*, 86.
19. Ren, S.; Ma, S.; Yang, Y.; Mao, Q.; Hao, C.; *Electrochim. Acta* **2015**, *178*, 179.
20. Sun, X.; Zheng, C.; Zhang, F.; Yang, Y.; Wu, G.; Yu, A.; Guan, N.; *J. Phys. Chem. C* **2009**, *113*, 16002.
21. Mirzaei, A.; Janghorban, K.; Hashemi, B.; Bonyani, M.; Leonardi, S. G.; Neri, G.; *Ceram. Int.* **2016**, *42*, 6136.
22. Gunnewiek, R. F. K.; Mendes, C. F.; Kiminami, R. H. G. A.; *Adv. Powder Technol.* **2016**, *27*, 1056.
23. Gharagozlou, M.; *J. Alloys Compd.* **2009**, *486*, 660.
24. Davis, J. C. In *Chemistry and Physics of Aqueous Gas Solutions*; Adams, W. A.; Greer, G.; Kell, G. S.; Desnoyers, J. E.; Oldham, K. B.; Atkinson, G.; Walkley, J., eds.; The Electrochemical Society: Princeton, NJ, USA, 1975, p. 393.
25. Chaves, J. A. P.; Araújo, M. F. A.; Varela, J.; Tanaka, A. A.; *Ecletica Quim.* **2003**, *28*, 2.
26. Ju, H.; Shen, C.; *Electroanalysis* **2001**, *13*, 789.
27. Cornell, R. M.; Schwertmann, U.; *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, 2nd ed.; Wiley: Weinheim, 2003.
28. Suresh, R.; Prabu, R.; Vijayaraj, A.; Giribabu, K.; Stephen, A.; Narayanan, V.; *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2012**, *42*, 303.
29. Bashir, S.; McCabe, R. W.; Boxall, C.; Leaver, M. S.; Mobbs, D.; *J. Nanopart. Res.* **2009**, *11*, 701.
30. Eigler, S.; Dotzer, C.; Hirsch, A.; Enzelberger, M.; Müller, P.; *Chem. Mater.* **2012**, *24*, 1276.
31. Sahoo, S.; Satpati, A. K.; *J. Electroanal. Chem.* **2017**, *801*, 416.
32. Wang, H. W.; Hu, Z. A.; Chang, Y. Q.; Chen, Y. L.; Zhang, Z. Y.; Yang, Y. Y.; Wu, H. Y.; *Mater. Chem. Phys.* **2011**, *130*, 672.
33. Kamali, K. Z.; Alagarsamy, P.; Huang, N. M.; Ong, B. H.; Lim, H. N.; *Sci. World J.* **2014**, DOI: 10.1155/2014/396135.
34. Cao, R. B.; Chen, X. Q.; Shen, W. H.; Long, Z.; *Mater. Lett.* **2011**, *65*, 3298.
35. Adekunle, A. S.; Ozoemena, K. I.; *Int. J. Electrochem. Sci.* **2010**, *5*, 1726.
36. Shahid, M. M.; Rameshkumar, P.; Basirun, W. J.; Juan, J. C.; Huang, N. M.; *Electrochim. Acta* **2017**, *237*, 61.
37. Xu, C.; Wang, X.; Zhu, J.; Yang, X.; Lu, L.; *J. Mater. Chem.* **2008**, *18*, 5625.
38. Yang, X.; Fan, K.; Zhu, Y.; Shen, J.; Jiang, X.; Zhao, P.; Li, C.; *J. Mater. Chem.* **2012**, *22*, 17278.
39. Scherrer, P.; *Nachr. Ges. Wiss. Goettingen, Math.-Phys. Kl.* **1918**, *2*, 98.
40. Bazrafshan, H.; Tesieh, Z. A.; Dabirnia, S.; Toubia, R. S.; Manghabati, H.; Nasernejad, B.; *Powder Technol.* **2017**, *308*, 266.
41. Cepriá, G.; Usón, A.; Pérez-Arantegui, J.; Castillo, J. R.; *Anal. Chim. Acta* **2003**, *477*, 157.
42. Oswald, H. R.; Asper, R.; *Preparation and Crystal Growth of Materials with Layered Structures*; Lieth, R. M. A., ed.; Reidel: Dordrecht, 1977, p. 73.
43. Barbieri, E. M. S.; Lima, E. P. C.; Lelis, M. F. F.; Freitas, M. B. J. G.; *J. Power Sources* **2014**, *270*, 158.
44. Gupta, A. K.; Gupta, M.; *Biomaterials* **2005**, *26*, 3995.
45. Kozhina, G. A.; Ermakov, A. N.; Fetisov, V. B.; Fetisov, A. V.; Shunayev, K. Y.; *Russ. J. Electrochem.* **2009**, *45*, 1170.
46. Nicholson, R. S.; Shain, I.; *Anal. Chem.* **1964**, *36*, 706.

47. Ribeiro, C. D. L.; Santos, J. G. M.; de Souza, J. R.; Pereira-da-Silva, M. A.; Paterno, L. G.; *J. Electroanal. Chem.* **2017**, *805*, 53.
48. Liang, Y.; Wang, H.; Diao, P.; Chang, W.; Hong, G.; Li, Y.; Gong, M.; Xie, L.; Zhou, J.; Wang, J.; Regier, T. Z.; Wei, F.; Dai, H.; *J. Am. Chem. Soc.* **2012**, *134*, 15849.
49. Fu, Y.; Wang, J.; Yu, H. Y.; Li, X.; Wang, H.; Tian, J. H.; Yang, R.; *Int. J. Hydrogen Energy* **2017**, *42*, 20711.
50. Sun, M.; Zhang, G.; Liu, H.; Liu, Y.; Li, J.; *Sci. China Mater.* **2015**, *58*, 683.
51. Bard, A. J.; Faulkner, L. R.; *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 2001.
52. Wang, K.; Wang, R.; Li, H.; Wang, H.; Mao, X.; Linkov, V.; Ji, S.; *Int. J. Hydrogen Energy* **2015**, *40*, 3875.
53. Mao, S.; Wen, Z.; Huang, T.; Hou, Y.; Chen, J.; *Energy Environ. Sci.* **2014**, *7*, 609.
54. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H.; *Nat. Mater.* **2011**, *10*, 780.

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