Switching effective oxygen reduction and evolution performance by controlled graphitization of a cobalt–nitrogen–carbon framework system†

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We report a purposely designed route for the synthesis of a promising carbon-based electrocatalyst for both ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) from zeolitic imidazolate frameworks (ZIFs). Firstly, precursor ZIFs are rationally designed with a blend of volatile zinc to induce porosity and stable cobalt to induce graphitic domains. Secondly, the self-modulated cobalt–nitrogen–carbon system (SCNCS) is shown to be an effective ORR catalyst after graphitization at mild temperatures. Finally, the best OER catalyst is developed by enhancing graphitization of the SCNCS. For the first time, solely by switching the graphitization conditions of SCNCS, excellent ORR or OER performance is realized. This approach not only opens up a simple protocol for simultaneous optimization of nitrogen doping and graphitization at controlled cobalt concentrations, but also provide a facile method of developing such active catalysts without the use of extensive synthesis procedures.

Energy storage and conversion technologies are critical for clean transport and renewable integration in smart grids.1,2 Nanoporous solids play a vital role in such technologies, including catalysis, charge-carrier storage and molecular sorption and separation.3–8 In particular, nanoporous carbons (NPCs) are highly desirable for such purposes, due to their high accessible specific surface area and pore volume, high chemical and mechanical stabilities, and good electrical conductivity.3,6–10 Functionalised NPCs are considered an emerging group of non-noble metal oxygen reduction and evolution electrocatalysts in fuel-cells and metal–air batteries.9–24 For example, nitrogen or sulphur doping and/or incorporation of transition metals in the carbon lattice induce significant surface charge and graphitization to enhance charge transfer capacity. Increasing accessible porosity (specific surface area (SSA), pore-size distribution (PSD) and pore volume ($V_p$)) of the NPCs facilitates fast mass or charge-carrier transfer. These properties can be enhanced with the selection of appropriate carbon precursors or chemical synthesis routes. Therefore advances in synthesis lead to new classes of functional NPCs. Carbon nanotube/graphene/graphene-oxide based metal–nitrogen–carbon structures are recent examples of such NPCs that show superior catalytic activities for ORR or OER, compared with expensive Pt or Ir and Ru oxides.9–11,13–18 However, developing such graphene/nanotube based NPCs usually involves extensive chemical processes, thus hindering large scale commercial implementation.

In contrast, the intrinsically open pore polymers with metal cores as sacrificial templates have proved extremely advantageous for the development of multifunctional NPCs.4,5,7,22–29 The best example of such templates are metal–organic frameworks (MOFs), which consist of small ligand molecules as linkers with metal centres to produce regularly ordered open frameworks of a high specific surface area.4,5 The carbonization of MOFs yields a new class of highly porous NPCs with simultaneous incorporation of intrinsic ligand heteroatoms and metal centres within the
similar synthesis conditions Co100–C results in more graphitized different structure and porosity characteristics. Zn 100–C NPCs observed by a well-defined and sharp cathodic current peak at an without zinc (Fig. 1e and f). For example, the ORR activity is graphitized Co100–C1000 after acid clean to remove cobalt metal carbonization of ZIF-8 (Zn 100–C) and Co–ZIF-8 (Co 100–C) exhibits microporosity and nitrogen doping (Tables S1 and S2, ESI†). The optimized NPCs are identified through extensive screening of samples obtained at different synthesis conditions, such as controlled cobalt- and nitrogen-concentrations, degree of graphitization, and OER activities directly without further chemical/acid treatment. The optimized NPCs are identified through extensive screening of samples obtained at different synthesis conditions, such as controlled cobalt- and nitrogen-concentrations, degree of graphitization, and OER activities directly without further chemical/acid treatment. The advantage of this approach is that functional and conducting NPCs can be easily developed from rationally designed MOFs, e.g. MOF-5 and ZIF-8.30,31 Imidazolate (H2C5N2) ligand based ZIFs, a sub family of MOFs with zeolitic structure, deserve a special mention. With the choice of enriched volatile (e.g., Zn) or stable (e.g., Fe, Co, Ni) metal centres, these ZIFs can generate metal free or metal-incorporated nitrogen-doped carbons with a significant degree of graphitization (see references Sb1–9, Sc1–22, Sd1–5 and Sc1–12 in the ESI†). More precisely, as shown in Fig. 1 and Fig. S1–S5 (ESI†), the carbonization of ZIF-8 (Zn100–C) and Co–ZIF-8 (Co100–C) exhibits different structure and porosity characteristics. Zn100–C NPCs are mainly amorphous in nature and exhibit a higher level of microporosity and nitrogen doping (Tables S1 and S2, ESI†). At similar synthesis conditions Co100–C results in more graphitized mesoporous NPCs with embedded crystalline cobalt. This graphitization is further confirmed by scanning and transmission electron microscopy (SEM and TEM) micrographs. Clearly, the graphitized Co100–C1000 after acid clean to remove cobalt metal shows enhanced electrocatalytic activity for both the ORR and OER compared with the amorphous Zn100–C1000 counterpart without zinc (Fig. 1e and f). For example, the ORR activity is observed by a well-defined and sharp cathodic current peak at an applied potential of around −0.15 V vs. Ag/AgCl. This is not observed in the N2 purged electrolyte (Fig. S6, ESI†). The enhanced ORR performance of Co100–C NPCs is also characterised by reduced onset and half-wave potentials, electron transfer and a steep reduction slope, i.e., a reduced Tafel slope (Fig. S6–S8, ESI†) with enhanced current density against sweeping potential. Furthermore, a considerable enhancement in OER activity is seen in the cobalt incorporated NPCs (Fig. S9, ESI†).

Interestingly, the thermogravimetric analysis of C100–C1000 accounts for 44% of cobalt by mass (Fig. S10, ESI†). This is very high and expected to limit the catalytic activity due to poor dispersion of active sites. Also note that the graphitized NPCs with or without cobalt at minimal nitrogen doping exhibits improved ORR and OER activities than the highest nitrogen doped amorphous NPCs. Thus we anticipate that fine control over graphitization, and nitrogen and cobalt concentrations would result in further improved catalytic activity of these NPCs.12–27

In principle, a precursor ZIF, designed rationally with a blend of volatile zinc to induce porosity and stable cobalt to induce graphitic domains, can generate optimized NPCs. This strategy also enhances the fine distribution of the active sites. For example, cobalt centres, facilitate fast electron-transfer kinetics for OER/ORR. In general, a higher effective surface area leads to higher electrocatalytic activity. However, research along this line has not been well explored.22,27 Also in most of the cases the MOF- or ZIF-derived NPCs were considered for ORR but rarely for OER [see references in the ESI†]. This is because most of those MOFs or ZIFs were subjected to a mild carbonization temperature and less annealing time. Thus, as demonstrated in Fig. 1, these structures exhibit very poor or no activity for OER. Furthermore, the range of graphitization conditions and metal concentrations for NPCs (other than the inherent metal of the MOF or ZIF) and their viability for complete electrocatalysis are yet to be explored.

Therefore, here we have performed a detailed investigation to explore the potential of these ZIF-based NPCs with a targeted synthesis from rationally designed bimetal (Co,Zn)x–ZIF-8 (Fig. 2 and Fig. S11–S13, ESI†). The bimetal ZIFs are converted to functionalized NPCs with a direct carbonization between (700–1100) °C with annealing for (2–10) h, i.e., mild to high graphitization under pure or control oxidative N2 atmosphere. The optimized NPCs are identified through extensive screening of samples obtained at different synthesis conditions, such as controlled cobalt- and nitrogen-concentrations, degree of graphitization, porosity and oxidation state of cobalt (Co(0)/C, Co(n)O@Co(n)/C and Co(n)/mOx/C). Thus obtained NPCs are investigated for both ORR and OER activities directly without further chemical/acid treatment. Throughout the text NPCs are named against the MOF type, and carbonization temperature and time, for example, Co,Zn100–x–ZIF-8 carbonized at 1000 °C for 10 h is named as Co,Zn100–x–C1000-10h. The NPCs are thoroughly characterized with complementary techniques, such as powder X-ray diffraction (PXRD), Raman spectroscopy, X-ray photoemission spectroscopy (XPS), electron microscopy (SEM and TEM), thermogravimetry and porosity (N2, CO2 and H2 uptake), see Fig. 3 and Fig. S14–S28, and Tables S3 and S4 (ESI†). An overview of structure–property
relationships is shown schematically in Fig. 2b. Clearly, the rationally designed $\text{Co}_x\text{Zn}_{100-x}$–ZIF-8 ($x = 25$ and $50$) derived NPCs show outstanding activity for both ORR and OER (Fig. 2b and Fig. S29, ESI†). More specifically, graphitization acts as a switch for high activity; ORR at $900 \, ^\circ\text{C}$ and OER at $1000 \, ^\circ\text{C}$.

We note that several factors play a decisive role, such as cobalt and nitrogen concentration, and graphitization temperature. We also note that the NPCs reported here are obtained by direct carbonization of ZIFs alone. In contrast, the literature often reports the addition of extra functional precursors, graphene or template support directed growth, and pre- and/or post-synthesis treatment [see references Sb1–9, Sc1–22, Sd1–5 and Sc1–12 in the ESI†]. Furthermore, as noted above the literature ZIF-carbons with high nitrogen content show a good ORR performance but have rarely being investigated for OER or clearly show poor or no activity for OER, see Fig. 1, 2 and Fig. S30 (ESI†).

The PXRD patterns of the NPCs show a clear transition from amorphous carbon to graphitized carbon with increasing substitutional cobalt for zinc (Fig. 3a and Fig. S14, ESI†). Carbonization temperature also plays a vital role in enhancing the crystallinity of carbon. Graphitization is also observed by sharp Raman D and G bands when going from $\text{Zn}_{100}$–C to $\text{Co}_{100}$–C (Fig. S15, ESI†). The transformation to a pure graphitic carbon phase with increasing temperature is suggested by a gradual narrowing and shift of a peak to a binding energy of $284.6$ eV (see deconvolution). The Co 2p spectra show mainly surface oxidation and nitrogen coordination. Note that in a control experiment, the oxidation of the samples to yield $\text{Co}_3\text{O}_4$/carbon shows different Co 2p and O 1s spectral peaks (Fig. S16–S19, ESI†).

$\text{N}_2$, $\text{H}_2$ and $\text{CO}_2$ molecular uptake isotherms of NPCs reveal a gradual reduction of microporosity with increasing substitutional cobalt (Fig. 3c and Fig. S20–S24 and Table S4, ESI†). A reasonable retention of porosity ($\approx 500 \, \text{m}^2 \, \text{g}^{-1}$ and $0.5 \, \text{cm}^3 \, \text{g}^{-1}$) is obtained at intermediate cobalt concentrations. It is worth noting that all the precursor ZIFs show a similar open pore framework structure.
The uneven trend in the porosity with respect to the carbonization temperature between (700 and 1100 °C) is directly linked to the framework decomposition at ≤700 °C and the competition between subsequent ligand decomposition, cobalt-induced graphitization at ≥700 °C, and also the vaporization of zinc at >900 °C (Fig. S27, ESI†). A framework decomposition/carbonization temperature is seen at 1000 °C, whereas Co25Zn75–C1000-10h show some clustering of cobalt and zinc metal centres within the disordered carbon, whereas Co25Zn75–C1000-10h show some clustering of cobalt and nanoribbons of carbon in locally graphitized carbon structure. For the first time the extent of graphitization is further analysed with the oxidation of carbon using thermogravimetric analysis under flowing air (Fig. S28, ESI†). With increasing temperature the CoZn100–x–C1000-10h and CoZn100–x–C1100-10h samples show different behaviours for mass loss. This is directly attributed to the different thermal stabilities associated with the amorphous and crystalline carbon. The cobalt-induced graphitization is evidenced by two-stage mass loss at ~300 °C (burning off of amorphous carbon) and ~400 °C (burning off of graphitized carbon) in CoZn100–x–C1000 samples. The samples with x = 25 and 50 consists of (60-80)% graphitized carbon. The residual mass at 700 °C estimates about (10-44)% cobalt by mass with respect to the carbon and nitrogen in CoZn100–x–C1000.

The chemical and structural transitions going from ZIF-8 to functionalized NPCs via framework and ligand decomposition† are further demonstrated with a combined thermogravimetry and mass spectrometry analysis (Fig. S27, ESI†). A framework decomposition/carbonization temperature is seen at ~600 °C, and evolution of various decomposed gaseous mixtures; C, CH, C2N or both, H2C3N2. Evidently, the increased cobalt substitution for zinc leads to a rapid ligand decomposition at reduced temperatures than in Zn-ZIF-8. The residual mass at the 1000 °C isothermal step in good agreement with the selected precursor composition to synthesize ZIFs. For example, each 50% increase in cobalt substitution for zinc shows an equally enhanced residual mass of ~14%. We also note that there is a large yield of NPCs, especially close to 50% by mass with respect to the bimetal ZIF-8. This is higher compared to the polymeric or biomass derived activated carbons.29,36

Next, the ORR and OER catalytic activity of the optimized NPCs is demonstrated, see Fig. 4 and Fig. S30–S40 and Tables S5 and S6 (ESI†). The carbonization temperature and thus graphitization, substitutional cobalt, nitrogen content and porosity in the samples play a key role in exhibiting high activities for both ORR and OER. For example, for the samples carbonized at ≤800 °C, a considerably enhanced ORR activity is seen when going from cobalt-free to cobalt-substituted carbons (Fig. S30, ESI†). This is characterized in terms of onset potential, half-wave reduction potential, Tafel slope, limiting current density and number of electron transfer steps. The highest ORR performance is obtained for the samples carbonized at 900 °C. Similarly, continuous improvement in the OER performance is seen with respect to cobalt-induced graphitization when increasing the carbonization temperature up to 1100 °C. Clearly, the carbonization temperature strongly influences ORR and OER activities – with 900 °C as the switching point for benefiting ORR or OER. More precisely, enhanced ORR ≤900 °C/1000 °C ≥ enhanced OER. For ORR activity a volcano behaviour is seen when going from 700 °C to 1100 °C with 900 °C being the optimal synthesis temperature.9 Similar behaviour is also observed when going from Zn100–C to Co100–C NPCs with Co25Zn75–C being an optimal structure at any given temperature.

A remarkable ORR performance is obtained with further tuning of carbonization conditions, such as controlling the period of carbonization and oxidation of cobalt to Co3O4 within the carbon matrix. As shown in Fig. 4a–d and Fig. S30–S32 (ESI†), the Co/C-5h and Co3O4/C-2h samples derived from Co25Zn75–ZIF-8 show better (steep slope/half-wave potentials and electron transfer number) or equivalent (onset potential and limiting current density) ORR performance to that of a reference Pt/C. The electron transfer number between 3.8 and
The stability of the NPCs, i.e. retention of a high current density against continuous operation, up to 20 h is further tested in both alkaline and acidic media (Fig. 4e, f and Fig. S37, ESI†). The Co25Zn75–C900-10h sample shows 9% and 36% drop in current density compared with 48% and 84% drop for Pt/C, respectively in 0.1 M KOH and 0.1 M HClO4.23 In particular, Co3Zn75–C900-10h maintains high stability in acidic medium than Pt/C. Furthermore, the NPCs show higher methanol oxidation tolerance than Pt/C. The Tafel plot slopes (Fig. S38, ESI†) and half-wave potentials (Table S6, ESI†) reveal that a high degree of graphitization is beneficial for fast reaction kinetics. The slope and half-wave potentials are continuously reduced with increasing carbonization temperature from 900 °C to 1100 °C. In contrast, the best positive onset potentials are observed at 900 °C with desired pyridinic and graphitic nitrogen functionality. Most of the samples exhibit faster reaction rates than Pt/C (Fig. S38 and Table S6, ESI†). The smaller Tafel slopes (48–50 mV decade−1) and half-wave potentials (e.g. 45 mV) are seen for Co3Zn100–C1100 (x = 10 and 25) compared to the high nitrogen content NPCs (at 900 °C) and Pt/C (82 mV decade−1 and 72 mV). These experimental observations are further probed by density functional theory calculations (see ESI† Fig. S42). These show that the addition of cobalt–nitrogen dopants render the OER process exothermic.

A remarkable OER performance of NPCs is observed at a controlled cobalt concentration in the Co3Zn100–x–NPCs (Fig. 1f, 4c–d and Fig. S9 and S30–S32, ESI†). The highest cobalt containing ZIF-67 derived carbon shows limited OER performance. Carbonisation temperature/graphitization and cobalt concentration strongly influences OER activity. The Co3Zn75–NPCs show the highest OER activity at any given carbonization condition among all the NPCs. At a benchmark current density of 10 mA cm−2, the best OER performance is observed at a potential of ≈(0.72–0.76) V vs. Ag/AgCl (or 1.67–1.71 V vs. RHE, reversible hydrogen electrode) for the Co3Zn100–x–C1100/1100 (x = 25 and 50). These potentials are very close to or better than the benchmark OER material, IrO2/C with 1.71 V vs. RHE.20 Note that the best OERRactive NPCs derived at mild graphitization conditions show very poor or no activity for OER. However, the same NPCs can be tuned into an effective OER or bifunctional (for both OER and ORR) catalyst by being simply subjected to high graphitization conditions.

The superior OER performance of Co50Zn50–C1100-10h is further demonstrated with stability and visible oxygen evolution, see Fig. 5 and Fig. S39 and S40 (ESI†). Improved OER performance with enhanced reaction kinetics is further observed in the Tafel plots (Fig. S40, ESI†) with smaller slopes (86–92 mV decade−1) than benchmark IrO2/C (93.2 mV decade−1).20 There is a continuous decrease in the Tafel slope with increasing cobalt concentration or carbonization temperature to facilitate fast electron transfer in the graphitized structures. The onset potential of ~1.57 V vs. RHE and potential (~1.7 V vs. RHE) required for generating a current density of 10 mA cm−2 are lower than or comparable to the best OER catalysts reported in the literature under the same experimental conditions.9,15,18,20,21,39–44

The literature indicates that the charge-transfer barrier and formation of O–O in the OOH adsorbate followed by deprotonation of the OOH group determines the catalytic efficiency of OER.46 The Co50Zn50–C1100-10h sample should exhibit the lowest charge transfer resistance due to its metallic cobalt core covered with a conducting graphitized carbon shell with few defects. The transition metals oxidation states readily participate in redox reactions.10 The metal–nitrogen–graphite system with more graphitic nitrogen is reported to show better OER activity.45 Furthermore, Chen et al. demonstrated a best OER activity from metallic CoN porous nanowire arrays.40 Positively charged metal-nitrogen sites or carbons adjacent to nitrogen (due to the electron-withdrawing nature of nitrogen in graphene) facilitate the adsorption of OH− and recombination of two adsorbed oxygens.9,16,21,45,46 As discussed in the theoretical calculations (ESI† Fig. S43), cobalt atoms have a large positive charge thus aiding OH− adsorption. This single precursor based self-modulated cobalt–nitrogen–carbon system can also be considered for complete water splitting.47

Conclusions

In summary, we have developed a simple and facile synthesis approach to realize high performance cobalt–nitrogen–carbon...
based electrocatalysts for ORR/OER. Samples derived from bimetallic $\text{Co}_x\text{Zn}_{1-x}$–ZIF-8 at mild graphitization of 900 °C show the highest activity for ORR (and the lowest activity for OER). Balanced ORR and OER activities are obtained with further graphitization at 1000 °C while the highest activity for OER occurs for samples graphitized at 1100 °C. In other words, high performance Co/C ($\text{Co}_x\text{O}_y$/C) NPCs for ORR and/or OER or vice versa can be realized by simply switching of the graphitization conditions. This is the first time that such an effective approach has been developed from a single source MOF or ZIF structure; typically additional factors such as extra functional precursor or carbon support or post-synthesis treatment are required. Our synthesis method only involves direct graphitization without the addition of any other functional precursors or extensive chemical treatment. Simple control over graphitization and cobalt-concentration produce balanced graphitic, nitrogen doped and cobalt embedded NPCs. These show highly effective catalytic performance for ORR and OER, equivalent to or better than benchmark Pt/C and IrO$_2$/C. From calculations of the energy diagram under an applied voltage $V$ we identify that the ORR reaction is significantly more exothermic for mixed cobalt–nitrogen doped systems than pure graphitic system. The reactivity (and thus efficiency) of the complete electrochemical cycle can be modified by tuning of the nitrogen content. Finally, characterization reveals that for OER nitrogen doping and cobalt concentration are primarily responsible for yielding notably more positive onset potentials. In contrast, for OER the combined graphitization and fine dispersion of cobalt metal concentration defines the reaction kinetics and the overall performance. Porosity with fine dispersion of active sites is the key in enhancing the overall activity. The results reported here can guide further advancement in targeted synthesis of nanoporous carbon-based high-performance bifunctional catalysts for high capacity metal–air batteries and overall water splitting.

Acknowledgements

This work was supported by the EPSRC (Grant No. EP/L018330/1 and EP/K002252/1). The authors also acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL) and the Grace High Performance Computing Facility (Grace@UCL).

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