A CoFe$_2$O$_4$/graphene nanohybrid as an efficient bi-functional electrocatalyst for oxygen reduction and oxygen evolution

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**Abstract**

Development of efficient electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) remain key issues for the commercialization of fuel cells and metal–air batteries. In this study, a CoFe$_2$O$_4$/graphene nanohybrid is facilely synthesized via a two-step process and applied as an electrocatalyst for the ORR and the OER. The as-prepared CoFe$_2$O$_4$/graphene nanohybrid demonstrates excellent catalytic activity for the ORR. At the same mass loading, the Tafel slope of CoFe$_2$O$_4$/graphene electrocatalyst for the ORR is comparable to that of the commercial Pt/C (20 wt% Pt on Vulcan XC-72, Johnson Matthey). The ORR on CoFe$_2$O$_4$/graphene mainly favours a direct 4e$^-$ reaction pathway. The CoFe$_2$O$_4$/graphene nanohybrid also affords high catalytic activity for the OER. The chronoamperometric tests show that CoFe$_2$O$_4$/graphene catalyst exhibits excellent stability for both the ORR and the OER, outperforming the commercial Pt/C. The high electrocatalytic activity and durability of CoFe$_2$O$_4$/graphene nanohybrid are attributed to the strong coupling between CoFe$_2$O$_4$ nanoparticles and graphene.

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1. Introduction

Electrocatalytic oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) play critical roles in the development of fuel cells and metal–air batteries, which are promising technologies for portable, residential and especially transportation applications [1–4]. The slow kinetics of the ORR and the OER at the cathode limits the efficiency of fuel cells and metal–air batteries [1,5–8]. Platinum-based materials are known to be the most active electrocatalysts for the ORR and the OER. However, the high cost and scarcity of Pt hinders the widespread commercialization of fuel cells and metal–air batteries.

Research efforts have been focused on replacing Pt with inexpensive materials. Mixed valence oxides of transition metals with a spinel structure have attracted much attention due to their high abundance, low cost, environmental friendliness and considerable catalytic activity for the ORR and OER [9–13]. More specifically, cobaltite spinel oxides $M_xCo_{3-x}O_4$ ($M = Co, Ni, Mn, Cu, Li$) have been shown as promising electrocatalysts for the ORR ($M = Co, Ni, Mn$) and the OER ($M = Co, Ni, Cu, Mn, Li$) [9–12,14–17]. Cheng et al. [10] have reported that nano-crystalline spinels of $Co_xMn_{3-x}O_4$ prepared by a rapid room-temperature synthesis method exhibited considerable catalytic activities for both the ORR and the OER. High electrocatalytic activities of $Cu_xCo_{3-x}O_4$ for the ORR and the OER have also been reported by Koninck et al. [14,15]. Recently, Yuan et al. reported the use of $Ni_xCo_{3-x}O_4$ spinel oxide as a bi-functional air electrode for zinc–air batteries [16]. Although cobaltite spinel oxides have been widely investigated as electrocatalysts for the ORR and the OER, the electrocatalytic activities of $M_xCo_{3-x}O_4$ with $M = Fe$ for the ORR and the OER are still seldom reported.

In order to obtain good catalytic activity, spinel oxides are usually attached to or supported on a conducting surface (like carbon) to assure fast electron transport since this type of oxides is a semiconductor. High electrical conductivity, chemical stability,
large surface area and open porous structure of graphene sheets [18–20] makes it an excellent substrate for spinel oxides. CoO4/graphene [11], MnCo2O4/graphene [12,13], NiCo2O4/graphene [21] have been reported to be promising bi-functional electrocatalysts for the ORR and the OER. In this work, we report the synthesis of CoFe2O4/graphene nanohybrid as an efficient bi-functional electrocatalyst for the ORR and the OER. To the best of our knowledge, few studies on the preparation and catalytic activity of CoFe2O4/graphene nanohybrid have been reported so far. Laouini et al. [22,23] and Cartaxo et al. [24] studied the electrochemical behaviour of CoFe2O4 electrocatalytic activity of which has not been reported. The electrocatalytic activities of the as-synthesized CoFe2O4/graphene nanohybrid for the ORR and the OER in alkaline media have been studied by using a rotating ring-disk electrode (RRDE) technique. The as-synthesized CoFe2O4/graphene nanohybrid exhibited high electrocatalytic activities for both the ORR and the OER with long-term stability in basic media, out-performing CoFe2O4 and graphene, respectively.

2. Experimental

2.1. Sample preparation

Graphene oxide (GO) is synthesized from natural graphite flakes by a modified Hummers’ method as described elsewhere [11,25]. GO was collected from the aqueous solution by centrifugation followed by lyophillization. 10 mg of the GO was dispersed in 30 ml of anhydrous ethanol. For the synthesis of CoFe2O4/graphene, 1 ml of 0.2 M Fe(NO3)3·9H2O and 0.5 ml of 0.2 M Co(NO3)2·6H2O (>99.0%, Guoyao Chemical Reagent Co. Ltd.) aqueous solution was added to the above GO ethanol suspension, followed by the addition of 2.50 ml of NH4OH at room temperature. The mixture was stirred at 80 °C for 12 h and then transferred to a 50 ml autoclave, sealed and heated at 180 °C for 5 h. After the autoclave is cooled to room temperature, the precipitate is collected by centrifugation and washed with ethanol and deionized water to remove any impurities. The final product was obtained after lyophilization. This hydrothermal step also reduced GO to rGO and the samples obtained were abbreviated to CoFe2O4/rGO. CoFe2O4 and rGO were also prepared with the same procedure for comparison.

2.2. Physical characterization

The crystal structure of the sample was examined with X-ray diffraction (XRD) using a Bede D1 X-ray diffractometer (UK, Bede Scientific Ltd.; Cu Kα radiation; operated at 40 kV, 45 mA; λ = 0.15418 nm), the diffraction angle ranging from 10° to 80° with a step of 0.02° and a rate of 1.2° min⁻¹. Surface analysis of the samples was performed with a SSI (Surface Science Instruments) X-ray photoelectron spectroscopy (XPS) spectrometer equipped with a hemispherical analyzer and using a monochromatized Al Kα (1486 eV) source with a 250 × 1000 mm illumination spot. The measurement parameters were as follows: 20 eV pass energy, 0.1 eV energy increments. The spectra were corrected for the background using the Shirley approach [26] and the composition of the films was determined by measuring the ratio of Co 2p to Fe 2p intensities (integrated peak area) normalized by their respective sensitivity factors [27].

The specific surface area and the pore structure of the samples were analyzed by adsorption/desorption measurements of nitrogen at 77 K (Quantachrome, QuadraSorb SI). Prior to measurements, the samples were degassed at 250 °C overnight under vacuum. Surface area was calculated by Brunauer–Emmett–Teller (BET) method. Pore size distributions were calculated using Barrett–Joyner–Halenda (BJH) method.

The morphology and microstructure of the synthesized sample were characterized by a transmission electron microscope (TEM, TecnaiG220 operating at 200 kV).

The amount of CoFe2O4 in CoFe2O4/rGO was measured with thermogravimetric analysis (TGA, PerkinElmer TGA7), which was calibrated with calcium oxalate.

2.3. Electrochemical measurements

Inks of the catalyst samples for CoFe2O4/rGO (the amount of CoFe2O4 in the composite was determined by to be 70 wt%), CoFe2O4 + rGO mixture (the ratio of CoFe2O4 to rGO is 70:30 by weight), rGO and CoFe2O4 (mixed with acetylene black (AB), the ratio of CoFe2O4 to AB is 70:30 by weight) were prepared by mixing 10 mg of powder, 5 µl of Nafion solution (5 wt% from Aldrich), and 350 µl of ethanol, followed by ultrasonication for 40 min. Seven µl of ink was pipetted onto a glassy carbon (GC) disk resulting in a powder loading of 1006 µg cm⁻². The same powder loading was used for commercial Pt/C (20 wt% Pt on Vulcan XC-72, Johnson Matthey) for comparison.

The electrocatalytic activity for the ORR of the samples on the GC disks was studied with the rotating ring-disk electrode (RRDE) technique using a Pine electrochemical system (AFMSRXR, and AFCBP1 biopotentiostat). The RRDE electrode consisted of a catalyst-coated GC disk (5 mm diameter, 0.196 cm² of geometric surface area) surrounded by a Pt ring (0.125 cm² of geometric surface area). The electrochemical measurements were conducted in a standard three-electrode electrochemical cell at room temperature. A Pt-foil was used as the counter electrode, and a Ag/AgCl (3 M Cl⁻, Cypress) reference electrode was used in a double-junction reference chamber. The electrolyte was 0.1 M KOH solution prepared from ultrapure water (Millipore, 18.2 MΩ cm). The working electrodes were the catalyst film-coated GC disks mounted in a disk-interchangeable rotating disk electrode (RDE, Pine Instruments).

The electrolyte was deaerated by purging high-purity Ar gas into the electrolyte for at least 30 min before each electrochemical measurement. The samples on the GC disks were first electrochemically cleaned by sweeping the potential in the range between −0.9 and 0 V (vs. Ag/AgCl) at 50 mV s⁻¹ in an Ar-saturated 0.1 M KOH solution until steady state cyclic voltammograms (CV) were obtained. For each catalyst tested, a CV was first collected in Ar-saturated 0.1 M KOH solution from −0.9 to 0 V at 10 mV s⁻¹ to determine the non-Faradaic current.

For the ORR test, the electrolyte was purged with high-purity O2 gas for at least 30 min to ensure O2 saturation. Linear sweep voltammetry (LSV) measurements during oxygen reduction were performed in O2-saturated 0.1 M KOH by sweeping the potential from 0 V cathodically to −0.8 V at 10 mV s⁻¹ with the electrode rotated at 400, 900, 1600 and 2500 rpm and O2 gas purged into the solution at a flow rate of 25 sccm through a 2 µm fritted tube (Ace Glass). Note that the LSV measurements on Pt/C were performed by sweeping the potential from −0.8 V anodically to 0 V at 10 mV s⁻¹ to avoid the initial oxidation of Pt surface at high potential [28,29]. The faradaic current density, i.e., the current due to the oxygen reduction alone, was obtained by subtracting the capacitive current (the current measured from the CV under Ar) from the ORR data and then normalized by the geometric surface area,

\[ j = -\left( j_{ORR} - j_{capacitive\text{-}Ar} - j_{CV} \right) / S_{geo} \]  \hspace{1cm} (1)

The kinetic current density for the ORR was derived from the Koutecky–Levich equation:
\[ j = j_k + j_d \]

where \( j \) is the measured disk current density; \( j_k \) and \( j_d \) are the kinetic and diffusion limiting current densities, respectively.

\[ B = 0.62nFD_O^2\omega^{-1/6}C_{O_2} \]

where \( n \) is the apparent number of electrons transferred in the reaction, \( F \) is the Faraday constant (96,485 C mol\(^{-1}\)), \( D_O \) is the diffusion coefficient of \( O_2 \) \( (D_O = 1.86 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \), \( \omega \) is the rotation speed of the disk electrode, \( C_{O_2} \) is the concentration of \( O_2 \) dissolved in electrolyte \( (C_{O_2} = 1.21 \times 10^{-6} \text{ mol cm}^{-3}) \) [28,30], and \( \omega \) is the electrode rotation speed. The ohmic resistances in the electrode contacts for the investigated samples were included in the corrections.

For all the RRDE measurements, the ring potential was held at 0.5 V vs. Ag/AgCl in order to oxidize any \( H_2O_2 \) produced in alkaline solution [31]. The % \( HO_2 \) produced in alkaline solution was calculated using the following equation [13,32,33].

\[ \%HO_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)} \]

where \( I_D \) is the Faradaic current at the disk, \( I_R \) is the Faradaic current at the ring, and \( N = 0.22 \) is the disk electrode collection efficiency.

For the OER test, the working electrode was scanned from 0 to 1.0 V vs. Ag/AgCl at a scan rate of 10 mV s\(^{-1}\) in a \( N_2 \)-saturated electrolyte with the electrode rotated at 1600 rpm to spin off the oxygen evolved during voltammetry testing.
3. Results and discussion

3.1. Structure of CoFe$_2$O$_4$/rGO nanohybrid

Fig. 1 shows the X-ray diffraction (XRD) profile of the CoFe$_2$O$_4$/rGO, the XRD profiles of CoFe$_2$O$_4$ and rGO are also included for comparison. The characteristic peaks in CoFe$_2$O$_4$/rGO can be well indexed as cubic spinel phase (PDF#22-1086) except the broad peak at around 23° corresponding to (002) peak of carbon in rGO. The average crystallite size of CoFe$_2$O$_4$ particles is estimated to be 4.9 nm for CoFe$_2$O$_4$/rGO nanohybrid by the Scherrer formula \[34\]. Two obvious diffraction peaks corresponding to (002) and (100) of carbon phase can be observed in rGO. The average crystallite size of pure CoFe$_2$O$_4$ is estimated to be 5.0 nm by the Scherrer formula, which is similar to that of CoFe$_2$O$_4$ nanoparticles in CoFe$_2$O$_4$/rGO nanohybrid.

The morphology and structure of the CoFe$_2$O$_4$/rGO was investigated by transmission electron microscope (TEM). As observed from Fig. 2a and b, CoFe$_2$O$_4$ nanoparticles were well dispersed on the graphene. The histogram of the CoFe$_2$O$_4$ particle size distribution in CoFe$_2$O$_4$/rGO nanohybrid is in the range of 3.0–6.5 nm with an average particle size of 4.8 nm (Fig. 2a), in good agreement with the value obtained from XRD. The crystal structure of the CoFe$_2$O$_4$ particles on graphene was further revealed by high-resolution TEM. The measured d spacing of 0.29 nm is assigned to the lattice spacing of the (220) plane of CoFe$_2$O$_4$ (Fig. 2c). Fig. 2d exhibits the selected area electron diffraction (SAED) patterns of the CoFe$_2$O$_4$ on graphene. The five most-distinct concentric diffraction rings from the centre can be assigned to the (220), (311), (400), (511) and (440) planes of cubic spinel CoFe$_2$O$_4$, which agrees well with the results obtained from the XRD pattern (Fig. 1). Note that the particle size of pure CoFe$_2$O$_4$ without any substrate is in the range of 10–20 nm as shown in the SEM image (Fig. S1), which is larger than that of mean crystallite size calculated from Scherrer formula (5.0 nm) due to the aggregation of the particles. In contrast, the smaller particle size of CoFe$_2$O$_4$ nanoparticles in CoFe$_2$O$_4$/rGO nanohybrid is due to the dispersing effect of graphene support in preventing the CoFe$_2$O$_4$ nanoparticles from aggregation.

To obtain the cation oxidation state and the surface chemical composition of CoFe$_2$O$_4$ on graphene, X-ray photoelectron spectroscopy (XPS) measurements were performed. As expected, the XPS survey spectrum given in Fig. 3a shows the Co 2p, Fe 2p, O 1s and C 1s peaks in CoFe$_2$O$_4$/rGO. The de-convolution of the Co 2p peak in CoFe$_2$O$_4$ and CoFe$_2$O$_4$/rGO shows four peaks (Fig. 3b). The peak at 780.7 eV is from Co$_2$p$_3$/2, while the peak at 796.3 eV is caused by Co$_2$p$_1$/2. The satellite peak at around 785.8 eV and 803.1 eV are two shake-up type peaks of Co at the high binding energy side of the Co$_2$p$_3$/2 and Co$_2$p$_1$/2 edge. The presence of Co$_2$p$_3$/2 and Co$_2$p$_1$/2 main peaks and shake-up satellite peaks indicates the presence of Co$^{2+}$ in the high-spin state \[35–37\]. The Fe2p spectra shows two peaks at a binding energy of around 710.9 eV and 724.2 eV, corresponding to Fe$_2$p$_3$/2 and Fe$_2$p$_1$/2, respectively, suggesting the presence of Fe$^{3+}$ cations \[35–37\]. Further quantitative analysis of the Co 2p and Fe 2p peaks gave a Co:Fe atomic ratio of about 1:2, which is consistent with the results of XRD. The O 1s spectra in CoFe$_2$O$_4$ and CoFe$_2$O$_4$/rGO show a large peak at 529.3 eV and 529.9 eV, respectively, corresponding to M–O–M, which is attributed to the lattice oxygen in the Co/Fe-oxygen framework \[21,36–38\]. The comparison of Co 2p and Fe 2p spectra in CoFe$_2$O$_4$ and CoFe$_2$O$_4$/rGO has revealed no shift in the binding energy of the peaks after the hybridization of CoFe$_2$O$_4$ and graphene sheets (Fig. 3b and c). However, a positive shift of about 0.6 eV in the binding energy for the O 1s peak is observed for CoFe$_2$O$_4$/rGO as compared to that of CoFe$_2$O$_4$ (Fig. 3d). This indicates that the
The coupling between CoFe$_2$O$_4$ and graphene occurs through the oxygen species of GO, which probably reacted with the metal precursors during the synthesis [21].

The N$_2$ sorption isotherm and the pore size distribution of CoFe$_2$O$_4$/rGO nanohybrid are shown in Fig. 4. The N$_2$-adsorption isotherm of the CoFe$_2$O$_4$/rGO exhibited Type IV isotherm, the hysteresis loop in the $P/P_0$ range of 0.5–1.0 is indicative of mesoporosity. The CoFe$_2$O$_4$/rGO displays a BET specific surface area of 173.12 m$^2$ g$^{-1}$ and a total pore volume of 12.57 cm$^3$ g$^{-1}$. A broad pore size distribution between 2 and 70 nm is clearly observed in Fig. 4b, which might come from the interlayer spacings and porous structure formed between graphene sheets. The high surface area of CoFe$_2$O$_4$/rGO provides a high surface exposure of active sites for the ORR. Meanwhile, the broad pore size distribution provides effective triple phase (solid–liquid–gas) regions required for oxygen reduction. Note that the specific surface area of the CoFe$_2$O$_4$/rGO nanohybrid is much lower than the theoretical value of graphene (2630 m$^2$ g$^{-1}$), which is due to the bigger weight contribution from CoFe$_2$O$_4$ nanoparticles on the surface of graphene sheets [39].

3.2. Catalytic activity of CoFe$_2$O$_4$/rGO nanohybrid for oxygen reduction and oxygen evolution

The ORR activity on CoFe$_2$O$_4$/rGO nanohybrid as measured with RRDE is shown in Fig. 5. To better understand the electrocatalytic performance of CoFe$_2$O$_4$/rGO during the ORR process, the ORR activities on CoFe$_2$O$_4$ (mixed with AB), rGO, CoFe$_2$O$_4$ + rGO mixture and commercial Pt/C are also included for comparison. The disk current densities ($i_d$) shown were measured at 1600 rpm and normalized by the geometric surface area. The ORR activity increases as follows: CoFe$_2$O$_4$ < rGO < CoFe$_2$O$_4$ + rGO mixture < CoFe$_2$O$_4$/rGO, as evidenced by the onset potentials for the ORR of these samples (Fig. 5a). The rGO has high electronic conductivity. The edge sites and defect sites of rGO prepared from graphite by a modified Hummer’s method could serve as active sites for oxygen reduction. Meanwhile the two-dimensional structure of rGO allows the easy access of O$_2$ from both sides to these active sites [40]. These facts result in the higher ORR activity of CoFe$_2$O$_4$ + rGO mixture than that of CoFe$_2$O$_4$(mixed with AB). A significant increase in the onset potential for the ORR of CoFe$_2$O$_4$/rGO (~0.136 V) as compared to that of CoFe$_2$O$_4$ + rGO mixture (~0.207 V) is indicative of the important effect of hybridization of CoFe$_2$O$_4$ and graphene on the ORR activity. The diffusion limiting current density of CoFe$_2$O$_4$/rGO reaches that of Pt/C though a negative shift of about 80 mV exists in the half-wave potential of CoFe$_2$O$_4$/rGO as compared to Pt/C. It should be noted that the
The diffusion-current-corrected Tafel plots of specific ORR activity of these samples are shown in Fig. 6. To construct the Tafel plots, the kinetic currents were derived from the mass-transport correction using Eq. (2). At low over-potentials, the Tafel slope is $75, 79, 78$ and $67 \text{ mV dec}^{-1}$ for CoFe$_2$O$_4$ (mixed with AB), rGO, CoFe$_2$O$_4$ + rGO mixture and CoFe$_2$O$_4$/rGO nanohybrid, respectively. The Tafel slope of CoFe$_2$O$_4$/rGO (67 mV dec$^{-1}$) is smaller than that of CoFe$_2$O$_4$, rGO and CoFe$_2$O$_4$ + rGO mixture, and is close to that of Pt/C (69 mV dec$^{-1}$). It approaches the theoretical value of $2.303RT/F$ (i.e., 59 mV dec$^{-1}$ at 25 °C), where $R$ is the universal gas constant, $F$ is the Faraday constant, and $T$ is absolute temperature. The low Tafel slope indicates the high intrinsic catalytic activity of CoFe$_2$O$_4$/rGO nanohybrid.

The polarization curves for the ORR on CoFe$_2$O$_4$/rGO nanohybrid at different rotation rates are shown in Fig. 7. They all reached well-defined diffusion limiting currents. The inset in Fig. 7 shows the corresponding Randles–Coulter plots obtained from the inverse current density ($j^{-1}$) as a function of the inverse of the square root of the rotation rate ($\omega^{-1/2}$) for CoFe$_2$O$_4$/rGO at $-0.22, -0.23, -0.25$ and $-0.36 \text{ V}$, respectively. These plots are linear and parallel, indicating the first-order dependence of the kinetics of ORR on the CoFe$_2$O$_4$/rGO surface. Each straight line intercept corresponds to the kinetic current $i_k$. The $B$-factor for CoFe$_2$O$_4$/rGO is 0.147 mA cm$^{-2}$ $\omega^{-1/2}$, determined from the slope of Randles–Coulter plots. The electron number $n$ calculated from the $B$-factor is in the range of 3.85–3.94. This is consistent with the result ($n \approx 3.84 – 3.90$) obtained from the RRDE measurements, suggesting that CoFe$_2$O$_4$/rGO favours 4e$^-$ reduction reaction process.

The catalytic activity of CoFe$_2$O$_4$/rGO nanohybrid for the oxygen evolution reaction (OER) was also investigated. Fig. 8 shows the anodic linear scanning voltammograms for the OER on CoFe$_2$O$_4$/rGO, CoFe$_2$O$_4$ + rGO mixture, rGO, CoFe$_2$O$_4$ (mixed with AB) and commercial Pt/C catalysts in N$_2$-saturated 0.1 M KOH solution at a corresponding rotation rate of 1600 rpm.
rotation speed of 1600 rpm. The CoFe$_2$O$_4$ + rGO mixture exhibits lower onset potential (0.62 V) and higher current density (19.4 mA cm$^{-2}$) for the OER than CoFe$_2$O$_4$ (mixed with AB). Similar to ORR, the edge sites and defect sites of rGO are active sites for OER and the two-dimensional structure of rGO allows the easy transfer of electrolyte/O$_2$ on both sides to/away active sites. Note that the activity of Pt/C is only slightly higher than that of CoFe$_2$O$_4$ and lower than that of the other three catalysts. This clearly shows that Pt/C is not a good catalyst for OER, which agrees well with the results reported by Liang et al. [11]. The OER activity is further improved on CoFe$_2$O$_4$/rGO nanohybrid, the onset potential on which is 0.54 V and the current density on which is 29.5 mA cm$^{-2}$. The high catalytic activity of CoFe$_2$O$_4$/rGO suggests that CoFe$_2$O$_4$/rGO is a promising bi-functional electrocatalyst for the ORR and OER. The results indicate the coupling between CoFe$_2$O$_4$ and rGO and the triple phase (solid—liquid—gas) region formed in CoFe$_2$O$_4$/rGO nanohybrid (similar to ORR) required for transport of reactants and products during the process of OER are important for the high activity of CoFe$_2$O$_4$/rGO nanohybrid.

The stabilities of CoFe$_2$O$_4$/rGO, CoFe$_2$O$_4$ (mixed with AB), rGO and commercial Pt/C catalysts for the ORR and the OER were examined with the chronoamperometric method in O$_2$-saturated 0.1 M KOH at 1600 rpm as shown in Fig. 9. The ORR current density of CoFe$_2$O$_4$ and rGO at $-0.8$ V decreases by 16.7% and 15.0%, respectively, after 43,200 s continuous operation, while a decrease of only 5.5% in current density is observed for the CoFe$_2$O$_4$/rGO catalyst (Fig. 9a). The worst case is Pt/C, the ORR current density of which decreases 52.4% after 43,200 s. For the OER stability, CoFe$_2$O$_4$/rGO catalyst shows a decrease of 8.7% in current density at 0.8 V after 43,200 s, which is much lower than that of CoFe$_2$O$_4$ (16.4%) and rGO (25.9%), respectively. And Pt/C degraded much more severely, showing a decrease of 71.3% in the OER current density after 43,200 s. It’s noticed that rGO exhibits more current decay in OER than in ORR, which is probably due to the oxidation of carbon at high potentials as reported by other groups [44,45]. The results reveal that the CoFe$_2$O$_4$/rGO nanohybrid is quite stable for both the ORR and OER, which most likely results from the strong coupling between CoFe$_2$O$_4$ and rGO. The strong coupling between CoFe$_2$O$_4$ and rGO prevents detachment and aggregation of CoFe$_2$O$_4$ during the process of ORR and OER, which improves the electrode cyclic stability.

4. Conclusions

In summary, CoFe$_2$O$_4$/rGO nanohybrid electrocatalysts were prepared via a two-step process. The CoFe$_2$O$_4$/rGO nanohybrid has shown high activity for the ORR in alkaline solutions and a four electron pathway is dominant for the ORR. Furthermore, high catalytic activity of CoFe$_2$O$_4$/rGO catalyst for the OER has also been demonstrated. This shows that CoFe$_2$O$_4$/rGO catalyst simultaneously owns promising catalytic activity for both the ORR and the OER. Meanwhile, the CoFe$_2$O$_4$/rGO is found to be quite stable for both the ORR and the OER, outperforming the commercial Pt/C. The improvement in the catalytic activity and stability in the CoFe$_2$O$_4$/rGO for the ORR and the OER mainly arises from the strong coupling between CoFe$_2$O$_4$ and rGO. The results indicate that CoFe$_2$O$_4$/rGO nanohybrid could be used as a potential bi-functional catalyst for metal—air batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.11.024.

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