CuCo$_2$O$_4$ nanoparticles on nitrogenated graphene as highly efficient oxygen evolution catalyst

Santosh Kumar Bikkarolla$^*$, Pagona Papakonstantinou$^*$

School of Engineering, Engineering Research Institute, University of Ulster, Newtownabbey BT37 0QB, UK

**Highlights**

- CuCo$_2$O$_4$ nanoparticles of size 4.0 nm were facilely synthesised on NrGO sheets.
- CuCo$_2$O$_4$/NrGO hybrid was explored as OER catalyst for the first time.
- CuCo$_2$O$_4$/NrGO shows high activity than any of the Cu—Co catalysts reported.
- The hybrid has shown good stability in alkaline media.
- High activity is due to presence of divalent copper ions at octahedral sites.

**Abstract**

Highly active, durable and cost-effective electrocatalysts for oxygen evolution reaction play a key role on developing energy-conversion technologies. Here, we report a composite material consisting of CuCo$_2$O$_4$ nanoparticles anchored on nitrogenated reduced graphene oxide (CuCo$_2$O$_4$/NrGO) as a highly efficient oxygen evolution electrocatalyst in both alkaline and neutral solutions for the first time. In 1 M KOH, 0.1 M KOH and 0.1 M PBS, CuCo$_2$O$_4$/NrGO catalyst exhibited a current density of 10 mA cm$^{-2}$ at a small overpotential of 0.36 V, 0.41 V and 1.15 V respectively, which are better than those of RuO$_2$ and IrO$_2$ catalysts. The CuCo$_2$O$_4$/NrGO exhibited good stability under strong alkaline conditions. The enhanced OER performance of CuCo$_2$O$_4$/NrGO is attributed to the presence of Cu$^{2+}$ ions at the octahedral sites, reduction in the size of the CuCo$_2$O$_4$ nanoparticles as measured by the TEM, enhancement of electrochemically active surface area (ECSA), and synergetic effect between CuCo$_2$O$_4$ nanoparticles and NrGO sheets. This cost effective and highly efficient catalyst can possibly replace the expensive catalysts such as RuO$_2$ and IrO$_2$.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Oxygen evolution reaction plays a key role in many energy conversion technologies such as solar fuel production, water electrolyser and rechargeable metal air batteries. The oxygen evolution reaction (OER) $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ (in acidic media) or $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ (in basic media) proceeds through a complex four electron transfer water oxidation process and it is kinetically sluggish [1–5]. This imposes considerable electrochemical overpotential requirements to achieve a current density of 10 mA/cm$^2$ or 10 A/g, which leads to significant losses in the energy conversion efficiency. Effective catalyst development is...
critical to address this challenge. Currently earth-limited RuO₂ and IrO₂ are considered as most active OER catalysts in both acidic and basic solutions [6]. However, the prohibited cost associated with these oxides has limited their deployment in large scale applications. Accordingly, extensive research efforts have been devoted to the development of alternative earth abundant OER electrocatalysts such as transition metal oxides [7–10], layered double hydroxides [11–13] and perovskites [14–16] that are inexpensive, sufficiently active, and stable upon prolonged exposure under oxidizing conditions.

Among all the catalysts, the spinel-type Co₃O₄, which consists of Co²⁺ at tetrahedral sites and Co³⁺ at octahedral sites, exhibited promising OER activities and corrosion stability in alkaline electrolytes [6–8]. Furthermore, the electrocatalytic efficiency of Co₃O₄ could be enhanced by the incorporation of additional metal ions (M = Zn, Cu, Ni, Mg, and Fe) into the oxide [9–14]. However, preparation of spinels by the traditional ceramic route, which involves high-temperature sintering and grinding, gives particles with limited electrocatalytic activity due to their low specific surface areas and inadequate conductivity for facilitating fast electron transport. Minimization of the particles size should enhance surface activity of the catalyst. Anchoring nanostructured oxides on a conductive support Results in an increase in rate and as higher OER activity. It is also believed that the synergistic chemical coupling effects between Co-based catalysts and conductive support contributes to substantial enhancement of the OER efficiency.

At present, a few studies have demonstrated that incorporating copper ions into Co₃O₄ lattice can expedite the OER by reducing the overpotential necessary to reach a current density of 10 mA/cm² [9,11]. Different studies reported various optimal compositions of copper, to achieve maximum OER performance [9,15,16]. The increase in the OER activity of Cu doped cobalt oxide is largely due to a decrease in the electrical resistivity [17]. Although it is clear that the OER performance of the Co₃O₄ nanostructures improves after doping with copper, there are contradictory reports regarding the OER stability of copper doped cobalt oxides. Jia et al. have shown copper doping increases the OER stability [17], whereas Berenguer et al. have shown decrease in the OER stability of copper doped spinel cobaltite oxides [18]. The parameters, which affect the OER performance, are size of the nanoparticles and electrical conductivity. However, in all of the reported studies the size of CuCo₂O₄ nanoparticles is typically greater than 10 nm and lack of any conductive support resulted in poor OER performance [9,11,19,20]. The OER performance of the CuCo₂O₄ integrated with NaGNO sheets has been reported in alkaline media [21].

Bearing these factors in mind, we have synthesized CuCo₂O₄ nanoparticles of average size 4.0 nm on NaGNO sheets by a simple solvothermal technique. Here we report for the first time the OER performance of 4.0 nm CuCo₂O₄ nanoparticles on nitrogenated reduced graphene oxide in alkaline and neutral media. The integrated CuCo₂O₄/NaGNO structure displays higher electrocatalytic activity towards OER, when compared to Co₃O₄/NaGNO, CuCo₂O₄ and Co₃O₄ counterparts. The overpotential of the CuCo₂O₄/NaGNO catalyst is smaller when compared to any previously synthesized Cu–Co compound [9,11,19,20] or to the most active cobalt based catalysts integrated with either carbon [22–26] or gold nanostructures [27,28]. The improved performance of the CuCo₂O₄/NaGNO hybrid is attributed to the following reasons: 1) CuCo₂O₄/NaGNO has spinel structure with Cu²⁺ ions at the octahedral sites [19,25,30]. The presence of Cu²⁺ ions at the octahedral sites of the spinel has been established by XPS spectra and an increase in the spinel lattice parameter (a₀) as revealed by XRD patterns. 2) Copper doped Co₃O₄ nanoparticles on NaGNO sheets have a smaller size and a high roughness factor. 3) The underlying conductive NaGNO provides strong coupling between the two catalysts and improves the electrical conductivity of hybrid, which leads to improved OER performance.

2. Experimental section

2.1. Chemicals

Graphite powder (particle size < 20 μm) was purchased from Alfa Aesar. Sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), ammonia hydroxide (30 wt% in H₂O), N,N-dimethylylformamide (DMF), cobalt chloride hexahydrate (CoCl₂·6H₂O) and copper chloride dihydrate (CuCl₂·2H₂O), alumina (particle size 0.05 μm) were purchased from Sigma Aldrich. All solutions used in experiments were freshly prepared with Millipore water of resistivity 15 MΩ.

2.2. Synthesis of graphene oxide

GO sheets were prepared from graphite flakes by a modified Hummer’s method. The starting material graphite powder with particle size 20 μm was ground for 30 min by using mortar and pestle. Ground graphite of 2.5 g was mixed with 2 g of NaNO₃ in 250 ml flask. 70 ml of sulfuric acid was added to the mixture and stirred until homogenized. The mixture was cooled in an ice bath and 10 g of KMnO₄ was added to the mixture and left over night followed by heating the mixture at 50 °C for 24 h. An additional 10 g of KMnO₄ was added to the mixture and slowly 70 ml of water was added to the mixture. The temperature of the mixture was raised to 50 °C and stirred for 24 h. The GO mixture was poured in 400 ml of ice water and 3 ml of H₂O₂ was added and stirred over night. The GO mixture was purified by dispersing in 500 ml aqueous solution of 3 wt% H₂SO₄ and 0.5 wt% H₂O₂. After 24 h the graphite oxide pellet was collected by centrifuging at 3000 rpm and the supernatant was removed. This process was repeated for 5 times. The solid product obtained after rigorous cleaning process was rinsed with copious amount water and dried in oven.

2.3. Synthesis of CuCo₂O₄/NaGNO hybrid, Co₃O₄/NaGNO hybrid, CuCo₂O₄ nanoparticles, Co₃O₄ nanoparticles and NaGNO

CuCo₂O₄/NaGNO hybrid was prepared by simple solvothermal method. In a typical synthesis, 20 mg of GO was dispersed in 14 ml of absolute ethanol and sonicated for 60 min. 1 ml of a 0.24 M CoCl₂·6H₂O and 1 ml of a 0.12 M CuCl₂·6H₂O were added to the GO solution and stirred for 30 min, followed by addition of 1 ml of NH₄OH to the mixture and stirred for another 30 min. After that, the reaction mixture was transferred to 23 ml Teflon lined autoclave for solvothermal reaction at 150 °C for 3 h. The resultant product was cleaned with ethanol and DI water and collected by centrifugation at 3000 rpm for 45 min. The material was dried by lyophilisation for 24 h and annealed in muffle furnace at 300 °C for 2 h. Co₃O₄/NaGNO was prepared by the similar procedure with 1 ml of 0.32 M CoCl₂·6H₂O and no Cu salt. CuCo₂O₄ and Co₃O₄ nanoparticles were prepared through the same steps without adding any GO. NaGNO was synthesized through the same steps without adding any Co and Cu salt.

2.4. Sample preparation for electrochemical characterization

A rotating disk electrode with a glassy carbon disk of 3 mm diameter was used in this study. Prior to surface modification the electrode was polished with alumina powder of particle size 0.05 μm and then cleaned by sonication in water for 2 min. The working electrode was prepared as follows: 5 mg of catalyst was dispersed in 1 ml of DMF and 50 μl of 35 wt% nafion by sonication
for at least 30 min. Then 2 μl of catalyst ink was spread on GCE and dried under infrared lamp, which results in a final loading of 0.14 mg/cm².

2.5. Electrochemical measurements

Electrochemical studies were carried out in a standard three electrode system controlled by a Metro Ohm electrochemical workstation. A Pt wire and Ag/AgCl electrode were used as collector and reference electrodes. The electrolyte (1 M KOH, 0.1 M KOH and 0.1 M PBS) was freshly prepared and experiments were carried out at room temperature. The electrolyte was saturated with O₂ by bubbling O₂ for 15 min. A flow of O₂ was maintained over the electrolyte during the measurements. Linear sweep voltammogram (LSV) was carried out at 1 mV/s for the polarization curves. All the catalysts were cycled at least for 30 times by cyclic voltammetry in the potential range 0.2–0.8 V (vs Ag/AgCl) in alkaline solutions and 0.6–1.2 V (vs Ag/AgCl) in 0.1 M PBS solution until stable CV curves were developed before measuring polarization curves. Electrochemical impedance spectroscopy (EIS) was recorded by overlaying an ac voltage of 10 mV to a dc offset of 0.58 V in 1 M KOH, 0.62 V in 0.1 M KOH and 0.8 V in 0.1 M PBS respectively. The frequency of the ac voltage was swept in the range of 1 MHz to 10 mHz by avoiding the instrumental noise at high frequency range. LSV and EIS were conducted at 1600 rpm to get rid of the oxygen bubbles. Stability tests were carried for 1000 cycles at a scan rate of 100 mV/s in the potential range 0.4 V–0.7 V in 1 M KOH, 0.45 V–0.8 V in 0.1 M KOH and 0.8 V–1.2 V in 0.1 M PBS at the end of every 500 cycles linear sweeps were measured at a scan rate of 1 mV/s. Potentials in the graphs were reported vs Ag/AgCl and overpotentials were calculated by using the relation \( \eta (V) = E_{R.H.E} - E_p \), where \( E_{R.H.E} \) corresponds to the potential at 10 mA/cm² and \( E_p \) corresponds to thermodynamic potential for water oxidation, being equal to 1.23 V vs R.H.E. The conversion between Ag/AgCl and R.H.E is given from the following equation between Ag/AgCl and R.H.E is given from the following equation:

\[
\eta = E_{Ag/AgCl} - 0.197 V + 0.0591 \times pH.
\]

The values of turnover frequency were determined in 1 M KOH by assuming every single metal atom is involved in the catalysis (lower TOF were calculated): [24,31,32].

\[
\text{TOF} = \frac{J_c \times S_{geo}}{F \times n} \quad (1)
\]

where \( J_c \) is the measured current density at overpotential \( \eta \), \( S_{geo} \) is the surface area of the glassy carbon disk electrode (0.07 cm²), the number 4 is due to the four electrons transferred per O₂ molecule, F is the Faraday constant (96,500 C/mol) and n is the number of moles of the metal atom on the electrode, which is calculated from the mass of the catalyst on the electrode and molecular weight. The values of specific current densities \( J_s \) were calculated by dividing the measured current density at a given overpotential by the roughness factor (RF), as described in equation (2).

2.6. Structural characterization

X-ray photoelectron spectroscopy was carried on a Kratos Axis Ultra DLD spectrometer. X-ray diffraction (XRD) analysis was performed on a Bruker D8-discover diffractometer fitted with global mirror (Cu Kα, radiation source, λ = 1.540 Å). Scanning electron microscopy images were obtained on FEI quanta 200 3D at 20 kV accelerating voltage. High resolution transmission electron microscopy (HRTEM) images were obtained on Jeol JEM 2011 at 200 kV accelerating voltage.

3. Results and discussion

CuCo₂O₄/NrGO and other control materials were prepared via a solvothermal process followed by annealing in air. Detailed information on synthesis is given in experimental section. The solvent in the solvothermal process was absolute ethanol. We have observed, that the presence of 10% water lead to growth of both nanowires and nanoparticles. At higher concentrations of water, both microstructures and nanostructures were observed with the resultant phase been Co₃O₄ or CuCo₂O₄. When absolute ethanol was used as the solvent, only cobalt oxide chloride hydrate (Co₉O₆Cl₄·7H₂O) nanoparticles were observed at the end of the solvothermal process. After annealing at 300 °C in air, the resulting phase was Co₃O₄ (Fig. S1). It has to be noted that the oxidation state of cobalt cations is +2 at the end of solvothermal process and only after annealing at 300 °C in air it leads to oxidation of Co²⁺ to Co³⁺ cations and formation of spinel cobalt oxides. The presence of ammonia in the solvothermal vessel is necessary for the growth of the nanoparticles on graphene sheets. In the absence of ammonia no growth of nanoparticles was observed on graphene sheets (Fig. S2). In addition ammonia acts as both a reducing agent and nitrogen precursor to graphene oxide to obtain NrGO sheets, which have higher conductivity, when compared to undoped reduced graphene oxide sheets.

The size, morphology and structure of the resulting materials were investigated by scanning electron (SEM) and transmission electron microscopies (TEM). SEM (Fig. 1) showed that both Co₃O₄ and CuCo₂O₄ nanoparticles are grown on a 3D flame like nitrogen doped reduced graphene oxide. TEM (Fig. 2a and c) showed that the graphene sheets are completely covered with nanoparticles. HRTEM (Fig. 2b and d) showed the crystal lattice fringes with d-spacing of 0.46 nm, 0.28 nm and 0.24 nm can be assigned to the 300, 211, (220) and (311) planes respectively of face centered cubic HRTEM (Fig. 2b and d) showed the crystal lattice fringes with d-spacing of 0.46 nm, 0.28 nm and 0.24 nm can be assigned to the 300, 211, (220) and (311) planes respectively of face centered cubic Co₃O₄ and CuCo₂O₄. The average size of the Co₃O₄ and CuCo₂O₄ nanoparticles on NrGO sheets is 6.4 nm and 4.0 nm respectively, which reveals a reduction in the size of the Co₃O₄ nanoparticles after doping with copper (distribution of nanoparticles on NrGO sheets is shown in Fig. S5).

The Cu₂O₃/NrGO XPS spectra for both Cu₂O₃/NrGO and Co₃O₂/Cu₃O₄/NrGO. The Cu 2p XPS spectra was fitted with two spin orbit doublets, assigned to Cu²⁺ and Cu³⁺ components and two satellite peaks assigned to Cu²⁺ and Cu³⁺ components. Similar fitting was also done for the Co 2p1/2 XPS spectrum [20,33,34]. The Cu 2p3/2 – Cu 2p1/2 spin orbit splitting is characteristic of Cu²⁺ and Cu³⁺ species. In both hybrids the spin orbit splitting for Cu²⁺ doublet is 15.0 eV and for Cu²⁺ doublet is 15.4 eV, which are characteristic of spinel cobalt oxides [20,33,34]. In the case of Co₂O₄/NrGO the ratio of Co²⁺ to Co³⁺ is 2:6, while this decreases to

**Table 1**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( \eta ) (V)</th>
<th>( \Phi = 10 \text{ mV/cm}² )</th>
<th>Tafel slope TOF</th>
<th>ECSA (cm²)</th>
<th>RF</th>
<th>( J_{s, 0.36 \text{ V}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCo₂O₄/NrGO</td>
<td>0.36</td>
<td>64</td>
<td>0.053</td>
<td>4.9</td>
<td>70</td>
<td>0.14</td>
</tr>
<tr>
<td>Co₃O₄/NrGO</td>
<td>0.4</td>
<td>57</td>
<td>0.011</td>
<td>1.2</td>
<td>17</td>
<td>0.12</td>
</tr>
<tr>
<td>CuCo₂O₄/NrGO</td>
<td>0.4</td>
<td>67</td>
<td>0.023</td>
<td>1.6</td>
<td>26</td>
<td>0.16</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>0.42</td>
<td>60</td>
<td>0.007</td>
<td>1.8</td>
<td>8.5</td>
<td>0.15</td>
</tr>
</tbody>
</table>
1.7 for CuCo2O4/NrGO, indicating a decrease of the Co2⁺ ions. However, in both the hybrids the concentration of Co2⁺ ions is greater than Co3⁺ ions [20]. Fig. 3c shows the Cu 2p XPS spectrum for CuCo2O4/NrGO. The Cu 2p3/2 curve region was fitted with three spin orbit doublets assigned to Cu⁺, Cu2⁺ and Cu3⁺ and two satellite peaks. The components at 931.9 eV, 934.1 eV and 937 eV correspond to Cu⁺ at the octahedral sites and Cu3⁺ at the tetrahedral sites [19,20,35]. The reason for the presence of the Cu⁺ ions can be due to the X-ray induced reduction of Cu2⁺ ions to Cu⁺ [19]. The most prominent peak in Cu 2p spectrum is at 934.2 eV, which indicates the majority of the copper ions are Cu2⁺ ions and these ions are at octahedral sites because the resulting structure is more energetically stable [19,20]. A decrease in the atomic ratio of Co2⁺ to Co3⁺ indicates that Co3⁺ ions replace Co2⁺ ions at the tetrahedral sites. Overall the amount of Co2⁺ ions decreases and the amount of Co3⁺ ions is unchanged due to Cu2⁺ substitution at octahedral sites. It has been found that in various substituted spinels the presence of divalent ions at the octahedral sites promotes the catalytic activity, when compared to divalent cations at the tetrahedral sites [19,29,30]. A detailed tabulated information (Table S1) is presented in the supporting information, showing the peak positions of components and concentration of Co2⁺, Co3⁺ and copper ions (Cu⁺, Cu2⁺ and Cu3⁺) in both materials. The overall atomic concentration of nitrogen in the NrGO sheets is 10 at %. The N 1s profile can be divided into three components pyridinic N (398.6 eV), pyrrolic N (399.9 eV) and substitutional (401.5 eV) as shown in Fig. 3d and these assignments are in agreement with the literature [36,37].

Fig. 4a shows the XRD of Co3O4/NrGO and CuCo2O4/NrGO powders prepared by solvothermal process followed by annealing under air at 300 °C for 2 h. Relative intensities of the diffraction lines of the Co3O4/NrGO and CuCo2O4/NrGO were consistent with face centered cubic Co3O4 (JCPDS-ICDD: 09–0418) and Cu0.95Co2.05O4 (JCPD-ICDD: 78–2177). The spinel lattice parameter (a0) calculated from the d spacings of the crystal planes of the CuCo2O4 nanoparticles in the hybrid is 8.133 Å, which is larger than that of Co3O4 (8.084 Å). The increase in a0 essential indicates the presence of Cu2⁺ ions at the octahedral sites of the spinel, which is consistent with the XPS observation [38,39]. From the XRD pattern (Fig. 4a), we observe that the full width at half maximum (FWHM) of the diffraction peaks is increasing, when cobalt ions are replaced with copper ions, which indicates that the size of CuCo2O4 nanoparticles is smaller to that of Co3O4. This observation is consistent with the HRTEM measurements. The decrease in the peak intensities and increase in the FWHM of the CuCo2O4 nanoparticles also reveals the poor crystallinity of the CuCo2O4 on NrGO sheets. The XRD pattern of CuCo2O4/NrGO is similar to Co3O4/NrGO with no additional peaks from the base center monoclinic CuO phase. Furthermore, the XRD of CuCo2O4/NrGO annealed at 300 °C in air for 2 h didn’t show any diffraction peaks corresponding to CuO phase (Fig. S4). This shows that the CuCo2O4/NrGO doesn’t contain any poorly crystalline CuO phase. However, in the case of the nanoparticles the XRD pattern of CuCo2O4 nanoparticles contains diffraction peaks from monoclinic CuO at 35.5° and 38.9° (JCPD-ICDD: 89–5895), which correspond to the crystal planes (111) and (111) (Fig. 4b).

The mass ratio of NrGO in the hybrid was determined by thermogravimetric analysis, in which the hybrid materials were heated in air at 550 °C for 2 h and a weight loss of 15% was measured in each hybrid. This corresponded to the removal of NrGO from the hybrid by oxidation. CuCo2O4 and Co3O4 was about 85 wt % in the hybrids.

The electrocatalytic activity of the samples was investigated in 1 M KOH, 0.1 M KOH and 0.1 M PBS (Figs. 5 and 6). All the catalysts were uniformly loaded on 3 mm glassy carbon electrode (GCE) with loading of 0.14 mg/cm² for measuring OER polarization curves at a
scan rate of 1 mV/s to reduce the capacitive currents. During the precondition procedure, the catalysts were not subjected to the positive and negative potential regions as this will cause the detachment of the nanoparticles from the graphene sheets [40,41]. Therefore the catalysts were cycled at least 30 times only in the potential range 0.2 V – 0.8 V in alkaline solutions and 0.6 V – 1.2 V in neutral solutions before recording the polarization curves. During the measurement of polarization curves, the working electrodes were rotating at 1600 rpm to eliminate the oxygen bubbles from the surface of the working electrode. The OER performance of each catalyst is reproduced at least on three electrodes.

The catalytic properties of all the catalysts were first investigated in 1 M KOH by measuring the linear sweep voltammogram (LSV). The overpotentials of CuCo2O4/NrGO, Co3O4/NrGO, CuCo2O4, and Co3O4 at 10 mA/cm² current density in 1 M KOH are presented in Table 1. The Co3O4 nanoparticles show more positive onset potential and the lowest current density, while CuCo2O4/NrGO shows the lowest onset potential for water oxidation and the highest current density at a given potential. In the case of Co3O4/NrGO, a current density of 10 mA/cm² is obtained at an overpotential of 0.4 V. After doping with the copper, the overpotential is shifted to 0.36 V. A shift of 40 mV is observed in the case of hybrids upon doping with copper. In the case of Co3O4 nanoparticles a current density of 10 mA/cm² is observed at overpotential of 0.42 V. After doping with copper the overpotential shifted to 0.4 V. A shift of 20 mV is observed in the case of nanoparticles after doping with copper. Importantly, in the high overpotential range, CuCo2O4/NrGO and Co3O4/NrGO show superior activity for water oxidation, when compared to CuCo2O4 and Co3O4 nanoparticles. The CuCo2O4/NrGO and Co3O4/NrGO hybrid afford nearly two times higher OER current densities than CuCo2O4 and Co3O4 nanoparticles at an applied potential of 0.7 V vs Ag/AgCl. This shows that the presence of NrGO sheets improves the current at higher overpotentials due to the synergetic coupling of the nanoparticles with the NrGO, which enhances the electron transfer during the OER process. The OER performance of the Co3O4/NrGO shown here is comparable to the best results in the literature, which include Co3O4 nanoparticles on NrGO sheets by Liang et al. and mesoporous Co3O4 nanostructures integrated with gold nanoparticles [28,41]. The OER performance of the CuCo2O4/NrGO is better, when compared to nickel doped Co3O4 nanostructures integrated with either carbon nanostructures or gold nanoparticles [22,23,27,42]. The overpotential of CuCo2O4/NrGO is smaller, when compared to RuO2, IrO2 nanoparticles catalyst [24,43] and comparable to the state of the art 20 wt % Ru/C and 20 wt % Ir/C catalysts for OER [44]. A more detailed comparison of our materials with the literature data is presented in the Supporting Information, in Tables S3 and S4 [9–11,22,24–27,31,32,42,43,45–47].

![Fig. 2. (a) TEM image of Co3O4/NrGO (b) HRTEM image of Co3O4/NrGO. (c) TEM image of CuCo2O4/NrGO (d) HRTEM image of CuCo2O4/NrGO.](https://example.com/f2.png)

We have investigated the OER stability of all the catalysts in 1 M KOH. Cycles were swept between 0.4 V and 0.7 V at 0.1 V/s for 1000
cycles in 1 M KOH. The anodic sweeps before and after the stability test are shown in Fig. 5b. Both the hybrid catalysts have suffered a small current decrease and a shift of approximately 10 mV in the overpotential towards positive potentials is observed after 1000 cycles. In contrast to previous reports [17,18] we observed equal corrosion stability for both CuCo2O4/NrGO and Co3O4/NrGO. In the case of CuCo2O4 and Co3O4 nanoparticles a shift of 18 mV and 23 mV is observed after 1000 cycles. It can be noticed that the Tafel slopes of all the catalysts are close to 60 mV/dec (Fig. 5c and Table 1), which indicates that the active species are Co4+ ions in all the catalysts [48]. In the case of cobalt oxides and doped cobalt oxides it has been well documented that the Co4+ ions promote OER. The role of the Co4+ cation in electrochemical water oxidation has been proposed by the Bell et al. [49,50]. As previously reported [25,27,49,50] one possible mechanism for OER is shown in equations (3)–(7), equation (5) is hypothesised as rate determining step.

The presence of Co4+ cations increases the electrophilicity of the adsorbed O and thus promotes the formation of OeOH and also believed to promote the deprotonation of OOH species via electron withdrawing inductive effect to produce O2.

\[
\begin{align*}
M + OH^- &\rightarrow M - OH + e^- \\
M - OH + OH^- &\rightarrow M - O + e^- + H_2O \\
M - O + OH^- &\rightarrow M - OOH + e^- \\
M - OOH + OH^- &\rightarrow M - O_2 + e^- + H_2O \\
M - O_2 &\rightarrow M + O_2
\end{align*}
\]

where M represents an active center.

Fig. 5d shows representative Nyquist plots of the EIS response of CuCo2O4/NrGO, Co3O4/NrGO, CuCo2O4, and Co3O4 at an applied potential of 0.58 V vs Ag/AgCl in 1 M KOH. The data were fitted using the equivalent circuit illustrated in the inset of Fig. 5d. From the fitting of the impedance spectra the electron transfer resistance for CuCo2O4/NrGO, Co3O4/NrGO, CuCo2O4, and Co3O4 are 61 Ω, 103 Ω, 88 Ω and 175 Ω respectively. The CuCo2O4/NrGO exhibits a smaller electron transfer resistance, when compared to Co3O4/NrGO, CuCo2O4, and Co3O4, which clearly demonstrates that the CuCo2O4/NrGO electrode possesses much faster transfer of electrons during OER. The CuCo2O4 nanoparticles have shown less electron transfer resistance than Co3O4/NrGO due to the higher current at an applied of 0.58 V.

OER performance of all the catalysts was also examined in both 0.1 M KOH (pH = 13.0) and 0.1 M PBS (pH = 7.6) solutions (Fig. 6). In 0.1 M KOH solution CuCo2O4/NrGO has exhibited overpotential of 0.41 V whereas in 0.1 M PBS solution CuCo2O4/NrGO exhibited overpotential of 1.15 V, which is due to the lower concentration of OH− in 0.1 M PBS solution [51]. In 0.1 M KOH solution all the catalysts have shown very good stability, where the hybrids have shown 10 mV increase in the overpotential and there is no change in overpotential in the case of the nanoparticles (Fig. 6b). Enhanced OER activity in neutral solutions is important due to the benign nature of the electrolyte, causing less corrosion to the electrode surface. However, observing good stability in neutral conditions is challenging, when compared to alkaline conditions, because the decrease in the pH at the electrode surface during the OER at high current densities can only get compensated at a certain reaction rate [52]. In addition the OER performance also decreases due to formation of passive layers on the catalyst surface and due to the aggregation of nanoparticles during the potential cycling [53,54]. In 0.1 M PBS solution all catalysts suffered significant increase in overpotential by 30 mV after the stability test (Fig. 6d). In 0.1 M PBS solution the OER performance and stability of the CuCo2O4
nanoparticles is poor, when compared to Co₃O₄ nanoparticles, due to the presence of the resistive phase CuO in the CuCo₂O₄ nano-
particles. Tafel plots and Nyquist plots in 0.1 M KOH and 0.1 M PBS solution are shown in Figs. S8 and S9.

To further evaluate their OER catalytic ability, the turnover frequencies (TOF) of the catalysts were measured at \( \eta = 0.36 \) V and presented in Table 1. The CuCo₂O₄/NrGO composite was found to exhibit the highest TOF of 0.053 s⁻¹ on the assumption that every metal atom is catalytically active. The ECSA of each material is calculated from the electrochemical double layer capacitances of each material by using Equation (8) [55,56].

\[
\text{ECSA} = \frac{C_{dl}}{C_s} \tag{8}
\]

In Equation (8), \( C_{dl} \) is electrochemical double layer capacitance, which was determined by measuring the CVs at various scan rates (100 mV/s to 10 mV/s) in the non-Faradaic region. CVs of the CuCo₂O₄/NrGO in 1 M KOH at various scan rates are shown in Fig. S10. The double layer charging current is equal to the product of scan rate (\( \nu \)) and \( C_{dl} \) [46,55-57]. Thus, a plot of \( i_C \) as a function of \( \nu \) yields a straight line with a slope equal to \( C_{dl} \) as shown in Fig. 7b for CuCo₂O₄/NrGO, Co₃O₄/NrGO, CuCo₂O₄ and Co₃O₄. \( C_s \) is specific electrochemical double layer capacitance of an atomically smooth surface, which will be typically 15–50 \( \mu \)F/cm² [58,59]. In this study the value of \( C_s = 40 \) \( \mu \)F/cm² for all the catalysts in 1 M KOH electrolyte. The roughness factor (RF) is obtained from the ratio of ECSA to the geometric surface area (0.07 cm²) of the electrode. CuCo₂O₄/NrGO exhibited ECSA and RF values of 4.9 cm² and 70, which are 4 times higher than those of Co₃O₄/NrGO (Table 1). It has been known that the only the surface atoms of the catalyst play a key role in the

Fig. 4. (a) XRD of CuCo₂O₄/NrGO and Co₃O₄/NrGO. (b) XRD of CuCo₂O₄ and Co₃O₄.

Fig. 5. (a) OER polarization curves of CuCo₂O₄/NrGO, Co₃O₄/NrGO, CuCo₂O₄, Co₃O₄ and NrGO measured on GCE at a scan rate of 1 mV/s (b) OER polarization curves before and after potential sweeps (0.4–0.7 V vs Ag/AgCl) for 1000 cycles. (c) Tafel plots derived from (a). (d) Nyquist plots at potential of 0.58 V (vs Ag/AgCl). All the measurements were performed in O₂ saturated 1 M KOH and 1600 rpm. Catalyst loading is 0.14 mg/cm² for all the samples.
OER process. Therefore, a larger RF means more accessible surface area for electrolyte permeation, which benefits the OER. The increase in the OER activity in the case of CuCo$_2$O$_4$/NrGO over Co$_3$O$_4$/NrGO and other catalysts is attributed to enhancement of ECSA, accrued from the copper doping and due to the synergetic coupling between graphene and CuCo$_2$O$_4$ nanoparticles, which make the hybrid more conducting when compared to nanoparticles.

4. Conclusion

In conclusion, this study reports a novel CuCo$_2$O$_4$/NrGO electrocatalyst for high-performance water oxidation. This electrocatalyst showed exceptional OER activity with a small overpotential of 0.36 V in 1 M KOH at the current density of 10 mA cm$^{-2}$ and large anodic currents, when compared to the CuCo$_2$O$_4$ nanoparticles. It is observed that the underlying nitrogen doped graphene network enhances electron transport, facilitating a high OER activity for the CuCo$_2$O$_4$ nanoparticles/NrGO sheets complex. This electrocatalyst has shown very good stability in alkaline solutions and outperforms precious metal oxide catalysts such as RuO$_2$ and IrO$_2$. This work opens up new possibilities in developing highly active and low-cost oxygen evolution electrocatalysts for energy applications such as water splitting and high performance rechargeable metal-air batteries.

Acknowledgments

SKB acknowledges support from the University of Ulster through the Vice-Chancellor’s Research Scholarship (VCRS) award.
Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.01.192.

References