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CO₂ turned into a nitrogen doped carbon catalyst for fuel cells and metal-air battery applications[†]

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Heteroatom doped metal-free catalysts are one of the most promising replacements for platinum for the alkaline oxygen reduction reaction (ORR). Due to the lack of metal atoms, they are extremely stable and environmentally friendly. However, production of carbon nanomaterials can have a very high CO_2 foot-print. In this study, we present ORR catalysts made directly from CO_2 *via* molten salt CO_2 electrolysis. The deposited carbon powder is doped with nitrogen using pyrolysis in the presence of dicyandiamide. The effect of molten carbonate electrolyte composition towards the final ORR activity in 0.1 M KOH is studied. A thorough physico-chemical study of the starting carbons and N-doped catalysts is presented with SEM and TEM imaging, BET analysis, Raman and X-ray photoelectron spectroscopy as well as the rotating disk electrode method. The onset potential and half-wave potential of the better catalyst were -50 and -175 mV vs. SCE in 0.1 M KOH, respectively.

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1. Introduction

Preserving the current way of life in the developed world while transitioning to a non-carbon energy cycle is among the most important challenges for mankind in the 21st century. Reducing CO₂ concentrations in the atmosphere requires a multi-pronged approach: the amount of CO₂ produced must be decreased while technologies for utilizing CO₂ also have to be developed to alleviate the effects that already affect our environment.^{1,2} The transportation industry, which makes up 14% of the total greenhouse gases,³ could be revolutionized by substitution of the internal combustion engine for polymer electrolyte fuel cells (PEMFCs), a device which converts hydrogen into electrical energy *via* controlled oxidation rather than burning to propel vehicles.⁴ Current PEMFCs use a considerable amount of platinum as a catalyst on the cathode side, hindering the commercialization as this noble metal makes up

40% of the price of the fuel cell.⁵ Platinum is needed to decrease the overpotential of the oxygen reduction reaction (ORR), especially under acidic conditions where PEMFC fuel cells traditionally operate. The emergence of highly conductive anion exchange membranes (AEMs) has meant that alternative, non-precious metal or metal free catalysts have become a viable alternative to platinum, because under alkaline conditions they can show similar or even higher activities.⁶

Recently, much attention has been focussed on non-precious metal catalysts, where the active sites (either metal-nitrogen coordination centres, M-N_x, or metal/metal oxide/metal carbide particles covered in nitrogen-doped graphitic carbon) have shown comparable or even higher activities in both acidic and alkaline media.7-12 Unfortunately, such catalysts suffer from an important setback as their stability is low, especially under fuel cell conditions.¹³⁻¹⁵ The quick loss in activity is commonly associated with either the demetallation of the metal atoms^{13,16} or corrosion of the underlying carbon structures.¹⁷ While these effects are known to be more detrimental under acidic (and thus more corrosive) conditions, they also deteriorate the catalysts in alkaline media.^{18,19} The second type of replacement catalysts developed forgoes metals entirely while focusing on maximizing the activity of nitrogen-doped carbon.²⁰⁻²⁴ Metal-free catalysts offer a couple of important advantages over metal-based catalysts, as the first mechanism of activity loss (demetalation of the active site) is not present here (thus these catalysts are intrinsically more stable) and also circumvent the use of metals in the synthesis, of which the production of some is actually quite bad for the environment (for example, Mn and Co-based catalysts).15,25-27

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Paper

Although metal-free N-doped carbon catalysts have become an increasingly researched topic in the last 10 years, the origin of ORR activity in N-doped carbon materials remains controversial. There is still an ongoing debate about the preferential spatial location (basal or edge sites) or chemical nature (which nitrogen moiety or combination is responsible for the ORR activity) of the N atoms.^{22,28} The lone pair of electrons on a pyridinic N atom (a nitrogen atom in a six-membered carbon ring bound to two carbons) has long been thought to be the site responsible for most of the ORR activity due to the π -conjugation it forms.^{29,30} Studies made with catalysts containing almost exclusively pyridinic N or with a high number of catalysts for comparison have confirmed the positive effect of pyridinic N on the ORR.^{29,31-34} Theoretical calculations as well as studies with real catalysts have proven that graphitic N (a nitrogen atom in a six-membered carbon ring bound to three carbon atoms) also contributes to the ORR activity of a N-doped carbon material.^{35,36} However, real life catalysts do not comprise of perfect sp^2 graphitic sheets, the material is often rather amorphous and defective. Indeed, a high number defects and edge sites is also a known descriptor for highly active N-doped carbon catalysts for the ORR.²¹ In addition to this, a large surface area is obviously needed for a high number of active sites on the surface.

Still, even when avoiding the environmental impact of platinum and other metals when creating ORR catalysts for fuel cells, the impact of synthesizing the carbon itself remains. It has been found that nanocarbon synthesis via conventional CVD methods can have a CO₂ footprint of up to 600 tons of CO₂ per tonne of carbon produced.³⁷ The electrochemical conversion of CO2 into solid carbon products in molten salts circumvents this problem as CO2 is instead consumed and turned into valuable nanocarbon products.² In this method, the carbonate salts in the electrolyte mixture are split into solid carbon and O₂ with the electrolyte then replenished using CO_2 from the surrounding atmosphere. The carbon can be designed according to the needs of the application via the selection of electrodes, salt mixtures and reaction temperatures.^{38–47} By varying these conditions, materials that are otherwise difficult to produce such as carbon nanotubes,⁴⁵ carbon nano-onions,43 and graphene44 have already been synthesized. The rate of CO2 electrolysis in molten salts is much higher when compared to that of aqueous solution based CO2 due to the increased electrical conductivity and high concentration of CO_3^{2-} , with electrical efficiencies of 95% already demonstrated in the literature, meaning that the production of carbon via this route can be easily and cheaply upscaled.48,49

In this study, we demonstrate for the first time highly active metal-free ORR catalysts synthesized directly from CO_2 . We compare the physico-chemical characteristics of two carbon materials synthesized from CO_2 , the changes that happen in them during nitrogen doping using a pyrolysis process with dicyandiamide (DCDA) and the effects of doping on their activity towards the ORR after nitrogen doping using a pyrolysis process with dicyandiamide (DCDA).

2. Experimental

2.1. Synthesis of carbon precursors from CO₂

For all carbon synthesis, a custom cylindrical reactor was used with an alumina crucible at the bottom containing the carbonate salt mixture. The carbonate salt mixture was heated to the desired temperature, after which electrodes were inserted into the molten salt. A cylindrical 304 stainless steel rod (metall24. ee, Estonia) was used as the anode and a DC01 steel sheet (metall24.ee, Estonia) as the cathode. Two different carbon materials were synthesized under differing conditions. For the first material, dubbed CO₂-1, a eutectic K₂CO₃-Li₂CO₃ (p.a., Lachner) mixture was used at 540 °C. The current density was 1.2 A cm^{-2} , which was applied for 1 hour using a power supply. The second material was synthesised in pure Li₂CO₃ at 770 °C, otherwise the conditions were the same. After synthesis the carbon was removed from the electrolyte and the electrode and then washed with 5 M HCl (Merck) multiple times for removing the salt until there was no visible gas evolution, after which the material was dried and collected.

2.2. N-Doping of carbon precursors

For doping the carbon materials with nitrogen, 100 mg of the material was first sonicated in isopropanol along with 10 mg of polyvinylpyrrolidone (PVP, Sigma-Aldrich) and 2 g of dicyan-diamide (DCDA, Sigma-Aldrich) for 2 hours. After that the material was dried and placed into a ceramic boat. The boat was placed into a tubular quartz tube, which in turn was in a tubular furnace. The furnace was purged with Ar, heated to 800 $^{\circ}$ C, after which the sample was quickly entered into the heating zone. The sample was pyrolyzed for 1 hour, cooled and then removed from the furnace.

2.3. Physical characterisation of CO₂-derived N-doped carbon catalysts

Surface morphology was studied using a ZEISS FE-SEM Ultra 55 scanning electron microscope (SEM). The acceleration voltage used in SEM measurements for high resolution imaging was 4.0 kV (In-lens SE detection). Transition electron microscopy (TEM) was performed using a Tecnai G2 F20, FEI. The samples for TEM analysis were dispersed in 2-propanol and dripped on a perforated carbon film on a 400-mesh copper grid (Agar Scientific S147-4).

The specific surface areas, $S (m^2 g^{-1})$, of the synthesized powders were analyzed by recording nitrogen adsorption–desorption isotherms using a NOVA 1200e instrument (Quantachrome, UK). The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and the porosity characteristics according to the quenched solid density functional theory (QSDFT). The electronic structure of the synthesized samples was characterized using the Raman system (Renishaw inVia Raman Microscope) using a 514 nm green laser (max 20 mW) with 1% laser power, 2 accumulations (extended) in the range of 150–4000 cm⁻¹ and an exposure time of 30 s. Following the treatment by Ferrari *et al.*,⁵⁰ a Lorentzian lineshape was used for the D-band, and a Breit–Wigner–Fano (BWF) lineshape for the G-band. The empirical Tuinstra–Koenig (T–K) relation was used to estimate the average grain size (L_a) of the carbon materials.⁵⁰

 $I_{\rm D}/I_{\rm G} = C(\lambda)/L_{\rm a}$ where $I_{\rm D}$ and $I_{\rm G}$ are the intensities of the D and G bands, $L_{\rm a}$ the average grain-size and $C(\lambda)$ a wavelength dependent constant (taken as ~0.44 nm with 514 nm excitation). Here it is assumed that the samples remain in the first stage of the carbon amorphization trajectory.⁵¹

To measure the XPS spectra, an XPS (ESCALAB 250 Xi) hemispherical analyser was operated at 20 eV pass and using Al-K α radiation, with an overall resolution of approximately 0.45 eV.

2.4. Electrode preparation and electrochemical characterisation

To test the electrocatalytic activity of the N-doped catalysts towards the ORR, the rotating disk electrode (RDE) method was utilized. First, a suspension was made of 2 mg of the catalyst in 1 ml of ethanol which contained 1 μ l of aQAPS-S₁₄ ionomer (Hephas Energy, China) per mg of catalyst material. 20 μ l of this suspension was pipetted onto 0.2 cm⁻² glassy carbon disk electrodes (GC, Goodfellow Cambridge Ltd, UK) which were pre-cleaned by polishing with 1 µm and 0.5 µm particle size alumina slurries and then sonicated first in isopropanol (Stanchem) and then in Milli-Q water for residue removal. The final loading of the catalyst on the electrodes was thus 0.2 mg cm⁻². A Pt/C material (HISPEC 5000) was used for comparison. In this case, the Pt loading on the electrode was kept at 40 μ g cm⁻² and the electrode was spin-coated for better Pt coverage on the electrode. Prior to measurements all glassware used was cleaned in piranha solution and rinsed with Milli-Q water to avoid contamination. The electrocatalytic activity was measured in 0.1 M KOH (VWR) saturated with oxygen (99.999%, Elme Messer AS, Estonia) in a five-neck glass electrochemical cell. The reference electrode was a saturated calomel electrode (SCE, SI Analytics) separated from the cell by a Luggin capillary, and a graphite rod separated from the cell via a glass frit was used as the counter electrode. Polarisation curves were recorded from 0 to -1.2 V vs. the SCE using the Gamry potentiostat 1010E (Gamry Instruments, USA) with a sweep rate of 1.67 mV s⁻¹. The rotation of the electrode was controlled by OrigaTrod apparatus (OrigaLys ElectroChem SAS, France). The rotation speeds of the electrode were as follows: (1) 400, (2) 800, (3) 1200, (4) 1600, (5) 1900, (6) 2400 and (7) 3600 rpm. To measure the stability of the CO₂-derived materials, they were cycled for 5000 polarization cycles in O₂saturated solution from 0 to -0.4 V vs. SCE with a sweep rate of 200 mV s⁻¹. After every 1000 cycles an O₂ polarization curve was recorded from 0 to -1.2 V vs. SCE at a sweep rate of 1.67 mV s⁻¹. The *n* value (electrons transferred per O_2 molecule) was calculated from the K-L equation:52

$$\frac{1}{j} = \frac{1}{j_{\rm k}} + \frac{1}{j_{\rm d}} = -\frac{1}{nFkc_{\rm O_2}^{\rm b}} - \frac{1}{0.62nFD_{\rm O_2}^{2/3}\nu^{-1/6}\omega^{1/2}c_{\rm O_2}^{\rm b}},\qquad(1)$$

where j is the measured current density, j_k and j_d are the kinetic and diffusion-limited current densities, respectively, k

is the rate constant for O₂ reduction, *F* is the Faraday constant (96 485 C mol⁻¹), ω is the rotation rate (rad s⁻¹), D_{O2} is the diffusion coefficient of oxygen $(1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$, ⁵³ C_{O2} is the concentration of oxygen in the bulk $(1.2 \times 10^{-6} \text{ mol cm}^{-3})^{53}$ and ν is the kinematic viscosity of the solution (0.01 cm² s⁻¹).⁵⁴ Electrochemical impedance spectra (EIS) were measured in N₂-saturated 0.1 M KOH from 10 kHz to 10 mHz. Gamry Echem Analyst software was used to fit the data.

3. Results and discussion

3.1. Physical characterisation of the pristine CO₂-derived carbons and N-doped materials

3.1.1. Morphology and textural properties of the pristine CO₂-derived carbons and changes taking place during N-doping. Scanning electron microscopy images of the starting carbons and N-doped materials were recorded to understand the morphology of the materials created from CO₂ and the effect of nitrogen doping on them. It has been found that the Li⁺ ions are necessary for direct solid carbon deposition at any appreciable rate, but unfortunately the melting temperature for pure Li₂CO₃ is relatively high (723 °C).^{2,55} Pure K₂CO₃ and Na₂CO₃, however, have melting points even beyond that (891 °C and 851 °C, respectively). Li₂CO₃ also has the highest conductivity among the three (at 900 °C), leading to lower ohmic losses during the electrolysis.⁵⁶ Mixtures of Li₂CO₃ with K₂CO₃ have a lower melting temperature which allows us to conduct the electrolysis and deposition of carbon from CO₂ at lower temperatures,⁵⁷ important for large-scale production as the process temperature can be kept lower along with the costs, which is why a eutectic mixture of Li₂CO₃ and K₂CO₃ was chosen as the first electrolyte media studied here. However, we also tried doping a carbon material deposited from pure Li₂CO₃ since the use of a pure carbonate would simplify the process by needing less control over the exact concentration of the electrolyte. The doping process was developed by us in previous studies and it has been successful in doping a variety of materials with nitrogen contents up to 5 at%.^{58,59} DCDA is a highly efficient nitrogen dopant due to its small size and C=N groups, which decompose at the pyrolysis temperature and readily bond to unsaturated carbon atoms.⁶⁰ The CO₂-1 material, shown in Fig. 1a-c, was very disordered, with visible porosity and no real defined particles. This is in accordance with results from CO₂-derived carbon synthesis in the literature, where a low electrolysis temperature (<700 °C) is known to create amorphous structures rather than ordered graphitic ones.³⁹ Increasing the synthesis temperature up to 770 °C and switching the electrolyte to pure Li₂CO₃ (material CO_2 -2, (Fig. 1d-f)) completely changed the morphology of the resulting carbon. A higher synthesis temperature alleviates mass transfer limitations in the electrolyte (the dynamic viscosity of pure molten Li₂CO₃ at 770 °C is 4.4 mPa s compared to 13.8 mPa s for the eutectic Li₂CO₃-K₂CO₃ mixture at 540 °C)^{56,61} and allows for the carbon material to deposit in a more ordered manner, creating spherical carbon particles



Fig. 1 Undoped CO₂-derived carbon materials: (a-c) CO₂-1, (d-f) CO₂-2.

(dubbed carbon "nano-onions"⁴³) and graphitic carbon sheets.⁴⁴ Fig. 2 shows the SEM and TEM images of the CO₂-derived carbon materials after doping with nitrogen. Fig. 2a–c

show the CO_2 -1-N material which retained its disordered porous structure, with some smaller graphitic regions also visible from the TEM image.



Fig. 2 Doped CO₂-derived carbon materials: (a-c) CO₂-1-N, (d-f) CO₂-2-N.



Fig. 3 Pore size distributions of the undoped and doped CO_2 -derived materials.

Table 1 Porosity characteristics of the CO₂-derived carbon materials: BET surface area (S_{BET}), specific surface area (S_{DFT}) and volume of micropores (V_{μ}) calculated according to the QSDFT model, total pore volume (V_{tot}), BET surface area (S_{BET}) and average pore diameter (d_p)

Catalyst	S_{BET} $(\text{m}^2 \text{g}^{-1})$	$ \begin{pmatrix} S_{\rm DFT} \\ (m^2 g^{-1}) \end{pmatrix} $	$\binom{V_{\rm p}}{({\rm cm}^3~{\rm g}^{-1})}$	V_{micro} (cm ³ g ⁻¹)	d _p (nm)
CO ₂ -1 CO ₂ -2 CO ₂ -1-N	451 480 430 39	519 545 520 26	0.379 0.434 0.413 0.049	0.194 0.204 0.186 0	1.3 1.6 1.6 3.8

The close-up in Fig. 2b and c shows an etched surface structure, due likely to the N-doping process, in which the CO₂-derived carbon is etched and replaced with nitrogen species on the surface. The CO₂-2-N material again has a very different structure, with both spherical carbon and carbon nanosheets, as seen in Fig. 2d-f. Extensive etching of the surface and graphitic domains are evident in this catalyst, which have important effects on its electrocatalytic properties as discussed in further sections. For understanding the porosity of the structures created from CO₂ and what happens to them during the N-doping process, the (BET) N₂ physisorption method was used; the pore size distributions are shown in Fig. 3 and the porosity characteristics calculated using QSDFT are given in Table 1. The CO₂-1 material had a surface area of 519 m² g⁻¹, with most of it in micropores and a second pore mode at 3-4 nm as visible from the PSD. During the doping process, the surface area did not change, but there was a small loss in microporosity, which is likely due to the closure of some pores due to ordering taking place at the high temperatures used for the pyrolysis process (800 °C). CO₂-2-N, again, was very different as the surface area decreased dramatically from 545 m² g⁻¹ to 26 m² g⁻¹ due to the etching and graphitization evident from TEM and Raman spectroscopy.

The samples were then characterised using Raman spectroscopy, and the results are given in Fig. 4. Fitted curves are shown in black and the individual bands in blue. The presented spectra are focused on the region characteristic of sp²hybridised carbons, showing the so-called D-band, located at



Fig. 4 (a and b) Raman spectra of the CO_2 -1 and CO_2 -2 samples, respectively. (c and d) Corresponding Raman spectra of the CO_2 -1-N and CO_2 -2-N systems. In all cases the red curves correspond to the raw experimental data, with the black line showing the result of the fitting procedure. Individual peaks are shown below the curves in blue.

around 1350 cm⁻¹, and the G-band found close to 1600 cm⁻¹, which dominate the carbon Raman spectrum under visible excitation.

Fig. 4a and b show the experimental Raman spectra (in red) for the CO₂-1 and CO₂-2 samples, respectively. The initial Raman responses of the systems are rather similar, with a high degree of overlap between the D and G bands, and the two peaks having similar absolute intensity. A second important feature is the width of the G-band, which should in principle increase with increasing disorder. For the undoped samples the I_D/I_G ratio was 1.1–1.2, values made apparent following fitting by the extremely broad D-band in each case. Applying the (T–K) relation, this would correspond to an average grain size of around 4 nm.

For analyzing the changes taking place in the carbon materials during doping, Raman spectra were also recorded for the N-doped samples (Fig. 4c and d). The Raman spectra for CO₂-1-N is shown in Fig. 4c. Following the fitting, it is apparent that there is little change in the position or width of the G-band, with only a slight decrease in the I_D/I_G ratio. The apparent change to the spectra instead emerges from a decrease in the D bandwidth, which in effect 'lends' less intensity to the G-band. The width of the G-band increases, along with a moderate increase in the I_D/I_G ratio. These changes suggest that graphitization is inhibited for CO₂-1-N, with the level of disorder being similar to that of the initial sample or even increasing. The inhibition of graphitization following nitrogen incorporation has been documented previously.^{62,63}

Fig. 4d shows the Raman response of the CO₂-2–N system. Here, the spectrum showed a reduction in I_D/I_G to around 0.8 ($L_a \sim 5$ nm), along with a reduction in widths of both bands. The high spectral region above 2500 cm⁻¹ also shows greater features (Fig. S1†). These changes are all consistent with a decrease in disorder and an increase in graphitic-like regions characteristic of the sample following high temperature treatment. The nitrogen doping has not been as successful (as also witnessed by XPS) and therefore, here, there is no inhibition of graphitization, resulting in a more graphitized material in the end.

3.1.2. Elemental content and surface moieties. The elemental surface composition in doped carbon catalysts is the most crucial factor for catalytic activity, since defects and nitrogen moieties are the active sites where the ORR takes place. Therefore, XPS analysis of the N-doped catalysts was performed. Fig. 5a and b show the C 1s and N 1s core level spectra for the CO₂-1-N catalyst. Overall, the carbon speciation in the samples was consistent, with the C-N and C=N peaks being more prominent in CO₂-1-N due to the high content of nitrogen in that sample. The surface nitrogen content for the CO₂-1-N material was 13.4 at%, which is spectacularly high compared to most of the catalysts seen in the literature and the highest so far achieved with DCDA-doping.^{22,33,58,59} This high level of nitrogen doping is achieved due to the amorphous nature of the starting material and its high initial oxygen content, which makes it very easy to dope with nitrogen. This also means that the CO_2 -derived material has potential for other surface modification methods. Most of the nitrogen in CO_2 -1-N was in the pyridinic N form, which is known to be one of the two most active nitrogen moieties for ORR catalysis.^{31,33} For the CO_2 -2-N sample (Fig. 5c and d), the relative N content was too low for deconvolution of the N 1s core level spectrum. Oxygen was also determined on the surface of both the catalysts, with the contents being 4.6 at% (CO_2 -1-N) and 21 at% (CO_2 -2-N).

3.2. Electrocatalytic activity of the CO₂-derived catalysts towards the ORR

The electrocatalytic activity of the catalyst materials made from CO_2 is presented in Fig. S2[†] and a short summary of the most important electrocatalytic properties of the CO2-derived materials is provided in Table 2. From the polarization curve series in Fig. S2a and b⁺ it is clearly visible that the N-doped material synthesized from the K2CO3-Li2CO3 melt at 540 °C is the better catalyst for the ORR. The onset potential for oxygen reduction on CO_2 -1-N was determined to be -50 mV vs. SCE, is extraordinarily positive for nitrogen-doped which carbon,58,64-66 proving the extraordinary structure created by reducing CO₂ into carbon and the successful nitrogen doping of this material. The half-wave potential $(E_{1/2})$ determined for the first reduction wave is -175 mV, which is also extremely positive for a metal-free catalyst. Fig. S2c and d† demonstrate the Koutecky-Levich (K-L) plots calculated from ORR polarization data and the number of electrons transferred per O_2 molecule (n) is shown in the inset. The average number of electrons transferred per O_2 molecule was around 4 in the entire potential range of oxygen reduction on CO2-1-N, meaning that the only product of electrocatalysis was OH⁻. For the CO₂-2-N material, it is clear from the K-L analysis that HO2⁻ was produced in addition to OH-. This can have important effects on the real utilization of these catalysts in fuel cells, as the efficiency is lower when HO2⁻ is produced instead of OH⁻ and it can also reduce the lifetime of the system. Table 2 shows the most important electrocatalytic properties of these catalysts, with the CO₂-1-N material clearly leading in both onset and half-wave potentials and also in the kinetic current (j_k) at 0.8 V vs. RHE and mass activity as well. The difference between RHE and SCE was determined by calibration in the same electrochemical cell by using a Pt wire as the working electrode in a H₂-saturated 0.1 M KOH solution ($E_{\text{RHE}} = E_{\text{SCE}} + 1.006$).

Fig. 6a shows a comparison of the ORR activity of all the CO_2 -derived N-doped materials as well as a blank glassy carbon electrode and non-doped carbon. The glassy carbon electrode itself shows very little activity towards the ORR, with the onset potential being -367 mV vs. SCE. The undoped carbon materials have a higher electrocatalytic activity towards the ORR with onset potentials of 219 mV and 205 mV for CO_2 -2 and CO_2 -1, respectively. With no nitrogen moieties in the catalysts, the main pathway of the ORR on these materials is the two-electron reduction to OH_2^- , with the second reduction wave starting from around -0.7 V being very prominent (according to either the further reduction of OH_2^- into OH^- or



Fig. 5 C 1s and N 1s core level spectra for (a and b) CO₂-1-N and (c and d) CO₂-2-N.

Table 2 Electrocatalytic properties of the CO2-derived catalyst materials and Pt/C

Catalyst	E_{onset} (mV vs. SCE)	$E_{1/2}$ (mV vs. SCE)	$j_{ m k}$ at 0.8 V vs. RHE (mA cm $^{-2}$)	Mass activity at 0.8 V vs. RHE (A g_{cat}^{-1})	
CO ₂ -1-N	-50	-175	8.0	40.1	
CO ₂ -2-N	-121	-277	1.0	5.2	
Pt/C (HISPEC 5000)	-25	-164	10.6	106	

a 2 + 2 electron pathway of the ORR). Clearly, better of the two N-doped materials is CO₂-1-N. As demonstrated by XPS, this catalyst contained the most surface nitrogen, mostly in the pyridinic form. This proves that nitrogen doping has a clear impact on the ORR activity of the material, by creating new active moieties (mostly pyridinic nitrogen) that catalyse the ORR. As the lone pair of electrons from the pyridinic nitrogen is donated to the π -bond system, the electron density of the system is increased, simplifying the electron transfer to O₂. The high pyridinic N content in CO₂-1-N thus has a substantial effect on the ORR activity as seen in Fig. 6a. CO₂-1-N also had the highest specific surface area after nitrogen doping, another factor responsible for the high electrocatalytic activity. CO_2 -2-N, which had the same surface area prior to doping, had nearly no microporosity left after the doping process and a very low SSA. N-doping with dicyandiamide is clearly more effective with the low-temperature, mixed electrolyte CO_2 -derived carbon material when compared to the higher-temperature pure Li₂CO₃-derived material. The reason for this might be that while the CO₂-1 material is comprised of an extensive amorphous structure, CO_2 -2 had spherical carbon phases and graphitic platelets, as seen from the SEM and TEM images, meaning that CO_2 -1 has deeper pores throughout the material, while the pores are more on the surface of the CO_2 -



Fig. 6 (a) Comparison of ORR polarization curves for all the CO_2 -derived undoped, N-doped materials as well as a commercial Pt/C catalyst and a blank glassy carbon electrode. $\omega = 1600$ rpm. (b) Corresponding Tafel plots with the linear fits used to determine the Tafel slope values.

2 material. Thus, in CO_2 -1, the DCDA is trapped in the amorphous pore structures and can dope the material more efficiently. Because the nitrogen doping process etches some of the carbon, there is a loss of surface area due to the etching of the porous phase on the surface of CO₂-2-N, significantly increasing the graphitization of the carbon (visible from the Raman spectra), which makes it very hard to dope (as witnessed by the low N content). The low N content, in turn, means that the activity towards the ORR is very low. Another notable effect comes from the oxygen content: an optimum oxygen content in carbon nanomaterials can increase the ORR activity somewhat since the oxygen species are also known to exhibit some activity towards the ORR, however a high concentration can lead to a decreased conductivity of the carbon material, which is overall detrimental since the electron transport to active sites is inhibited.

Table 3 shows the properties derived from fitting the EIS spectra (Fig. 7a) measured for the two catalysts: R_{Ω} (uncompensated resistance), $R_{\rm ct}$ (charge transfer resistance), $C_{\rm dl}$ (double layer capacitance), and τ (time constant of oxygen diffusion through the ionomer layer). The equivalent circuit used is shown in Fig. 7b. The uncompensated resistance for the CO₂-2-N material was somewhat higher, showing that the contact resistance and resistance of the material itself were increased in this case (all other elements in the system being equal), the bigger effect can be seen from the charge transfer resistance, which was much higher in the case of CO₂-2-N. In

 Table 3
 Properties of the two CO₂-based catalysts calculated by fitting the EIS spectra

Catalyst	$R_{\Omega}\left(\Omega\right)$	$R_{\mathrm{ct}}\left(\Omega\right)$	$C_{\rm dl}$ (F)	τ (s)	α	X^2
CO ₂ -1-N	35.3	10.6	$7.8 imes 10^{-3}$	0.21	0.83	60.0×10^{-6}
CO ₂ -2-N	38.7	38.7	$2.8 imes 10^{-3}$	0.31	0.92	273.9×10^{-6}

CO₂-1-N, the oxygen content was at an optimal level, whereas in CO₂-2-N the O content was too high. Compared to a commercial Pt/C catalyst (HISPEC 5000), the CO₂-1-N material also performed very well, with the $E_{1/2}$ being only 11 mV more negative and reaching 75% of the kinetic activity of the Pt/C catalyst at 0.8 V vs. RHE, which is remarkable considering that CO₂-1-N is a metal-free ORR catalyst. A key issue when replacing Ptbased catalysts (which is the final goal of carbon-based ORR electrocatalysts) is reaching the activity targets while keeping the cost and the environmental impact as low as possible. With all other carbon precursors, from expensive MOF-derived catalysts to cheap biomass-based materials, there is always CO_2 created, not captured, during the synthesis. This is the key problem that is solved by using CO2-derived electrolytic carbon. We demonstrate that not only is it possible to use this carbon as a starting material for a N-doped ORR catalyst, but also to dope it with a very cheap and abundant nitrogen source (DCDA) to create a very competitive catalyst material. By exposing the exact reasons for the high activity of this CO₂derived catalyst, this work can act as a starting point for future research on CO2-derived ORR catalyst materials with a much lower cost and environmental impact as the preceding generations of catalysts. Fig. 6b shows the Tafel plots derived from the polarization curves in Fig. 6a along with linear fit lines that were used to calculate the Tafel slopes of the presented catalyst materials. The Tafel slope of the Pt/C catalyst was 63.6 mV dec⁻¹, which is around the average value commonly found for Pt/C materials (60 mV dec^{-1}). Compared to the commercial Pt/C catalyst, the CO2-1-N material had a Tafel slope of 67.6 mV dec⁻¹ and the CO₂-2-N material 75.4 mV dec⁻¹. A Tafel slope similar to that of Pt/C is commonly accepted as a sign of the same rate-determining step and reaction mechanism.⁶⁷ However, as previously discussed, N-doped materials have multiple electrocatalytically active sites, as well as competing inner- and outer-sphere reactions of ORR taking place



Fig. 7 (a) Nyquist plots of CO₂-1-N and CO₂-2-N measured at OCV from 10 kHz to 10 mHz in N₂-saturated 0.1 M KOH. (b) Equivalent circuit used for fitting the data.

at the same time, making it difficult to point to a sole ORR mechanism. Tafel analysis, as powerful a tool as it might be, still determines the average response of the system and cannot differentiate between different active sites and reaction mechanisms proceeding in the same system. All in all, these catalysts present a very interesting new class of carbon materials with very high activity towards the ORR. Since the morphology can be easily changed by using different current protocols and electrolyte (mixtures), this work presents not only a new type of catalysts, but a new strategy for catalyst morphology optimization, which can lead to important advancements in the rational design of ORR catalysts. The most important thing to be considered, however, is the environmental advantage a CO₂-derived material has over all the other materials proposed in the literature. To date, N-doped carbon for ORR catalysis has been produced from basically everything, from expensive CVD graphene⁶⁸ to bird feces.⁶⁹ Although using waste material as the source can reduce the carbon footprint of the catalyst enormously when compared to CVD, for example, it cannot make it negative. In comparison with other types of carbon materials used as the precursors to catalysts, the main advantage of CO₂derived carbon is that it captures CO₂ during its synthesis instead of producing it. In addition, it has been shown in the literature as well as in this work that the properties of the electrolytic carbon are easily tuneable. This means that by coupling it with a well-understood doping method, such as nitrogen doping with DCDA, as in this work, the final properties of the catalyst can be rationally designed to fit the purpose (in the scope of this work, ORR, but we imagine that other catalytic reactions can also be driven by CO₂-derived catalysts). By using CO2 as the resource from which a high-performance ORR catalyst is produced, we combine carbon capture and fuel cell technologies to alleviate global warming with a two-pronged strategy that directly reduces both the current CO₂ levels and the future ones. The results of stability testing during 5000 polarization cycles from 0 V to -0.4 V vs. SCE (this translates to 1.0 to 0.6 V vs. RHE, as recommended by the Depatment of



Fig. 8 ORR polarization curves of CO₂-1-N during 5000 cycles. ω = 800 rpm.

Energy) are shown in Fig. 8. The figure shows ORR polarization curves recorded before stability testing, after 1000, 2000 and 5000 cycles. During the whole test, there was practically no change in activity (negative $E_{1/2}$ shift of 1 mV), compared to typical shifts of 8 mV or more^{66,70–72} seen for heteroatom-doped metal-free catalysts in 0.1 M KOH, showing the superiority of CO₂-derived carbon as a template for N-doped carbon catalysts.

4. Conclusions

A novel type of metal-free catalyst material for the ORR was synthesised directly from CO_2 . The solid carbon product of CO_2 electrolysis in a molten Li_2CO_3 - K_2CO_3 eutectic mixture or pure Li_2CO_3 was doped with nitrogen using dicyandiamide and tested for electrocatalytic activity towards the ORR in 0.1 M KOH. A high current density (1.2 A cm⁻²) electrolysis of CO_2 in a eutectic Li₂CO₃-K₂CO₃ mixture at 540 °C produced a better carbon material for further N-doping and ORR electrocatalysis. The onset potential and half-wave potential of the better of the two catalysts were -50 and -175 mV vs. SCE in 0.1 M KOH, respectively, owing to the extraordinarily high nitrogen content of this catalyst (13.4 at%). In addition to the excellent activity, the CO₂-derived catalyst presented high stability: the half-wave potential shifted only 1 mV to more negative after 5000 cycles. Thus, we report a new concept to synthesize ORR catalysts from CO₂, connecting the fields of carbon capture and fuel cell research.

Conflicts of interest

There are no conflicts to declare.

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