One-step synthesis of carbon-protected \( \text{Co}_3\text{O}_4 \) nanoparticles towards long-term water oxidation in acidic media

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Keywords: Oxygen evolution reaction; Noble metal-free electrocatalysts; PEM water electrolysis; Hydrogen generation.

Abstract

The design and development of a highly efficient and stable Oxygen Evolution Reaction (OER) electrocatalysts in acid media are important for various renewable technologies. In this work, an advanced \( \text{Co}_3\text{O}_4 \) electrocatalyst supported on a mesoporous hydrophobic carbon paper (Co/29BC) was formed via a simple one-step thermal decomposition of cobalt nitrate. Through this novel approach, the amorphous carbon layer resulting from the thermal decomposition of carbon-containing species in the mesoporous layer provided enhanced electronic conduction and protection against corrosion to the \( \text{Co}_3\text{O}_4 \) nanoparticles. Equally important, the OER performance was found to be correlated to the morphology and surface composition of \( \text{Co}_3\text{O}_4 \). With optimized \( \text{Co}^{3+} \) active sites and oxygen vacancies at the metal oxide surface, the \( \text{Co}_3\text{O}_4 \) catalyst showed superior OER performance and durability in a PEM water electrolyser, with a small overpotential (350 mV) at a constant current density of 10 mA.cm\(^{-2}\) for over 50 h. Accordingly, this work provides new insights...
toward the design of high-performance and highly stable OER electrocatalysts in corrosive acidic environments.

1. Introduction

With the increase in energy demand, hydrogen is believed to be a promising energy carrier to store and transport energy across small- to large-scale applications. However, the lack of a cheap and efficient way to produce renewable hydrogen hinders its large-scale implementation. Currently, hydrogen is still primarily (94%) produced via steam reforming of natural gas leading to additional CO$_2$ emissions. In comparison, renewable water electrolysis is a clean and efficient way to produce hydrogen. This not only provides stability to the electricity network, but also captures the otherwise wasted economic values of renewable energy. Among all the water electrolysis technologies, Proton Exchange Membrane Water Electrolysis (PEMWE) leads to high current density (~2 A cm$^{-2}$), high efficiency (80 - 90%) and hydrogen purity (99.99%), and PEMWE can be operated to produce pressurised hydrogen without the need of compressors.$^{[1]}$ However, efficiencies depend heavily on the kinetics of the Oxygen Evolution Reaction (OER), involving the complex four proton- coupled electron transfer processes. As a result, noble metals (e.g. Pt and IrO$_2$) are always required as electrocatalysts due to their high electronic conductivity, superior activity and stability under acidic conditions.

Several promising noble metal-free electrocatalysts, in particular Co-based materials, have shown reasonable OER performance due to their good electrical conductivity, possible electron hopping between metal centres of different valence states, as well as rich redox sites at the surface of oxides enabling the adsorption and activation of oxygen.$^{[2]}$ However, the electrocatalytic activity of non-noble OER electrocatalyst has mainly been reported under alkaline and neutral pH conditions. Significant fundamental challenges, including high overpotentials, low Faradaic efficiencies, and metallic dissolution remain for enabling the use of non-noble OER catalysts under acidic conditions relevant to PEMWE. Recently, some approaches to enhance the stability of transition metal oxides
in a strong acid environment have been reported. These include: 1) the addition of conductive corrosion-resistant elements or support,\cite{3,4} 2) methods for enhanced electrical and mechanical interfaces between the active materials and the support,\cite{5} and 3) the precise control of the operating window.\cite{6} Through these approaches extended stabilities (>12 h) at 10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$ have been reported. In particular, carbon-coated Co$_3$O$_4$ nanosheets showed very low OER in 0.5 M H$_2$SO$_4$ with a small overpotential of 370 mV, and a long lifetime of 86.8 h at a constant current density of 100 mA cm$^{-2}$.\cite{7} Further downsizing the catalyst nanoparticles to Single-Atom metal Catalysts (SACs) anchored on conductive three-dimensional (3D) supports, such as hetero-N-coordinated Co single sites, have shown more promising results through a maximum atom utilization.\cite{8} However, the stability of single metal atoms is challenging because of the high surface energy involved and the difficulties in avoiding the surface diffusion and agglomeration of the single metal atoms, which in fine results in a lower number of active sites.

The challenge of transition metal oxides as practical OER electrocatalysts in an acidic environment remains the limited activity and long-term stability. Herein, inspired by previous findings, a one-step synthesis of Co$_3$O$_4$ nanoparticles is reported whereby the direct decomposition of cobalt nitrate on a hydrophobic carbon gas diffusion layer (29BC), led to a superior catalytic material. Remarkably through this synthetic approach, a layer of amorphous carbon was formed at the surface of the Co$_3$O$_4$ nanoparticles (<10 nm), enabling an enhanced electronic conductivity of the oxide materials while enabling protection against corrosion. We examined the catalytic OER performance of the Co/29BC electrode in 0.5 M H$_2$SO$_4$, and its correlation with the particle size, active sites and adsorbed oxygen of Co$_3$O$_4$. Besides, we demonstrated the direct application of the Co/29BC electrode in a full PEM water electrolyser, showing outstanding performances and stability owing to the unique structure of the cell.

2. Results and discussion

2.1 Preparation and characterization of Co/29BC electrode

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As shown in Figure 1a, the cobalt oxide catalyst layer was prepared by direct decomposition of cobalt nitrate on a hydrophobic carbon substrate (29BC). The 29BC carbon substrate was placed on a hotplate at various calcination temperatures (i.e. 250, 300 and 350 ℃) and the resulting materials were denoted as “Co-250”, “Co-300” and “Co-350”, respectively. XRD analysis (Figure 1b) of the as-prepared electrodes confirmed the formation of a highly crystalline cubic phase Co₃O₄, with the space group of Fd-3m. The main peak at 39.6° corresponds to the (311) plane, indicating that Co₃O₄ preferentially grew along the <311> direction. The effect of the calcination temperature on the crystalline size of Co₃O₄ was also investigated by XRD. In this case, the main (311) peak became broader as the calcination temperature increased, indicating a decrease in Co₃O₄ crystallinity. The average crystalline size of Co₃O₄ along the (311) plane was further estimated by using the Scherrer equation. The average grain sizes of Co₃O₄ at 250, 300 and 350 ℃ were calculated to be 29, 20 and 13 nm, respectively. Hence, the grain size of the Co₃O₄ nanoparticles was reduced with calcination temperatures. As shown in the digital image of the electrode surface (Figure 1c), the Co/29BC electrode showed a uniform loading of Co₃O₄ with strong binding to the carbon substrate, and very little catalysts were removed upon sonication of the electrode for over 30 min. The cross-section section of the Co/29BC electrode (Figure 1d) was further examined by SEM. It can be seen that a uniform layer of Co₃O₄ catalyst with a thickness of approximately 100 µm was formed on the carbon substrate. The thickness of the carbon paper shown in the SEM image was around 150 µm while the original thickness of the 29BC carbon paper is approximately 235 µm. This suggested that some of the Co₃O₄ catalysts had penetrated the mesoporous layer of the 29BC, resulting in the strong adhesion. Element maps using STEM coupled with EDS, confirmed that Co and O were present in the Co₃O₄ layer and C and F were present in the hydrophobic carbon substrate. The signal of Co and C were well separated, indicating that the Co₃O₄ catalyst layer was well supported by the carbon substrate.

TEM and high-resolution TEM (HR-TEM) (Figure 2) were used to reveal the structures of the Co₃O₄ nanoparticles that were sonicated off from the Co/29BC electrode. It can be seen in Figure...
2a that Co$_3$O$_4$ nanoparticles with a diameter between 10 - 40 nm were interconnected with each other to build up a porous architecture. As shown in Figure 2b, Co$_3$O$_4$ nanoparticles were embedded in an amorphous carbon layer, which means that the carbon simultaneously formed at the surface of the Co$_3$O$_4$ nanoparticles during the decomposition process of cobalt nitrate at the 29BC substrate. This may be due to the diffusion and precipitation of carbon onto the surface of the catalytic Co$_3$O$_4$ nanoparticles. Indeed, under high carbon content, it has been reported that carbon diffusion and deposition occur at the surface of metallic nanoparticles.\cite{9} In the current work, it is believed that the carbon source is possibly a mixture of carbon black, hydrophobic dispersion agents (i.e. PTFE), and solvents present in the microporous layer of our carbon fiber substrate.\cite{10} The HR-TEM image and corresponding electron diffraction (FFT – Fast Fourier Transform) pattern in the insert showed lattice spacings of 0.47 and 0.24 nm, corresponding to the Co$_3$O$_4$ crystal planes (111) and (311), respectively. This confirms that the encapsulated core is Co$_3$O$_4$ nanoparticles in agreement with the XRD observation.

Further analysis by SEM of the electrode surface indicated the uniform loading of Co$_3$O$_4$ particles (Figure S1). At low magnification, a high porosity of the Co$_3$O$_4$ catalysts layer could be seen, suggesting the good gas permeation of the prepared electrode. At higher-magnification, the nanoparticles were found to be agglomerated into spherical aggregates with a size of 60 - 200 nm (average 105 nm) when the decomposition was carried out at 250 °C (Figure S1a). it is noteworthy that when the synthesis temperature was increased to 300 and 350 °C, the average particle size was reduced to 85 and 50 nm, respectively (Figure S1b and c). In general, an increase in temperature results in an increase in particle size due to Ostwald ripening.\cite{11} In this case, the nucleation and growth of the Co$_3$O$_4$ nanoparticles are governed by the decomposition rate of the cobalt precursors and the evolution of gaseous products. Therefore, a higher temperature may lead to faster decomposition of the cobalt precursor and higher water evaporation rates, leading to faster nucleation and thus smaller particles with a narrower size distribution.

### 2.2 OER performance in three-electrode and two electrode systems

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The OER activity of the Co/29BC electrodes was firstly investigated using LSV in O$_2$-saturated 0.5 M H$_2$SO$_4$ (pH 0.3) with a scan rate of 10 mV s$^{-1}$ using a three-electrode setting at 25 °C. Figure 3a shows plots of the current density vs potential for Co/29BC, with commercial IrO$_2$ catalysts sprayed on 29BC (IrO$_2$/29BC) as a comparison. The Co/29BC electrodes require overpotentials over 450 mV to achieve a current density of 10 mA.cm$^{-2}$. In comparison, IrO$_2$/29BC had an overpotential of 330 mV at the same current density. It is noteworthy that the OER activity of Co$_3$O$_4$ was found to be dependent on the calcination temperature. Co-250 exhibited a slightly higher overpotential of 490 mV, while raising the calcination temperature to 300 and 350 °C resulted in a reduction in overpotentials by 40 and 30 mV, respectively. As observed in SEM images, higher temperatures resulted in a lower agglomeration of particles, which could lead to a higher surface area, and thus a higher electrochemical surface roughness.[5]

Tafel analysis (Figure S2a) provided insights into the kinetics of the OER catalysis of Co$_3$O$_4$ and the associated rate-determining step.[12] The slopes of the Tafel plots were calculated to be of 235, 179 and 172 mV dec$^{-1}$ for the Co-250, Co-300 and Co-350, respectively in 0.5 M H$_2$SO$_4$. In comparison, IrO$_2$/29BC showed a Tafel slope of 118 mV dec$^{-1}$. The typical values of Tafel slopes for the OER of Co$_3$O$_4$ in neutral and alkaline aqueous electrolyte is around 60 mV dec$^{-1}$.[13, 14] However, this value is generally larger in the acidic condition, due to the slow dissolution of Co$_3$O$_4$ in the acid condition.[5, 15] It is believed that a Tafel slope much larger than 120 mV dec$^{-1}$ indicates that the rate-determining step is a single electron transfer process with a very high symmetry factor ($\beta$), or a chemical process occurring from the resting state of the catalyst.[16] However, Yan et.al reported a similar Tafel slope of 219 mV dec$^{-1}$ for Ag-doped Co$_3$O$_4$ nanowires, with high activity (overpotential of 680 mV) in 0.5 H$_2$SO$_4$.[17] It is thus uncertain whether one can use only Tafel slopes to determine the rate-determining step, since other factors (other than electrocatalytic reactions) such as conductivity and catalyst/substrate interfaces can also lead to an increase in Tafel slope.[18] EIS analysis of the as-prepared electrodes was also carried out in the three-electrode system to provide an insight into the acidic OER performance of the Co/29BC electrodes. Figure
S2b shows the Nyquist plots of Co-250, Co-300 and Co-350 in the three-electrode system. One single semicircle in the high-frequency region could be observed, revealing the charge transfer resistance from the electrode to the electrolyte. From this result, it can be seen that the charge transfer is very similar for all the materials prepared, in agreement with the LSV measurements. However, the slope of the Nyquist plots at low frequency (i.e. mass transfer) for Co-300 is slightly larger, and this may be explained by the higher activity of this catalyst at higher potential windows (Figure 3a).

The stability of Co-300 was then investigated in a three-electrode setting. Galvanostatic experiments (Figure 3b) confirmed that the Co/29BC electrode prepared at 300 °C was capable of sustained oxygen production for over 12 h at a current density of 10 mA cm\(^{-2}\) with only negligible changes (~30 mV) in the recorded overpotentials. From the electrochemical measurement in a three-electrode system, it can be seen that the Co/29BC electrodes exhibited remarkable catalytic performance and stability in an acidic environment, although cobalt oxides generally undergo rapid dissolution in strong acid at anodic potentials. In the current investigation, the superior stability of the material synthesised is possibly due to the carbon layer formed at the surface of the Co\(_3\)O\(_4\) nanoparticles. Notably, Co\(_3\)O\(_4\) has superior catalytic performance upon carbon-coating, suggesting that the carbon layer is probably porous to allow for the exposure of active sites of Co\(_3\)O\(_4\).

To confirm the improvements observed through the initial characterisations, we further investigated the OER performance of Co/29BC in a complete PEM water electrolysis cell.[19] Figure 4b shows the potential-current density plot for Co/29BC calcined at different temperatures. Co-250, Co-300 and Co-350 exhibited very similar activities at low anodic potential, with an overpotential of 330 - 370 mV at 10 mA cm\(^{-2}\), which is 120 mV lower than in the three-electrode system. In comparison, the overpotential for IrO\(_2\)/29BC is 240 mV at 10 mA cm\(^{-2}\) instead of 330 mV in the three-electrode system. This is surprising, since the overpotential generally increases due to the increase in ohmic resistance in a full cell set-up. In our study, a water-absorbing electrolyte water electrolyser was used. In this configuration, pressurised water is injected through the electrolyte instead of the anode. This article is protected by copyright. All rights reserved
side, ensuring good water supply and minimal dehydration of the membrane.\textsuperscript{[20]} This means that the anode electrode experiences less mechanical stress from the injected water, and this prevents the detachment of the catalysts and therefore lowers the overpotential of the cell. While the 330 mV overpotential of the Co/29BC electrode at 10 mA cm\(^{-2}\) is higher than IrO\(_2\)/29BC, it is significantly improved relative to other earth-abundant metal-based OER catalysts (Figure 4d). Additionally, Co-300 showed the highest current density of \(\sim 245\) mA cm\(^{-2}\) at 2.2 V. In comparison, Co-250 showed limited current density at much lower potentials, while Co-350 started to experience limiting current at potential above 1.9 V. Such a behaviour could be explained by a range of factors, such as particle size effects and the gas permeation level of the catalysts layer, which will be determined in further studies. Nonetheless, it can be concluded that Co\(_3\)O\(_4\) prepared at 300 °C showed the best performance in both the three-electrode system and full water electrolysis cell.

The gas evolution of the cell was determined and compared to the theoretical values calculated by Faraday’s Law (Figure S3). It can be seen that both the hydrogen and oxygen evolution rate obeys Faraday’s Law, with a Faradic efficiency above 95%. This quantitative hydrogen and oxygen evolution rate suggest that the cross leaking of gases is minimum and almost all of the generated gases are collected outside the cell without dissolution into the liquid water phase. This also suggests that the Co/29BC electrodes remained highly porous and had good gas permeability.

The stability of the Co-300 electrode was tested under a constant current of 10 and 50 mA cm\(^{-2}\) (Figure 4c). At 10 mA cm\(^{-2}\), the potential increased by 30 mV from 1.57 to 1.6 V (1.9 % increase) in the first 1 h. Similar behaviour was also observed for commercial IrO\(_2\)/29BC, where an increase of potential from 1.39 to 1.43 V (2.8 % increase) was detected in the same time frame. Co-300 exhibited a high overpotential but a similar stability as compared to IrO\(_2\)/29BC, where cell voltage of 1.61 V remained remarkably stable at 10 mA cm\(^{-2}\) for over 50 h. At high current density (i.e. 50 mA cm\(^{-2}\)), the activity of Co-300 quickly degraded, and the voltage increased by more than 200 mV from 1.78 to 2.0 V in 24 h. SEM analysis of Co-300 after stability testing (Figure S4) revealed that
the morphology of the Co-300 nanoparticles remained spherical and well distributed even after 50 h of operation at 10 mA cm\(^{-2}\). However, the particles started to look more agglomerated, which is consistent with the increase in overpotential observed. To identify the dissolution rate of Co\(_3\)O\(_4\) in the full water electrolysis cell, inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of soluble cobalt species after stability tests was carried out. The average Co dissolution rate for Co-300 held galvanostatically at 10 and 50 mA cm\(^{-2}\) was 11.2 and 13.4 ng cm\(^{-2}\) h\(^{-1}\), respectively. This is significantly lower than previously observed dissolution rate for other Co\(_3\)O\(_4\) (i.e. 140 ng h\(^{-1}\) for Ag-Co\(_3\)O\(_4\) at ~1 mA cm\(^{-2}\))\(^{[21]}\) and Ir-based (~72 ng cm\(^{-2}\) h\(^{-1}\) at 10 mA cm\(^{-2}\)).\(^{[22]}\) Therefore, it can be concluded that a lower current density is more favourable to suppress the dissolution of Co and maintain the spherical morphologies of the Co\(_3\)O\(_4\) nanoparticles, resulting in significantly higher performance and longer operation times. Notably, the sample preparation temperature in this work is lower than the temperatures used in other studies, which could enable a smaller average particle size and a lower degree of agglomeration.\(^{[23]}\)

### 2.3 Surface structures and composition of the electrocatalyst

XPS measurements were carried out to determine the atomic composition and chemical state of Co\(_3\)O\(_4\). Figure S5 showed the survey scan in the region of 0 - 1000 eV for Co/29BC calcined at different temperatures. The narrow scans of Co 2p spectra were investigated to identify the electronic states of Co atoms with different valences (Figure 5a). It revealed peaks around 795.6 and 780.2 eV, corresponding to the Co2p\(_{1/2}\) and Co2p\(_{3/2}\) peaks of Co\(_3\)O\(_4\). After detailed fitting, the peaks located at around 781.2 and 796.5 eV were assigned to Co\(^{2+}\), and the peaks at 794.7 and 779.8 eV were assigned to Co\(^{3+}\).\(^{[14]}\) The oxidation state of Co has been reported to be an important factor in the electrocatalytic activity of Co\(_3\)O\(_4\).\(^{[21, 24, 25]}\) Previous studies\(^{[24, 26]}\) have indeed confirmed the superior activity of Co\(^{3+}\) sites over Co\(^{2+}\), owing to its good electronic conductivity as well as fast adsorption-desorption and good activation of oxygen species. It is believed that the higher electron-donating ability of Co\(^{3+}\) can improve the O\(^{2-}\)/OH\(^-\) displacement during the OER processes, compared to Co\(^{2+}\). As summarized in Table 1, the ratios of Co\(^{3+}\) and Co\(^{2+}\) were found to be...
increasing as the calcination temperature increased. This suggests that higher calcination temperatures are more favourable for the formation of octahedrally coordinated Co$^{3+}$ sites.

Three peaks were found in the narrow scan spectra of O1s (Figure 5b), including the superoxide ions (531.8 eV), peroxide ions (531.0 eV), and lattice oxygen (529.6 eV). Superoxide ions (O$_2^-$) and peroxide ions (O$_2^-$) correspond to hydroxyl and oxygen vacancies (O$_{\text{vac}}$) at the Co$_3$O$_4$ surface, respectively, where the lattice oxygen (O$_{\text{lat}}$) is a reflection of the metal-oxide bond in the lattice.[27] The ratio between the O$_{\text{vac}}$ and O$_{\text{lat}}$ was found to be as high as 0.63 for Co-300, indicating higher oxygen vacancies at the surface of Co$_3$O$_4$ nanoparticles. Both experimental results and theoretical calculations showed that oxygen vacancies can generate new bandgap states in Co$_3$O$_4$ and delocalize the two electrons previously occupied oxygen 2p orbitals around the defect states, resulting in an enhanced electronic conductivity of Co$_3$O$_4$. Along with the superior Co$^{3+}$ active sites and oxygen vacancies at the Co$_3$O$_4$ surface, the Co/29BC electrode is expected to give distinct OER performance.

XRD and XPS analysis of the electrodes after water electrolysis at different voltages was also performed. XRD showed the formation of a small amount of graphitic carbon when a voltage was applied (Figure S6a). It is possible that the oxygen evolution at the electrodes created some pores on the catalysts layer and led to the exposure of the carbon paper substrate. Therefore, the carbon black contained in the carbon paper was detected as the graphite carbon peak. However, the crystalline structure of Co$_3$O$_4$ remained unchanged. Narrow scan of Co2p confirmed the stability of Co$^{2+}$ and Co$^{3+}$ in the materials, with the ratio between Co$^{3+}$ and Co$^{2+}$ remaining similar at low voltage and a slight decrease at 2.0 V (Figure S6b). However, a change of oxygen composition at the electrode surface was observed, as shown in the oxygen narrow scan of Co-300 at different voltages (Figure S6c). Upon water electrolysis at a voltage of 1.6 and 1.8 V, the main peak of lattice oxygen in Co-300 remained at 529.6 eV, while it slightly shifted to 529.4 eV when 2.0 V was applied to the electrode. A decreasing trend was observed in the level of oxygen vacancies, along with an increasing amount of hydroxyl group as cell voltage increased (Figure S6d). This may be
caused by the instability of oxygen vacancies under OER conditions and an increase in the amount of adsorbed oxygen (OH) at the surface of the electrocatalyst, which actively participates in the oxygen evolution reactions at the surface of the electrode.\textsuperscript{[29]}

2.4 Pathways towards high OER activity and stability in acid media

It is well known that cobalt oxides dissolve during water electrolysis, especially under acidic conditions, with a dissolution rate of over 1200 ng cm\(^{-2}\) h\(^{-1}\). Despite that, emerging Co-based materials such as carbon-coated Co\(_3\)O\(_4\) nanoarrays\textsuperscript{[7]}, highly crystalline Co\(_3\)O\(_4\)\textsuperscript{[5]}, Ag-doped Co\(_3\)O\(_4\) nanowire arrays\textsuperscript{[17]} have been reported to be stable in acid media. However, a comprehensive understanding and mitigation of catalyst degradation still remain the major challenges. In this work, we have demonstrated a one-step synthesis of a carbon protected Co\(_3\)O\(_4\) nanoparticles on a hydrophobic carbon paper, and provided unique insights into the enhancement of Co\(_3\)O\(_4\) OER activity and stability in acidic condition via a combination of: i) the morphology, particle size and surface composition tuning, ii) an improvement in catalyst and substrate adhesion and iii) the use of a conductive and corrosion-resistant protective carbon layer.

Firstly, the electrocatalytic activity of cobalt oxide is highly dependent on its surface area and electronic states. From the morphology observation of the Co/29BC electrode, it was found that the particle sizes and agglomeration of Co\(_3\)O\(_4\) nanoparticles could be tuned by the calcination temperature, enabling a higher surface area and more exposure of the active sites for OER reactions. Meanwhile, in this study, it was found that the higher calcination temperature also favoured the exposure of Co\(^{3+}\) active sites and the formation of oxygen vacancies at the surface of the Co\(_3\)O\(_4\) nanoparticles, which are the key influencer on the electronic properties and catalytic performance. Herein, the synergistic effect of the surface atomic arrangement of Co\(^{2+}\)/Co\(^{3+}\) active sites and defects of Co\(_3\)O\(_4\) nanoparticles resulted in a superior electrocatalyst for OER. Secondly, the direct synthesis of size-controlled nanoparticles on carbon support materials along with control of the calcination process can result in a sufficiently strong adhesion between the catalyst and substrate to
overcome the mechanical and electronic stress associated with the water electrolysis process and bubble formation. Indeed, studies have stressed the important role of catalyst adhesion on the support for long-term stability.[30] Furthermore, the use of a porous and hydrophobic carbon paper as a substrate has demonstrated the formation of a corrosion-resistant carbon layer on the Co$_3$O$_4$ surface. Thermal decomposition of 29BC (Figure S7) suggested 7.1 mass% weight loss between 100 and 350 °C, and a rapid weight loss above 400 °C. This is corresponded to the gradual decomposition of PTFE starting at around 260 °C, followed by a rapid decomposition above 400 °C. Therefore, it is believed that the source of carbon is mainly attributed to the partial decomposition of PTFE, while the contribution from the solvent used in the preparation of the microporous layer of 29BC cannot be ruled out completely. The carbon layer acted as a protection layer to decrease the dissolution rate of Co$_3$O$_4$ by trapping the nanoparticles inside the carbon pores. Meanwhile, the conductivity of carbon materials can improve the electronic conductivity of the Co$_3$O$_4$, leading to a reduction in the overpotential. In addition, the low cost and simple fabrication of the carbon paper-based electrodes in this work has great potential to be directly implemented in electrochemical devices, in particular PEM water electrolyzers and metal-air batteries. The more conventional antimony or fluorine-doped tin oxide and tin-doped indium oxide used under the harsh oxidizing conditions of OER are not practical for real water electrolysis applications.

3. Conclusion

In conclusion, a carbon-protected Co$_3$O$_4$ electrocatalyst layer was synthesized by the direct decomposition of a cobalt nitrate precursor on a commercial hydrophobic carbon paper. Half-cell measurement showed that Co-300 can achieve an overpotential of 460 mV at 10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$, with a stability of more than 12 h. Additional testing of this catalyst in a full PEMWE cell, showed that the overpotential was further reduced to 350 mV for Co-300. Attributed to the carbon protection layer and the strong catalysts adhesion to the substrate, the Co/29BC electrode showed superior stability (>50 h at 10 mA cm$^{-2}$) and a much suppressed Co dissolution (8.8 ng h$^{-1}$). A combination of SEM, XRD, XPS and EIS analysis also evidenced that control over the particle size,
Co^{3+} active sites and oxygen vacancies of Co$_3$O$_4$ nanoparticles by the calcination temperature could lead to further enhancement in activity and robustness of the catalyst. This opens new avenues for the preparation of efficient and stable earth-abundant OER catalysts in acidic environments by the combination of morphology, chemical state, surface composition and catalyst /substrate interface tuning.

**Experimental Section**

**Materials and method**

Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99.95%) was received from KANTO CHEM and used as received. Throughout the study, distilled water (Elix Advantage3; Merck Millipore Co.) with a resistivity of 15.0 MΩ was used. All chemicals were used without purification. Micro-porous layer coated carbon paper (MPL/CP; SGL29BC), Pt-C, and IrO$_2$ inks were purchased from Chemix Co. Ltd. Hand-punch (Nogamigiken Co., Ltd.) was used to cut $\phi$10 and $\phi$16 mm diameter carbon paper for spraying the catalyst ink.

**Preparation of Co$_3$O$_4$ on 29BC (Co/29BC)**

Co$_3$O$_4$ electrocatalyst layer was prepared by the direct decomposition of Co(NO$_3$)$_2$·6H$_2$O on a hydrophilic 29BC substrate. First, a 3.0 × 3.0 cm 29BC carbon paper was placed at the centre of a hotplate. A rectangular ceramic disc wrap with an aluminium foil was placed at each corner of the carbon paper to hold the carbon paper in place. The whole setup was heated to the desired temperature (i.e. 250, 300 and 350 °C, respectively).

A 4.0 M Co(NO$_3$)$_2$·6H$_2$O solution was prepared by dissolving 11.64 g of Co(NO$_3$)$_2$·6H$_2$O solid in 10 mL of distilled water. The mixture was put under ultra-sonication for 5 min to ensure the full dissolution. The nitrate solution was poured into a spray-gun and directly sprayed on the pre-heated carbon paper. The Co(NO$_3$)$_2$·6H$_2$O rapidly decomposed into a black/dark grey solid on the carbon paper. The calcination was allowed to proceed in air for 5 min. The resulting electrode was rinsed with distilled water and sonicated for 10 seconds in distilled water. Finally, the electrodes were...
dried in an oven at 60 °C for 2 hours before used. The electrode was punched with a hand-punch into a 10 mm disc for the water electrolysis test in the designed cell.

**Preparation of reference electrocatalysts layer**

Electrocatalyst layers were prepared by a spraying method using the following procedure. The purchased ink was poured into the spray-gun reservoir and directly sprayed on the surface of the 29BC substrate at 70 °C on hot-plate by using a spray-gun. The catalyst loadings at the cathode (Pt-C: 0.5 mg.cm\(^{-2}\)) and anode (IrO\(_2\): 1.5 mg.cm\(^{-2}\)) electrodes were controlled by weighing the substrate before and after sprayed. After that, the coated 29BC substrates were further heat-treated for 30 min at 60 and 120 °C, respectively, in order to evaporate the remaining solvent.

**Electrochemical Measurements.**

All electrochemical measurements were performed using a CH electrochemical workstation. A saturated Ag/AgCl electrode (SCE) was used as the reference electrode and a platinum rod was used as the counter electrode for all electrochemical measurements.

Measurements at pH 0.3 were performed in high purity 0.5 M H\(_2\)SO\(_4\) (99.99%) using a one-compartment, three-neck glass cell. The pH of the electrolyte was adjusted by altering the concentration of H\(_2\)SO\(_4\). The cell was purged with O\(_2\) for approximately 15 min before each set of experiments. During all electrochemical measurements, the solution was not stirred and was kept blanketed under an atmosphere of O\(_2\). The OER activity of Co/29BC was evaluated by measuring polarization curves with linear sweep voltammetry (LSV) at a scan rate of 10 mV.s\(^{-1}\). The stability test was performed with the time-dependent potential measurement, where a constant current density (10 mA.cm\(^{-2}\)). All data were presented without iR correction.

**Full PEM water electrolyser cell assembly and electrolysis test**

The MEA for water electrolysis cell testing was fabricated using the following procedure. Firstly, the anode was fixed on a 10 mm porous titanium mesh holder with a ring of tape on the side of the carbon paper. The cathode was placed on a 16 mm porous titanium mesh holder and then covered
by a sheet of Nafion 117. A round silicone gasket and stainless-steel plate were placed in such order on the cathode side of the cell to fix the cathode and Nafion in place. The anode side of the cell was then placed on top of the cathode side and the cell was then screwed together with a torque wrench with 0.3 - 0.8 N m to promote the contact between the two electrodes. The water was directly injected into the cell and water pressure of 0.05 MPa was applied using a nitrogen gas cylinder.

**Characterization and Instruments**

The particle size distribution, morphology analysis of Co$_3$O$_4$ particles was performed by a Transmission Electron Microscopy (TEM) using a JEM-ARM200F operated at 200 kV. The surface structure of the Co/29BC electrode was investigated via Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis on a Scanning Transmission Electron microscope (STEM), using a FEI VersaTM 3D DualBeamTM operated at 20 keV.

The crystalline nature of the materials was determined by X-ray Diffraction measurement (XRD) using a Rigaku, Ultima IV X-ray diffractometer operated at 40 mA, 40 kV with a monochromatic Cu-Kα radiation. The chemical properties of the surface of the nanoparticles were further characterised by X-Ray Photoelectron Spectroscopy (XPS) using an Ar Cluster Ion Beam XPS/PHI5000VersaProbe II (base pressure below 10$^{-5}$ Pa). The XPS spectra were collected using a monochromatic Al Kα (1486.7 keV) X-ray source operated at 150 W. Survey scans were collected at 186 eV pass energy with an energy step of 0.2 eV, while detailed scans were acquired at 20 eV pass energy and 0.1 eV energy step. The data were analysed using the Multipeak software.

In the electrolysis experiment, the current was measured for the applied voltage using the Potentiostat/Galvanostat instrument (HA-151B). The generated gases species (hydrogen and oxygen) were measured with the help of a carrier gas (Ar: 20 mL.min$^{-1}$) by gas chromatography (GC) with an Agilent 300A Micro GC (column: Molsieve, 14m × 320μm × 120 μm). The GC was calibrated by using 1% H$_2$/Ar. During water electrolysis experiment, carrier gas was flown across each side of the electrodes and the outlet gas stream containing carrier gas and the produced gases.
hydrogen or oxygen were characterised. The outlet gas flow rate was measured with a flow meter and the hydrogen and oxygen concentration was measured with the GC. Both values were measured three times over a period of 10 min and the average values were used to calculate the exact amount of hydrogen or oxygen in the outlet stream to compare with the theoretical value.

Supporting Information

SEM images of as-prepared and used Co/29BC electrode; Tafel slopes and EIS of Co/29BC electrode in 3-electrode electrochemical measurement; Gas evolution profile of Co/29BC in a PEM water electrolyser; XRD and XPS analysis of Co/29BC electrode after water electrolysis experiment.

Acknowledgments

This work was supported by JSPS KAKENHI Project Number 19F19707. Dr Qiwen Lai is an International Research Fellow of Japan Society for the Promotion of Science (Postdoctoral Fellowships for Research in Japan (Standard)). We appreciate the performance of TEM instruments by Dr Yoonyoung Kim from Ishihara Laboratory and the use of electrochemical instrument in Nakashima Laboratory in Kyushu University.

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Table 1: Summary of electrochemical performance and surface oxidation states of Co/29BC electrodes calcined at different temperatures.

|        | Overpotential at 10 mA cm<sup>-2</sup> (mV) | Current density at 2.2 V (mA cm<sup>-2</sup>) | Ratio of Co<sup>3+</sup>/Co<sup>2+</sup> | Ratio of O<sub>vac</sub>/O<sub>lat</sub> |
|--------|------------------------------------------|-----------------------------------------------|-----------------------------------|-------------------------------------|
|        | Three-electrode system (0.5 M H<sub>2</sub>SO<sub>4</sub>) | Full PEM water electrolysis cell | Full PEM water electrolysis cell |                                      |
| Co-250 | 490                                      | 380                                           | 115                               | 1.08                                | 0.24                               |
| Co-300 | 450                                      | 350                                           | 245                               | 1.33                                | 0.63                               |
| Co-350 | 460                                      | 330                                           | 216                               | 1.45                                | 0.54                               |
Figures

Figure 1. (a) Schematic representation of the Co/29BC electrode preparation procedure. (b) XRD patterns for the Co/29BC electrode prepared at different calcination temperatures. (c) Digital image of the top view of the Co/29BC electrode surface. (d) Typical SEM images of a cross section of the Co-300 electrode, and corresponding element maps and EDS of Co and O in the Co$_3$O$_4$ catalyst, as well as C in the 29BC carbon paper.
Figure 2. (a) TEM image and (b) HR-TEM images of Co$_3$O$_4$ nanoparticles sonicated off from the Co/29BC electrode. (insets are the size distribution of the Co$_3$O$_4$ nanoparticles and diffraction pattern)
Figure 3. (a) OER polarization curves for Co-250, Co-300 and Co-350 electrodes in 0.5 M H$_2$SO$_4$. Commercial IrO$_2$ anode (IrO$_2$/29BC) results are included for comparison. (b) Galvanostatic measurements at 10 mA.cm$^{-2}$ for Co-300 electrode 0.5 M H$_2$SO$_4$. 
Figure 4. (a) The structure of the Kyudai PEM electrolyser used in this study. Water is injected through the polymer electrolyte (i.e. Nafion) instead of the anode electrode. (b) I-V performance of PEM water electrolyser at 25 °C, using Pt/C as the cathode and Co/29BC electrodes prepared at different temperatures as anode. (c) Time dependence of the cell voltage at 10 and 50 mA cm$^{-2}$ (at 25 °C, without ohmic resistance correction), using Pt/C as the cathode and Co/29BC electrodes prepared at different temperatures as anode. Commercial IrO$_2$ as anode (IrO$_2$/29BC) results are included for comparison. (d) Overpotentials and stability of various 3d-metal OER catalysts in acidic media in previous reports,$^{[3, 5-7, 17, 21, 31]}$ compared with our catalyst in terms of activity, stability at 10 mA cm$^{-2}$. 
Summary

A novel non-noble carbon-coated $\text{Co}_3\text{O}_4$ electrocatalyst layer, with optimised $\text{Co}^{3+}$ active sites and oxygen vacancies at the metal oxide surface, showed superior OER performance and
durability in a PEM water electrolyser, with a small overpotential (350 mV) at a constant current density of 10 mA cm\(^{-2}\) for over 50 h.