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A study of plasma−porous carbon−CO₂ interactions: Ammonia plasma treatment and CO₂ capture

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Abstract

Owing to its high porosity and tunable surface chemistry activated carbon (AC) is considered a promising material for CO₂ adsorption. Functionalising porous materials by plasma is challenging but if successful, it could enhance the CO₂ uptake capacity of AC via chemisorption. This work presents an in-depth analysis of the interactions between ammonia plasmas and the porous surface of AC monolithic samples. The treatment involved an ammonia based atmospheric-pressure dielectric barrier discharge and a low-pressure radio frequency plasma. Unique plasma reactor designs for treating 3-dimensional, electrically conducting and non-conducting monolithic structures at atmospheric pressure with versatile applications are presented. The plasma-surface interactions were analysed using emission spectroscopy and X-ray photoelectron spectroscopy. High surface N containing AC samples were then used to assess the treatment effect on the subsurface. A much lower although a still significant amount of N was found at depths of ~30 µm. A simple fit of the results showed that the ratio of plasma species reaching the surface with higher to lower sticking probability was 4:1. A slight decrease in the microporosity of the plasma treated samples was found and attributed to pore blocking by the grafted N species. Plasma treated AC with high N showed an improved CO₂ adsorption capacity of up to 14 % and selectivity against CH₄ and N₂ adsorption showed that the treatment was selective primarily towards CO₂.

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Keywords: ammonia plasma; activated carbon; reactor design; porous monolith functionalization; x-ray photoelectron spectroscopy; CO$_2$ adsorption

1 Introduction

With the world’s ever-increasing energy demands and the continued emission of greenhouse gases, investigating technologies for efficiently capturing and utilising CO$_2$ remains indispensable. Amongst various methods of CO$_2$ capture, absorption by aqueous alkanolamine solutions is considered the most mature technology. Due to its major drawbacks including energy intensiveness, corrosion and solvent degradation, other methods involving physisorption or chemisorption to solid adsorbents, where regeneration of the adsorbent requires much less energy, are being investigated. Owing to its many advantages such as high porosity and surface area, ease of regeneration and versatile chemical properties activated carbon (AC) is one such material that is being investigated for CO$_2$ capture. There are several ways to increase the CO$_2$ uptake of a solid adsorbent like AC, including increasing the surface area, increasing the enthalpy of adsorption and pore engineering. These strategies must also take into account their impact on the ease of sorbent regeneration, for example, increasing the enthalpy of adsorption could make the regeneration process more energy intensive. Furthermore, under realistic conditions, the presence of other competing species in an exhaust gas stream could affect the material’s CO$_2$ uptake capacity with respect to that under idealised mono-species conditions. Thus, it is important to be able to fine-tune the material properties to control its affinity towards CO$_2$ and achieve a judicious combination of adsorption efficiency, sorbent regeneration and adsorption selectivity.

As a first step towards achieving this ambitious goal, we investigate a versatile method focussing on enhancing the CO$_2$ capture capacity and selectivity of industrial ACs by increasing the energetic interactions between CO$_2$ and the surface via chemical functionalisation. CO$_2$ being a Lewis acid, the most logically intuitive way to increase its adsorption enthalpy is to introduce onto the surface amine functional groups, which are Lewis bases. This will promote chemical acid-base reactions and enhance the CO$_2$ uptake capacity.
There are two approaches to introduce amine groups, (i) impregnation, or (ii) grafting. Impregnation involves physical adsorption of the amines onto the porous surface via weak bonds such as dipole-dipole interactions and van der Waals forces which makes them prone to desorption during the sorbent regeneration step. On the other hand, grafting involves chemically attaching the amines onto the surface which makes them more resistant to desorption during regeneration, thus making grafting the preferred technique. Attention to pore blocking is important during surface modification which can occur if the grafting species is a large macromolecule with respect to the pore size of the AC. Several techniques are used to graft amine groups onto ACs including amination, silylation with aminosilanes and nitration followed by reduction of nitrated AC. However, many of these techniques are multistep wet chemical methods that involve harmful solvents (e.g. 3-aminopropyltriethoxysilane, HNO₃, H₂SO₄) and complicated waste-handling procedures.

Non-thermal plasma processing, owing to its versatility, clean and dry (solvent-free) technique, is widely being investigated to make surfaces more reactive without altering the material’s bulk properties. It involves two main approaches, (i) plasma based film deposition wherein an organic precursor is used to deposit a thin film on the surface, and (ii) plasma treatment or so-called ’grafting’ during which chemical functional groups are attached to the surface via plasma-induced substitutive radical reactions. Studies have been done using both these approaches to introduce nitrogen functionalities to carbonaceous materials. For example, Orfanoudaki et al. used ethylene/nitrogen and propylene/nitrogen low-pressure (LP) radio frequency (RF) plasmas to deposit thin films on activated carbon fibres (ACFs) aiming to improve their molecular sieving properties, or more specifically, to improve the separation of CO₂ from CH₄ by forming pore constrictions in the fibres. This approach is based on separating gases by the different size and shape of the molecules. Although the pore constrictions achieved through film formation hindered the diffusion of both gases, the selective adsorption of CO₂ over CH₄ was favoured due to acid-base interactions between the CO₂ molecules and the nitrogen functional groups introduced from during the plasma process. Huang et al. studied the
1 Introduction

functionalisation of ACFs by an atmospheric-pressure (AP) dielectric-barrier-discharge (DBD) using N\textsubscript{2} as the precursor at different operating conditions. The external surface of the ACFs was etched and increased in roughness at a longer treatment time of 30 minutes as opposed to when the fibres were treated for only 10 minutes in which case, no such etching effect or surface roughness was observed. The highest N content determined by X-ray photoelectron spectroscopy (XPS) was reported as 2.98 at.% and was observed at the highest treatment time, 30 minutes. They also reported a loss of the graphitic structure of the ACFs after the plasma treatment. A more recent study by Moosburger-Will et al.\textsuperscript{26} investigated the surface modification of ACFs using a LP RF ammonia plasma. The authors observed a continuous increase in the average surface N content with increase in treatment time, the lowest N content being reported as 6.2 at.% after only a 2 minute treatment and the highest being reported as 12.9 at.% after a treatment duration of 16 minutes. They also observed a reduction in the surface N content on fibres taken from the centre of the tow (\(~5\text{ at.\%}, 16\text{ min}\) as compared to those at the top of the tow (\(~12.9\text{ at.\%}, 16\text{ min}\). Thus, the authors reported that the plasma treatment predominantly affects the outermost surface and poses a "shadowing" effect on the inner fibres of the tow. This effect on the inner surface is important to consider when treating porous materials for adsorption applications and is investigated in the present work.

Out of all nitrogen functionalities, amine groups are of primary interest and owing to their role in biomedical applications many studies have been published over the past few decades on improving the content of amine groups added onto surfaces via plasma methods.\textsuperscript{23,27–30} Ammonia and N\textsubscript{2}/H\textsubscript{2} are the commonly used precursors to graft amine groups by plasma treatment.\textsuperscript{23} Variation of plasma parameters has been found to control the selective grafting of amine groups over other N functionalities. Here, it must be highlighted that a reliable method for quantifying amine groups grafted by plasma is not yet well established\textsuperscript{31} owing to the variety of different N species present in a plasma and the difficulty of reliably distinguishing between these groups on the surface using the traditional methods such as FTIR and derivatisation techniques. Therefore, it is uncertain as to which choice of precursors would give rise to higher concentrations of
amine groups. Since the -NH₂ group is already present in the ammonia molecule and since the formation of the -NH₂ group using a mixture of N₂ and H₂ would require a more complex mechanism involving multiple steps of bond breaking and forming, ammonia is the preferred gas to render better amine selectivity provided the careful choice of plasma operating conditions. Moreover, surfaces treated with NH₃ plasma were found to be more stable in air over 90 days as compared to those treated with a N₂/H₂ plasma. Some studies have used ammonia along with hydrogen to improve amine selectivity. Here, atomic hydrogen is thought to play a role in reducing all other nitrogen functionalities such as imines and nitriles into amines and even volatile ammonia.

In this work, we use ammonia plasma treatment to functionalise AC monolithic structures with the aim of understanding the complex plasma-porous surface interactions and subsequently improving the AC’s CO₂ adsorption capacity and selectivity. Functionalising the material directly in its desired physical form, which in this case is a monolith, rather than in a different form such as that of the raw material i.e. the AC powder, is of importance since the process of creating the monolith from the powder usually results in a considerable loss of its original adsorption capacity. Due to its high porosity and compact design, functionalising AC monoliths is challenging and to the best of our knowledge, there have been no reports on ammonia plasma functionalisation of such porous carbon monolithic structures.

The plasma treatment is carried out using two types of reactors: (i) a home-built AP DBD uniquely designed to treat AC monolithic structures at ambient pressure as well as to enable, in a future work, the simultaneous desorption and in situ conversion of the desorbed CO₂ by plasma, and (ii) a home-built versatile LP plasma system to create a homogeneous discharge evenly over the sample surface that could also functionalise the inner pores. Along with the AC materials, cordierite monolithic samples were also included in the study as a non-porous material as well as owing to its interest as a well-known catalyst support. Furthermore, it is known to be used as an ingredient during the production of certain ACs and therefore, is used in this work to elucidate the surface chemistry of such ACs upon plasma treatment. The influence of plasma parameters such
as the power on the surface modification achieved from both plasma reactors is studied. The plasma is analysed by emission spectroscopy and surface chemical characterisation is done by XPS and high-resolution (HR)-XPS. Functionalisation of the inner pores is investigated by performing XPS on the subsurface, the average depth of which is measured by profilometry. CO\textsubscript{2} adsorption capacity is assessed by performing CO\textsubscript{2} adsorption isotherms at 30°C. Any plasma-induced alteration of the porous structure is determined by examining the samples’ micro- and mesopore distributions obtained from CO\textsubscript{2} and Ar adsorption isotherms.

2 Experimental methodology

2.1 Materials

Three activated carbon (AC) monoliths of unknown composition were obtained from three independent industrial sources, names of which are not disclosed due to confidentiality. They are labelled AC-A, AC-B and AC-C. The monolithic structure consists of square-shaped channels with wall thicknesses ca. 0.73, 0.50, 0.33 mm and channel widths ca. 0.7, 2.0, 1.3 mm for AC-A, AC-B and AC-C, respectively. The cordierite (CDR) monoliths, also obtained from an industrial source, were standard catalyst supports used in the automotive industry, with 400 cells per square inch. Pictures of the monoliths are presented in Fig. 1. Prior to functionalisation, all monolithic samples, cut into appropriate sizes which are specified in the next sections, were dried in an oven at 110°C for 24 h and stored in a desiccator over solid NaOH for at least 24 h before use. High-purity gases, ammonia and helium (ca. 99.96 % and \geq 99.999 % respectively, Air Liquide, Belgium) were used for the plasma treatment.

2.2 Atmospheric-pressure plasma treatment

Fig. 2 illustrates the AP plasma system used for treating the AC samples. It comprised of a DBD ignited between the grounded electrode being the conductive AC monolith and the high voltage (HV) electrode being the Cu wires inserted into thin alumina tubes which were in turn inserted into each of the monolith channels. The alumina tubes of 1.19
Experimental methodology

Figure 1: The activated carbon and cordierite monoliths.

mm out. dia. and 0.39 mm wall thickness, served as the dielectric. The tubes were fixed firmly to the reactor to ensure that they were well-centred within and throughout the channels of the sample. Only monolithic samples of AC-B and AC-C could be treated by AP DBD. The AC-A monolith could not be modified in a similar AP plasma setup since its channels were too small which made it impractical to pass sufficiently thin alumina tubes through them. The samples of the AC-B and AC-C monoliths used in this setup comprised of nine 30 mm long channels in a 3 x 3 configuration. The same reactor system was adapted to treat both AC-B and AC-C samples. Ammonia gas flow rate was kept constant at 1000 mL\textsubscript{n}/min and 500 mL\textsubscript{n}/min during treatment of AC-B and AC-C, respectively. Helium flow rate was varied between 100 and 1000 mL\textsubscript{n}/min. Experiments were conducted with pure ammonia plasma and in mixtures of ammonia and helium. With a discharge gap of less than 1 mm and in the range of working powers used, both flow compositions produced diffused discharges as observed by the naked eye.

The DBD setup used to treat CDR samples is presented in Fig. 2b. The sample was layered between two 3 mm thick quartz slides which served as the dielectric barrier. Two 26 x 46 mm stainless steel meshes were used as the HV (top) and grounded (bottom) electrodes. A typical CDR sample was 30 x 4.4 x 50 mm and comprised of 69 channels in a 3 x 23 configuration. Possibly due to the relatively large discharge gap of \( \approx 4.4 \) mm (defined by the sample height), the plasma needed to be ignited first with a pure He flow of 500 mL\textsubscript{n}/min. After 1 min, NH\textsubscript{3} was admitted at 50 mL\textsubscript{n}/min for 4 min resulting in a total treatment time of 5 min and a total final flow rate of 550 mL\textsubscript{n}/min.
Figure 2: Conceptual sketches (left) and to-scale overall schematic views (right) of the dielectric barrier discharge (DBD) systems used to treat the (a) AC and (b) CDR samples.
Gas flow was restricted to the channels of the monolithic samples and controlled using electronic mass flow controllers (Bronkhorst). After placing the sample (AC or CDR), the system was purged with precursor gas flow for approximately 5 min before initiating the discharge. A sinusoidal voltage was then applied across the electrodes using a commercial power source and transformer (AFS generator G10S-V, 1000 W maximum output) and monitored via a digital oscilloscope (Tektronix DPO 3032). A typical frequency of 25 kHz and a peak-to-peak voltage of 5 kV were recorded with the DBD for AC samples; 20.5 kHz and 16-30 kV were recorded with the DBD for CDR samples. The actual power delivered to the system was calculated by the voltage and current measured using a HV probe (Tektronix P6015A) and a Rogowski coil (Pearson 2877), respectively.

2.3 Low-pressure plasma treatment

Fig. 3 presents the LP plasma system which consisted of a 32 mm out. dia. and 28 mm in. dia. quartz tube connected to stainless steel vacuum flanges. Reactor pressure was monitored by a compact Pirani gauge (Balzers TPR 250). The chamber was evacuated using a two-stage rotary vane pump through an activated carbon adsorption filter (Pfeiffer Vacuum FAK 025) used for trapping moisture and corrosive media. Thanks to the filter, the ultimate base vacuum that could be reached in the reactor chamber was \( \leq 5 \times 10^{-4} \) mbar. Ammonia gas was admitted via electronic mass flow controllers (Brooks Instrument) at a constant flow rate of 20 mL\(_n\)/min. The operating pressure was maintained at 80 Pa using a manual gate valve. With the help of an impedance matching network (Huttinger PFM 1500 A), a 13.56 MHz RF power from a generator (Huttinger PFG 300 RF) was applied to a thin 1 cm wide Cu strip wrapped externally around the tube at the centre. The stainless steel connections on either end of the quartz tube were grounded and the capacitively-coupled glow discharge ignited spanned the entire visible region of the tube which was 214 mm long. Samples were placed on top of a 22 mm wide, 143 mm long, 3 mm thick quartz slide whose position inside the tube was kept the same throughout all experiments. Samples were at floating potential. Experiments were conducted with samples placed either at position I which is near the end of the tube or
position II which is at the centre of the tube as indicated in Fig. 3.

Figure 3: Schematic of the low-pressure (LP) capacitively-coupled RF plasma reactor system used for treating both AC and CDR monolithic samples.

In the case of both the AP and LP plasma systems, the treatment time was set to 5 min, since in both setups longer treatment times did not improve the N content on the sample surface. Moreover, in the AP DBDs, shorter treatment times were preferred to avoid excessive localised heating.

2.4 Plasma diagnostics

The plasma was characterised by optical emission spectroscopy (OES) using an Andor Technology spectrometer (SR-500i-D2-R) coupled with a CCD camera (Andor DU420A-OE). Spectra in the range 200-900 nm were acquired using a 1800 L/mm grating providing a resolution of 0.02202 nm. In every acquisition, 5 spectra were accumulated each with an exposure time of 2 s in the Full Vertical Binning mode. The entrance slit width used was 0.16 mm. Spectra were acquired at Pos I and Pos II of the plasma. At Pos I, the optical fibre was placed perpendicular to the quartz tube whereas at Pos II, it was placed at an angle of 57° to the tube in order to fully capture the bright zone at Pos II (see Fig. 3). Therefore, the optical-fibre-to-quartz-tube distance (9 mm Pos I, 17 mm Pos II) and the plasma length (26 mm Pos I, 32 mm Pos II) probed were different at the two positions; nevertheless, it does not have any significant effect on the analysis of the
2 Experimental methodology

results presented. The height of the optical fibre was kept the same at both locations. Atomic lines and molecular bands in the spectra were identified as per literature.

2.5 Material characterisation

Once the samples were plasma treated they were immediately placed in petri dishes, wrapped in parafilm and stored in a freezer at -20°C until they were analysed or transferred into a glovebox maintained under inert conditions within 2 hours of the plasma treatment. This procedure ensured that ageing of the treated surfaces when exposed to ambient air, reactions which are known to occur on plasma modified surfaces, was slowed down, reduced and kept consistent for all samples. In fact, with ammonia plasma treated glassy carbon samples, we observed negligible change in the surface chemistry upon storage at -20°C up to 14 days.

Samples that were prepared for XPS measurements were cut into ca. 7 mm long pieces consisting of a single layer of 3 channels. XPS analyses were performed in a PHI 5000 VersaProbe II instrument, using monochromated Al Kα X-rays of energy 1486.6 eV. Spectra were acquired at a 45° emission angle over a circular analysis area of 200 µm diameter. Wide scans were acquired with a step size 0.8 eV, pass energy 187.85 eV, dwell time 200 ms in the range 1200 to -10 eV. Narrow scans were acquired for the C1s peak with step size 0.1 eV, pass energy 23.5 eV, dwell time 200 ms in the range 300 to 275 eV. The quantification was performed using the CasaXPS software (version 2.3.22) which uses the following relative sensitivity factors for C1s, N1s and O1s: 1, 1.8, 2.93. The binding energy (BE) scale was calibrated with respect to the carbon (C1s) peak at BE = 285 eV.

Access to the subsurface region of the plasma treated sample was gained by gently scraping off the top layer of the surface using a cutter knife and removing any loose material using a high-purity nitrogen flow (≥99.8 %, Air Liquide, Belgium) which also eliminates contamination by any N containing fragments from the top layer. The average step height (ASH) of the step created was measured by a profilometer (DektakXT).

The porosity of the monolith was characterized using Ar and CO2 porosimetry using

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an Autosorb-1 (Quantachrome Instruments, Odelzhausen, Germany). The Ar isotherm at 87 K was treated with the Quenched Solid Density Functional Theory to determine the micro- and mesopore (0.8–50 nm) size distribution and pore volume. The CO$_2$ isotherm at 273.15 K was analysed using the Nonlocal Density Functional Theory to gain insight on the (ultra)micropores which are not accessible for Ar (0.3–1.5 nm).

CO$_2$ adsorption capacity was measured by performing CO$_2$ adsorption isotherms (Autosorb-1 Quantachrome Instruments, Odelzhausen, Germany) at 30°C. The samples, after plasma treatment, were stored in a glovebox under a N$_2$ atmosphere to prevent ageing until analysis. They were activated for 4 h in deep vacuum (<0.013 Pa) prior to the isotherm measurements. Activation temperatures of 30°C, 100°C and 200°C were used. CH$_4$ and N$_2$ isotherms at 30°C were performed on the modified samples to gain information on the effect of the plasma treatment on selectivity. High-purity CO$_2$, CH$_4$ and N$_2$ gases (<99.995 %, Air Liquide, Belgium) were used. With the LP plasma setup, in order to treat the monolithic samples evenly on all surfaces, the sample was hung on a Cu wire attached to the glass slide placed in the quartz tube.

3 Results and discussion

The elemental composition of the untreated materials as measured by XPS is presented in Table 1. Fig. 4 presents typical XPS survey spectra of an untreated and a plasma treated high-N sample of each AC and CDR. The main constituents common to all ACs include C and O. The O atoms are known to be present in ACs in the form of different functionalities of which the widely accepted predominant groups being carboxyls, lactones, anhydrides, phenols, carbonyls and quinones. Aside from C and O, Si and Al are observed in good proportions on AC-B and AC-C, suggesting a prior modification of these industrial ACs. Trace quantities of several other elements are also observed in all materials. The main constituents of the CDR sample include O, Al, Si and adventitious C. As seen in Fig. 4, characteristics of cordierite are reflected mostly on the AC-B spectra but also on that of AC-C which indicates the potential involvement of cordierite in the production of these ACs. The high content of O on both AC-B and AC-C, compared
to that on AC-A, implies that O on these samples are likely to occur also in the form of inorganic aluminium and silicon oxides similar to that in cordierites.\textsuperscript{39,40} In fact, ACs modified with aluminosilicates are known for applications related to adsorption and catalyst supports.\textsuperscript{41–43}

Table 1: Elemental composition of the non-treated ACs and CDR samples.

<table>
<thead>
<tr>
<th>Elements</th>
<th>AC-A (at.%)</th>
<th>AC-B (at.%)</th>
<th>AC-C (at.%)</th>
<th>CDR (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85</td>
<td>8</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>11</td>
<td>54</td>
<td>41</td>
<td>49</td>
</tr>
<tr>
<td>Si</td>
<td>2</td>
<td>27</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1</td>
<td>7</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;1</td>
<td>2</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>N</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>&lt;1</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>-</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Unlike in Table [1], note that in the figures presenting the elemental composition as measured by XPS, the N and O contents reported are atomic percentages of the total amount of C, N and O atoms only. Other elements such as Al and Si are omitted for a simpler and consistent presentation for all samples. This has no significant effect on the results analysis given below.

3.1 Atmospheric-pressure plasma treatment

Fig. 5a and b show the effect of the applied power and the presence of helium on the N and O contents of the AC-B and AC-C samples modified by the AP DBD. The large variation in the data is attributed to the combined effect of the inhomogeneity of the non-treated AC surfaces and of the discharge under current experimental conditions; especially in the case of the AC-B sample which was more inhomogeneous and the discharge gap of which was higher than that of the AC-C. For AC-C samples, with the increase in applied power, an increasing trend in the average N content is seen, which is due to the increase in the formation of reactive excited N species that then interact with and graft onto the surface. With the addition of He, an increase in the N content is observed because of an increase
Figure 4: Typical XPS survey spectra of non-treated and plasma treated high-N (a) AC-A, (b) AC-B, (c) AC-C and (d) CDR samples.
3 Results and discussion

Figure 5: N and O contents of samples treated with the atmospheric-pressure DBD; (a) AC-B with 1000 mL/min NH₃, (b) AC-C with 500 mL/min NH₃ and (c) CDR with 50:500 mL/min NH₃:He.

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in the reactive N species owing to better ionisation of the precursor by the high energy He metastables\textsuperscript{44,45}. As a consequence, the average N content is increased also with the increase in the He flow rate.

A very low N percentage is grafted onto the CDR surface (Fig. 5c) for which the main cause is likely the low ammonia flow rate relative to the high He flow rate used; higher flow ratios of NH$_3$:He could not ignite a plasma in this setup and further investigation was not prioritised since it is not the main goal of the study. Nevertheless, it shows that a simple flat DBD setup can be used to ignite a plasma at atmospheric pressure within the channels of a CDR monolithic structure and that N groups can successfully be grafted onto its surfaces.

Both of these plasma systems designed for treating AC and CDR monolithic structures can also be used for converting CO$_2$ using an AP plasma. In the case of AC monoliths saturated with adsorbed CO$_2$, igniting a plasma within its channels in a similar setup where the monolith acts as one of the electrodes, can result in the desorption of the CO$_2$ due to electrical heating of the monolith during the plasma ignition. As the CO$_2$ desorbs it could be converted immediately by the plasma. This setup for ACs can, therefore, be used not only for surface modification but also it can potentially be used for simultaneous CO$_2$ desorption and conversion by AP plasma. A similar demonstration was recently presented by Li et al.\textsuperscript{46} where hydrotalcite pellets were used as the CO$_2$ sorbent and were packed into a coaxial cylindrical AP DBD reactor. As per our knowledge, this is the first time an AP DBD setup specifically designed for a strong CO$_2$ sorbent such as an activated carbon in a compact monolith form, which can take advantage of its electrical conductivity for efficient desorption, is presented for this application. As for the CDR setup, it can also be used for CO$_2$ conversion by plasma coupled with a catalyst coated onto the CDR. With both the CDR and catalyst being dielectrics, a plasma can be ignited at atmospheric pressure within the channels of the CDR monolithic sample which allows for plasma-catalytic conversion of CO$_2$ using this system design.
3 Results and discussion

3.2 Low-pressure plasma treatment

Fig. 6 presents the emission spectra of a pure ammonia discharge acquired at Pos I and Pos II of the LP plasma at 10 W. Under LP RF plasma conditions, ammonia is considered to decompose into successive intermediate species, NH\textsubscript{2} and NH, which is followed by the bimolecular recombination of NH to produce N\textsubscript{2} and H\textsubscript{2}. In our experiments, the main emission bands and lines observed were attributed to NH [A\textsuperscript{3}\Pi \rightarrow X\textsuperscript{3}\Sigma \textsuperscript{-}] at 336.0 nm, N\textsubscript{2} 2nd positive system [C\textsuperscript{3}\Pi \textsubscript{u} \rightarrow B\textsuperscript{3}\Pi \textsubscript{g}] with band heads at 297.6, 315.9, 337.1, 357.6, 380.4, 399.7 nm, N\textsubscript{2}\textsuperscript{+} 1st negative system [B\textsuperscript{2}\Sigma \textsubscript{u} \rightarrow X\textsuperscript{2}\Sigma \textsubscript{g} \textsuperscript{+}] with band heads at 358.2, 391.4, 423.6, 427.8 nm and the H Balmer lines, H\alpha at 656.3 nm, H\beta at 486.1 nm and H\gamma at 434.0 nm. In line with the high brightness observed by the naked eye, the overall spectral intensity was much higher at Pos II, where the stronger electric field leads to stronger ionisation of the precursor and thus, electron density, thereby resulting in greater electron- led processes such as species fragmentation, ionisation, recombination and excitation. While the spectra presented were acquired in the absence of a sample, no clear differences in the type of emitting species were observed irrespective of the presence of any sample. Any C or O containing species were not evident suggesting no apparent signs of etching of the bare sample. The peak at 388.4 nm may be regarded either as one of the N\textsubscript{2}\textsuperscript{+} 1st negative system or that of a CN band at 388.3 nm. However, it is unlikely to stem from a CN band since these spectra were acquired with pure ammonia in the absence of any sample. Interestingly, N\textsubscript{2}\textsuperscript{+} species were detected only at Pos II as shown in the inset of Fig. 6. This clearly indicates stronger ionisation of species due to higher electron density and thus, electron impact processes at this position. Due to a significant presence of N\textsubscript{2}\textsuperscript{+} species, the sheath surrounding the sample at Pos II would be of greater potential and thickness compared to that at Pos I.

Ammonia plasmas produce a complex variety of reactive species. Their interactions with the equally complex porous surface of ACs which contain a variety of O-groups as well as other inorganic moieties, results in an unknown mixture of C-N and C-N-O species, not to mention the possible formation of any N containing inorganic groups. Thus, the fitting of XPS high-resolution (HR) spectra can be very challenging. To obtain a general...
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Figure 6: Emission spectra of the LP capacitively coupled RF plasma acquired at Pos I and Pos II at 10 W, NH$_3$ flow rate 20 mL$_{min}$/min and pressure 80 Pa.

understanding of the effect of the LP plasma treatment on AC, the HR-C1s peaks of these materials have been carefully fitted following a procedure commonly used for N-plasma treated surfaces to minimise subjectivity of the analysis. O$_{1s}$ and N$_{1s}$ HR spectra were also acquired (cf. Supporting Information), however, owing to the unknown mixture of co-existing complex functionalities typically found on plasma treated surfaces, peak fit analysis of these peaks is not straightforward.

Fig. 7 presents the HR-XPS C1s peak fitting of the non-treated and LP plasma treated AC-As. The C1s spectrum of the untreated AC was fitted which was then used as a basis for the fitting of the respective treated samples. Background subtraction was performed according to a Tougaard model incorporated within the CasaXPS software and a mixed Gaussian/Lorentzian peak shape was used for all components. Based on the procedure of Estrade-Szwarckopf for C1s peak fitting of graphitic materials, the spectra were deconvoluted into an asymmetric sp$^2$ C component denoting the graphitic C in ACs and an sp$^3$ C component to account for the non-crystalline amorphous regions which are considered to serve as favourable sites for grafting of functional groups. Additional peaks include sp C, $\pi - \pi^*$ shake-up components and plasmon loss peaks, the latter

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two accounting for the characteristic losses associated with the unsaturated C moieties and interaction with electrons in the bulk or surface plasmons of the material. Peaks accounting for O-functional groups -C-O, -C=O, O-C=O are attributed to C1, C2, C3 in the order of increasing electronegativity. Upon plasma treatment, an additional functional group component, C0, representing -C-N was added and attributions of N groups -C=N, -C≡N, N-C-O, N-C=O were included in the C1 to C3 components in the order of increasing electronegativity. Table 2 summarises the different components and their attributions. The peaks were placed at BEs relative to the sp$^3$ C component which is referenced at 285.0 eV. Constraints on FWHM and BE values of individual components were applied based on previous studies$^{37,48–50}$ and the best overall fits calculated by CasaXPS.

<table>
<thead>
<tr>
<th>Component name</th>
<th>BE (eV)</th>
<th>Assignment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp-C</td>
<td>283.9±0.2</td>
<td>C≡C, C≡C=C sp C</td>
</tr>
<tr>
<td>sp$^2$-C</td>
<td>284.5±0.2</td>
<td>Graphitic sp$^2$ C</td>
</tr>
<tr>
<td>sp$^3$-C</td>
<td>285.0</td>
<td>C-C, C-H in non-graphitic sp$^3$ C</td>
</tr>
<tr>
<td>C0</td>
<td>285.8±0.2</td>
<td>(C-N amines)</td>
</tr>
<tr>
<td>C1</td>
<td>286.8±0.2</td>
<td>C-O in aliphatic alcohols, phenols (C≡N imines, C≡N nitriles)</td>
</tr>
<tr>
<td>C2</td>
<td>287.8±0.2</td>
<td>C=O in carbonyls, quinones (N-C=O amides, N-C-O)</td>
</tr>
<tr>
<td>C3</td>
<td>289.1±0.2</td>
<td>O-C=O in carboxylic acids, anhydrides, lactones</td>
</tr>
<tr>
<td>π − π*</td>
<td>290.6±0.2</td>
<td>losses due to π − π* transition in C</td>
</tr>
<tr>
<td>plasmons</td>
<td>292.5±0.2</td>
<td>losses due to interactions with bulk or surface plasmons</td>
</tr>
</tbody>
</table>

*Given within () are additional assignments for the plasma treated samples.

It is clear that AC-A is comprised predominantly of a graphitic structure which is signified by the sharp narrow peak with the characteristic long tail on the high BE side which is reflected in the prominent sp$^2$ component. Upon functionalisation at Pos I, a clear raise in the shape of the tail of the C1s spectra with an increase in the functional group components, particularly the C2 peak is observed. In order to understand this observation, we consider possible reactions between the N plasma species and the chemical groups originally present on the samples. As previously mentioned, the dominant plasma emission lines detected corresponded to the NH[A$^3\Pi \rightarrow X^3\Sigma^-$] at 336.0 nm, N$_2$[C$^3\Pi_u \rightarrow B^3\Pi_g$] at 337.1 nm, the H Balmer lines H$\alpha$ at 656.3 nm and H$\beta$ at 486.1 nm. Thus, excited NH species (NH*) are expected to play a major role in grafting of N functional groups. They
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Figure 7: C1s peak fitting of the untreated and LP plasma treated AC-A samples at 5 W, 80 Pa, 20 mL/min for 5 min.

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can react with pure hydrocarbon (HC) moieties on the samples as well as those containing different O-groups. Upon reaction with the pure HC regions, they are grafted in the form of primary, secondary or tertiary amines involving hydrogenation with H radicals from the plasma or dehydrogenation. Reaction with the O-groups can produce several types of N functional groups such as amides, imines and amines. Possible reaction schemes of NH* with the typical O functional groups of ACs under plasma conditions, are as follows.

With aliphatic alcohols to form primary amines:

\[
R{-}OH + NH^{*} \xrightarrow{2H} R{-}NH_2 + H_2O \quad (1)
\]

With phenols to form imines or nitriles:

\[
R{-}OH + NH^{*} \xrightarrow{H} R{=}NH + H_2O \quad (2)
\]

\[
R{-}OH + NH^{*} \rightarrow R{=}N + H_2O \quad (3)
\]

With aldehydes, ketones, quinones to form imines:

\[
R{=}O + NH^{*} \xrightarrow{2H} R{=}NH + H_2O \quad (4)
\]

With lactones to form primary amides:

\[
R^1{-}C(=O)-O-R^2 + NH^{*} \xrightarrow{2H} R^1{-}C(=O)-NH_2 + R^2OH \quad (5)
\]

where $R^1$ and $R^2$ of the lactone are part of the same ring.
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With carboxylic acids to form primary amides:

\[ R-C(=O)-OH + NH_2^* \xrightarrow{2H} R-C(=O)-NH_2 + H_2O \]  

(6)

With anhydrides to form primary amides:

\[ R^1-C(=O)-O-C(=O)-R^2 + NH_2^* \xrightarrow{2H} R^1-C(=O)-NH_2 + R^2-C(=O)-OH \]  

(7)

where \( R^1 \) and \( R^2 \) of the anhydride are part of the same ring.

Note that the primary amines, imines and amides formed in the above schemes may undergo dehydrogenation to form their secondary and tertiary counterparts. From above schemes, the increase in the C2 peak upon plasma treatment at Pos I in all samples can be attributed to the formation of amide groups. Furthermore, of all the O-groups only reactions with aliphatic alcohols can potentially produce amines and the presence of other O-groups on the samples is not a desirable condition for plasma grafting of amines.

Fig. 8 presents the surface chemistry of AC-A, AC-B, AC-C and CDR samples treated with the LP ammonia RF plasma. A low range of powers from 2 W to 15 W was chosen in order to avoid excessive fragmentation of \( NH_3 \) and to preserve the amine functionality in the plasma. The homogeneity of the LP discharge allows for more consistent modifications which were difficult to achieve with the AP DBDs. In the case of AC-A, samples placed at Pos I clearly showed a higher surface N content than those that were placed at Pos II under the same operating conditions. Considering the species created and processes occurring under a LP RF ammonia discharge, as discussed previously with Fig. 6, the less N content on samples treated at Pos II is attributed to the region’s high electron density which causes a high degree of \( NH_3 \) fragmentation via electron impact collisions leading to increased dehydrogenation and formation of more stable \( N_2 \) and \( N_2^+ \) which are unlikely to contribute towards grafting of N. Similar observations are made with AC-C and CDR samples, however, the opposite is seen with the AC-B sample where N is better incorporated when placed at Pos II rather than at Pos I. This observation is related to

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the structure of the AC-B sample where the C atoms were found to be predominantly in the sp\(^3\) hybridised state characteristic of amorphous C rather than in a sp\(^2\) graphitic state (Fig. S3). The sp\(^3\) regions in graphitic materials (termed as ”defects”) play an important role in grafting of molecules.\(^5\)\(^6\)\(^7\)\(^8\) As opposed to sp\(^2\) graphitic C, the sp\(^3\) C containing regions, being less stable, are easily activated by radicals, neutrals, ions and UV radiation to create reactive sites for the grafting of N groups from the plasma. Hence, owing to the higher electron density, a higher overall density of heavy species, UV light and ion bombardment at Pos II, more favourable sites are created and made available on the surface of the AC-B for more efficient N grafting, overriding the counter-effect from the stronger fragmentation of ammonia and the production of more stable species in this region. One may ask then how does CDR not show a similar behaviour as AC-B since in both materials carbon is predominantly in a more amorphous sp\(^3\) hybridised state. This is attributed to the higher organic oxygen content on the non-treated AC-B present in the form of aliphatic alcohols and phenols that act as preferential binding sites for N and are readily activated by the more intense ion bombardment and UV radiation at Pos II (Fig. S3).

The increase in N content with the increase in power is due to the stronger ionisation and excitation of N species leading to more reactive surface interactions. The decrease in N content with further increase in power is the result of a high degree of fragmentation of NH\(_3\) at higher powers leading to the formation of more stable and less reactive N\(_2\) and/or N\(_2^+\) which leave the reaction zone as exhaust. The differing inherent surface chemistries of each substrate material clearly also influences the degree and the type of N functionalities introduced at each power as seen with the aforementioned AC-B samples.

Comparing the different materials in terms of the overall quantity of surface N content is not straightforward due to the different and complex chemical nature of each material. Nevertheless, the XPS survey spectra (Fig. 4) clearly indicates that more N is grafted onto the AC-A material and a very low amount onto the others. This points back to the potential modification of AC-B and AC-C with inorganic compounds such as cordierite in which case the amount of organic functional groups available is strongly limited by the
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Figure 8: Effect of plasma power and the sample position on the N and O contents of (a) AC-A, (b) AC-B, (c) AC-C and (d) CDR samples treated with the LP capacitively coupled RF plasma using an NH$_3$ flow rate of 20 mL/min and a pressure of 80 Pa for 5 min.

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abundance of inorganic groups that provide less preferential sites for N-functionalisation.

The O content of the LP plasma treated AC-A samples show no particular trend and it seems to be related to an inherent variation in the O content of the non-treated AC-A samples whose influence on the N content grafted, if any, is unclear. The O content of the AC-B, AC-C and CDR samples show the opposite trends of their N contents which is likely due to these reported quantities being relative and not absolute amounts. Some increase in the O content with the increase in power, for example in AC-C Pos II, is expected due to the inevitable post-plasma oxidation of long-lived radicals or dangling bonds (referred to as ‘ageing’) that may increasingly be created at higher powers.

3.3 Subsurface treatment analysis

Subsurface treatment analysis was conducted on LP plasma modified AC-A samples owing to their high surface N content. Fig. 9 presents the effect of the treatment below the outer surface of AC-A samples for two plasma power conditions. In order to gain access to the subsurface to perform XPS, a portion of the top surface was removed by gently scraping it off with a cutter knife and creating a step which was later measured by profilometry as the average step height (ASH). On the untreated sample, an inherent N content of $\approx 1$ at.% was found on the surface and $<1$ at.% on the subsurface up to a depth of ca. 50 $\mu$m. The O content of the untreated sample was around 12–16 at.% on the surface and 3–9 at.% on the subsurface at the same depth of ca. 50 $\mu$m. Surprisingly, upon plasma treatment N was detected at levels above that of an untreated sample at depths of about 30-40 $\mu$m. The plasma is usually not considered to reach such depths in nanoporous substrates and only few studies have investigated plasma functionalisation of porous structures

In a recent study, LP (50 Pa) plasma polymerisation of cyclopropylamine on a variety of substrates with different 3D geometries was investigated in terms of the deposition penetration depth and the uniformity of film chemistry. One of the substrates studied was polycaprolactone nanofibrous mats which had an average pore diameter of $\approx 1$ $\mu$m. The authors observed deposition penetration depths of several tens of micrometers. It

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Figure 9: Effect of treatment on the subsurface regions of AC-A samples treated by LP plasma at (a) 5 W and (b) 10 W, with NH$_3$ flow rate 20 mL$_m$/min and pressure 80 Pa for 5 min.
was clear that this effect was not caused by the local activation of monomer molecules in the mat considering the relatively large Debye length ($\approx 0.3 \text{ mm}$) due to which the plasma could not have penetrated into the pores. Moreover, the plasma sheath being further away from the inner pore surfaces, any contribution to film formation from ion bombardment directly through mass transport or indirectly through the creation of active sites on the surface were ruled out. The mean free path of over 100 $\mu$m, i.e. greater than the pore diameter, at a pressure of 50 Pa indicated that transport within the nanofibrous mat was driven by Knudsen diffusion. It was revealed that at least two populations with two different sticking probabilities were present in the plasma. A significant proportion (24 %) of film-forming species in the plasma had a lower sticking probability and it was due to this reason that species were able to reach the inner pores via Knudsen diffusion after undergoing many collisions with the surface.

At a pressure of 80 Pa used in our experiments, the Debye length is in the order of $10^{-1}$ mm similar to that in ref. 54. At this Debye length, which is much greater than the pore widths of the AC-A sample estimated to be $\approx 0.5 \text{ nm}$, $\approx 1 \text{ nm}$, $\approx 4 \mu\text{m}$ by CO$_2$, Ar and Hg porosimetry respectively, the plasma could not have extended into such depths. Additionally, the mean free path which is typically in the order of $10^{1}-10^{2} \mu\text{m}$ at 80 Pa, is also larger than the pore diameters suggesting that transport within the porous structures is indeed driven by Knudsen diffusion. Thus, similarly to the case of the nanofibrous mats, the presence of N deep into the AC-A is due to species with a lower sticking probability which are transported into the inner pores via Knudsen diffusion. Furthermore, our results suggest that more than one population of species each with a different sticking probability is present and that the decrease in the N content which we observe on the subsurface is due to more N-species with a higher sticking probability being grafted at the top surface regions.

We can summarise the explanations for the observations in Fig. 9 as follows. The grafting of N species (NH in our case) onto the surface is dependent on (i) the amount of those species that are transported to the surface from the bulk of the plasma and (ii) the fraction of those species that can react with the surface functional groups which
lead to grafting. The transport to the surface is dependent on the density of those species in the plasma and the nature of the sheath containing positive ions which in our case would mainly be $\text{N}_2^+$. The fraction of species that would undergo successful grafting is dependent on their sticking probability and the reactivity of the sample surface. Accordingly, considering the presence of two populations of N grafting species, one with a higher sticking probability and the other with a lower sticking probability, the following approximations can be made on the trends observed in Fig. 9.

For the observation of two times higher N content at Pos I than that at Pos II on the surface:

$$a^I N^I \approx 2 \cdot a^II N^{II}$$

where $N$ is the total amount of reactive N species (mainly NH, excluding N$_2$ and N$_2^+$) reaching the surface and $a$ is the fraction of reactive N species with a higher sticking probability. The superscripts $I$ and $II$ indicate Pos I and Pos II, respectively.

For the observation of two times higher N content at Pos I than that at Pos II on the subsurface:

$$b^I N^I \approx 2 \cdot b^II N^{II}$$

where $b$ is the fraction of reactive N species with a lower sticking probability, and $a + b = 1$ at each position.

For the observation of four times lower N content on the subsurface than that at the top surface:

$$a \approx 4 \cdot b$$
Solving the above yield,

\[ N' \approx 2 \cdot N'' \]

\[ a' \approx a'' \]

\[ b' \approx b'' \]

\[ a \approx 0.8, \ b \approx 0.2 \]

In general, \( N' > N'' \) and \( a >> b \)

Thus, the amount of reactive N species reaching the surface at Pos I is more than that reaching the surface at Pos II. Although the high electron density at Pos II produces a larger amount of reactive N species in the plasma via ionisation and fragmentation of more precursor molecules, the higher floating sheath potential and thickness populated by the less reactive \( \text{N}_2^+ \) greatly hinders the transport of the more reactive neutral N species onto the surface at Pos II.

### 3.4 Porosimetry analysis

After having successfully grafted N functionalities onto the porous ACs, we investigated the effect of the plasma treatment on the porous structure since high porosity and surface area are vital properties for a good CO\(_2\) adsorbent. Information on pore volume and specific surface area obtained from performing Ar adsorption isotherms on the three untreated AC materials is presented in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>AC-A</th>
<th>AC-B</th>
<th>AC-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume (cc/g)</td>
<td>0.340</td>
<td>0.024</td>
<td>0.289</td>
</tr>
<tr>
<td>Surface area (m(^2)/g)</td>
<td>1239</td>
<td>72.90</td>
<td>387.9</td>
</tr>
<tr>
<td>Pore width - mode (nm)</td>
<td>1.066</td>
<td>0.573</td>
<td>0.818</td>
</tr>
</tbody>
</table>

Owing to its much larger specific surface area, the untreated AC-A showed the highest CO\(_2\) adsorption capacity among the three ACs. Thus, the effect of plasma treatment on the porosity was investigated for AC-A and Table 4 presents the summary of the LP plasma modified AC-A samples for pore width ranges 0.3–1.5 and 0.8–50 nm. Fig. 10 presents the corresponding pore size distribution and cumulative pore volume. While the
effect of the plasma treatment on the micropore size distribution (left of Fig. 10a) is unclear, a decrease in the cumulative micropore volume (right of Fig. 10a) of the treated samples starts to become evident at pore widths >0.55 nm. Upon plasma treatment, a 6–8 % decrease in the cumulative pore volume within 0.3–1 nm pore diameters is observed. This decrease in micropores cannot be due to destruction caused by ion bombardment since the plasma sheath is further away from the bulk of the material. Instead, it is explained by the partial blockage of these pores by the grafted N species whose diameters are ca. 0.3 nm similar to that of an ammonia molecule, resulting in a decrease in the respective micropore volumes. Accordingly, a decrease in the specific surface area in this pore width range 0.3–1.5 nm is found as indicated in Table 4.

Table 4: Pore information of the LP plasma treated AC-A samples

<table>
<thead>
<tr>
<th></th>
<th>Pore widths 0.3–1.5 nm</th>
<th>Pore widths 0.8–50 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unt</td>
<td>Pos I</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Pore volume (cc/g)</td>
<td>0.364</td>
<td>0.336</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>1234</td>
<td>1164</td>
</tr>
<tr>
<td>Pore width - mode (nm)</td>
<td>0.548</td>
<td>0.501</td>
</tr>
</tbody>
</table>

Note: ‘Unt’ refers to the untreated AC-A. The LP plasma treatment was at 10 W, 20 mLₐ/min NH₃ and 80 Pa.

Fig. 10b shows the mesopore size distribution and the respective cumulative mesopore volume. Clearly, the amount of mesopores which are defined as pores with diameters in the range 2–50 nm are very limited (left of Fig. 10b). However, we observe a peak around 1.1 nm pore diameter, which has significantly been altered by the plasma treatment. This is reflected in the cumulative pore volume (right of Fig. 10b) as an initial decrease compared to that of the untreated sample which is also attributed to the partial blockage of these pores by the grafted N groups. A final net increase in the cumulative mesopore volume is observed which is merely due to a very small although almost continuous increase in pores with diameters >1.5 nm in the plasma treated samples. Since the amount of such pores observed in the mesopore size distribution curves (left of Fig. 10b) is very low, this net increase in the cumulative mesopore volume upon plasma treatment is considered negligible. Thus, the observed increase in the specific surface area of the
Figure 10: Pore size distribution (left) and cumulative pore volume (right) in the pore width range of (a) 0.3–1.5 nm and (b) 0.8–50 nm of AC-A samples, both non-treated and LP plasma treated at 10 W, 20 mL/min NH$_3$ and 80 Pa.
plasma treated samples in the pore width range 0.8–50 nm, presented in Table 4, is also considered negligible.

It is worth noting that a 60 min long plasma treatment at Pos II does not change the porosity any more significantly than a 5 min treatment does. This suggests that under the studied plasma conditions, the interactions between the plasma and the surface leading to any changes in porosity, occurring directly or indirectly through diffusion processes, reach an equilibrium within quite a short period of time. Additionally, the difference in the effect of treatment at Pos I and II on the porosity is also negligible. This is probably due to the amount of N species grafted in the inner pores, in the bulk of the sample used for the porosity measurements, being relatively low as shown previously in Fig. 9. Therefore, the difference in the amount of N species grafted in the inner pores at Pos I and II, does not seem large enough to be clearly reflected in the porosity measurements.

3.5 CO₂ adsorption and selectivity

![Figure 11: 30°C CO₂ adsorption isotherms of non-treated AC-A, AC-B and AC-C samples activated at 150°C.](image)

Fig. 11 shows the CO₂ adsorption isotherms of the non-treated ACs at 30°C. Out of the three, AC-A performed the best with a final adsorbed CO₂ amount of ≈3.3 mmol/g at 1 bar. This is not surprising given that it has a very high specific surface area as

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presented in Table 3. With the specific surface areas of AC-B and AC-C being 17 and 3 times lower than that of AC-A, they both show much lower adsorption capacities which are 5 and 3 times lower than that of AC-A, respectively. Despite the stark difference in their specific surface areas with the area of AC-B being five times lower than that of AC-C, their CO\(_2\) adsorption capacities do not reflect this difference to the same extent. More specifically, the adsorption capacity of AC-B, although lower than that of AC-C, is still relatively high. There are many factors that affect CO\(_2\) adsorption. Apart from the surface area and the porous structure, the type of CO\(_2\)-surface interactions and the stability of the resulting complexes formed could significantly influence the adsorption. CO\(_2\) may bind to a surface either through physical interactions (physisorption) or chemical reactions with the surface (chemisorption). During physisorption, it may bind to saturated HCs via weak acid-base interactions giving rise to complexes with low stability. With unsaturated HCs, the bonding occur via \(\pi\) interactions, Lewis acid-base interactions and H-bonding. The resulting complexes are expected to be more stable, with those formed with aromatic HCs to be the most stable. Further, CO\(_2\) interactions with functionalised HCs are considered to form even more stable complexes. For example, CO\(_2\) is expected to interact more strongly with functionalities such as hydroxyls, carbonyls and carboxyls via non-covalent forces including Lewis acid-base interactions \((\text{C}=\text{O} \cdots \text{C}(-\text{O})_2)\) and hydrogen bonds \((\text{C-O-H} \cdots \text{O}=\text{C}=\text{O}, \text{C-H} \cdots \text{O}=\text{C}=\text{O})\) to form more stable complexes. In addition, the presence of more CO\(_2\) molecules in the system may lead to larger increases in the stability of the complexes formed. More information on CO\(_2\) interactions with organic surfaces during physisorption can be found in ref. \(^{56}\). In the case of AC-B and AC-C, the closeness of their CO\(_2\) adsorption capacities, despite the large difference in their specific surface areas, is explained by the relatively higher proportion of organic oxygen functional groups found on the AC-B (Fig. S3). This would greatly improve the CO\(_2\) adsorption capacity of AC-B due to the formation of much more stable complexes as explained above, thereby compensating for its low specific surface area.

Among the different N functionalities that are grafted onto the surface, amine groups are of great interest since they allow for the chemisorption of CO\(_2\), increasing the enthalpy
of adsorption and thus improving the material’s CO₂ uptake capacity much more than physisorption alone would allow for. The work of Said et al.\textsuperscript{12} shows that the CO₂ reaction with supported amines occurs via a six-membered mechanism involving the nucleophilic attack of CO₂ by a Lewis base (amines, OH) assisted by a Brønsted base (amines, OH) to form a carbamate, carbamic acid or a bicarbonate depending on the amine surface density and whether the feed gas is dry or humid. Under dry conditions, at high amine surface density, the nucleophilic attack of CO₂ by amines is assisted by a neighbouring amine to form an ammonium carbamate. At low amine loading, nucleophilic attack of CO₂ by amines may be assisted by hydroxyl groups to form carbamic acid or hydronium carbamate. Under humid conditions, water may play the role of the nucleophile or the assisting species to form either ammonium bicarbonate or hydronium carbamate. The amine-CO₂ reaction mechanism in much more detail can be found in this work.\textsuperscript{12}

The effectiveness of the ammonia plasma treatment on the CO₂ adsorption capacity of the ACs was tested and an improvement was seen only with the AC-A samples. No significant change in the adsorption capacity of either AC-B or AC-C was observed. The main reason for this is most likely the very low amount of N that could be grafted onto these samples. Moreover, since not all of the N grafted is in the form of amines but rather can be in other forms like amides, nitriles and imines that are chemically more stable with CO₂, the fraction of the useful N functionalities grafted may very well be too small to produce any significant improvement in the CO₂ adsorption capacity of these two ACs.

Fig. 12 presents the CO₂ adsorption capacity of the AC-A samples, untreated (the reference) and LP plasma treated at 10 W for 5 min at Pos I and Pos II. Along with a deep vacuum, an activation temperature of 30, 100 or 200°C was used to "activate" or fully evacuate any adsorbed species from the sample prior to performing the adsorption isotherms. The reference curve shown is the same for all activation temperatures and so is the case with the treated samples where no difference in the adsorption capacity is observed with the different temperatures. This indicates that the effect of the modification is thermally stable up to 200°C and the amine functionalities were able to withstand the higher temperatures. Additionally, since the different activation temperature measure-
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Figure 12: 30°C CO₂ adsorption isotherms of AC-A samples, untreated and LP plasma treated at 10 W, 20 mL/min NH₃ and 80 Pa for 5 min.

ments were conducted on the same treated sample and all three isotherms perfectly align with each other, it alludes to the full regeneration of the sample without compromising the chemical stability of the treatment upon several adsorption-regeneration cycles. Since the focus is on enhancing the CO₂ adsorption capacity, a detailed discussion on the desorption behaviour is considered out of the scope of this study. CO₂ adsorption kinetics of the treated AC-A was performed and results indicate good kinetics of the sample with 80 % of the CO₂ being adsorbed within the first 2 seconds of equilibration (Fig. S6), thereby suggesting that the adsorption of CO₂ is not hindered by the plasma treatment.

Soon after the LP plasma treatment, samples were stored in a glovebox under nitrogen until the adsorption measurements were done in order to minimise the effect of ageing. As shown in Fig. 12, an improvement in the adsorption capacity with the increase in N content is observed; a 14 % increase with the 12 at.% N sample treated at Pos I, and an 8 % increase with the 6 at.% N sample treated at Pos II. We presume that this is caused by the higher enthalpy of adsorption resulting from the chemical reactions between CO₂ and the successfully grafted amine groups, as opposed to mere physical interactions that governed the adsorption process prior to plasma functionalisation. The higher adsorption capacity of the sample treated at Pos I strongly suggests that more of the N groups grafted were
in the form of amines. On the other hand, the lower enhancement in the CO$_2$ adsorption capacity of the sample treated at Pos II is an indication of less amines being grafted at this position. This is in good agreement with the stronger precursor fragmentation and dehydrogenation that occur, as previously discussed, at Pos II which favour the grafting of unsaturated species like imines and nitriles which are unreactive towards CO$_2$.

In order to check the effect of ageing, the high N content sample was left exposed to ambient air for 14 days before re-measuring. Indeed, a reduction in its adsorption capacity down to the level of the untreated sample is observed as shown by the red dotted dashed line labelled 'Air' in Fig. 12. This is expected since upon exposure to air, amines are known to undergo oxidation to form more stable amides which are no longer chemically reactive towards CO$_2$. Unfortunately, it is not possible to fully avoid the ageing process but methods to minimise this process in plasma modified surfaces are being investigated, especially for plasma deposited thin films. Nevertheless, this result re-confirms that the improvement in the CO$_2$ adsorption capacity was indeed due to the presence of amines on the sample that allowed for the chemisorption of CO$_2$.

It must be mentioned that not all plasma treated samples, for example those treated at 5 W and the 60 min long treatments, were able to show a similar increase in the adsorption capacity despite the high N contents. The reason for this can be related to various factors that could affect the amount and the type of amines formed, whether primary, secondary or tertiary, the reactivity of such amines in different chemical environments and so on. For example, at 5 W, as the amine structure would be better preserved due to lower electron bombardment and precursor fragmentation in the plasma, more primary amines may be grafted. In dry conditions, tertiary and secondary amines are more basic and thus are considered to be more nucleophilic than primary amines although other factors may also play a role. Many of such considerations in the amine-CO$_2$ reaction alone are taken into account in the work of Said et al. While expanding on this very complex chemistry is beyond the scope of the present work, it shows that rigorous testing of the effect of various different plasma parameters is essential and that plasma conditions can certainly be tuned to achieve the desired chemistry on surfaces of substrates as complex
as porous carbon.

Figure 13: 30°C adsorption isotherms of CO$_2$, N$_2$ and CH$_4$ on AC-A samples, untreated and LP plasma treated at 10 W, 20 mL$_n$/min NH$_3$ and 80 Pa for 5 min.

Considering that under realistic conditions there will be other competing species for adsorption, the effectiveness of the plasma treatment relative to the adsorption of methane and N$_2$ was tested considering their relevance as typical constituents of biogas and fuel gas. In addition, water vapour adsorption isotherms on the treated and untreated samples as a function of relative humidity were also obtained. However, without breakthrough measurements which involve sophisticated equipment and data analytics, relating the water isotherms to CO$_2$ selectivity is not straightforward since adsorption kinetics will play a major role. Nonetheless, the maximum water adsorbed on both the treated and untreated samples were found to be comparable and owing to the hydrophilicity of the grafted amine groups, the treated sample showed adsorption of water starting at a lower relative humidity (see supplementary information for more details). For methane and N$_2$, the respective adsorption isotherms were conducted separately as a first step towards selectivity testing. Fig. 13 shows the capacity of both treated and untreated AC-A to adsorb methane and N$_2$ relative to CO$_2$. With the untreated sample, all three gases bind to the surface via physical interactions, with CO$_2$ showing the highest adsorption followed by a considerably lower adsorption of CH$_4$ and even lower for N$_2$. The kinetic diameters of
Results and discussion

CO$_2$(0.33 nm), CH$_4$(0.38 nm) and N$_2$(0.36 nm) being close to each other, are unlikely to have contributed largely to this difference in adsorption. Instead, it is most likely to have resulted dependently on the type of interactions between the gases and the surface. CO$_2$ being a Lewis acid, forms stronger non-covalent bonds such as acid-base interactions and π interactions with the aromatic and O-groups on the AC, resulting in being more easily adsorbed. N$_2$ being non-polar shows minimal adsorption due to weak van der Waals interactions. CH$_4$ owing to its slightly better polarisability and weakly acidic nature, could form weak acid-base interactions with the functionalised HC regions, thus showing better adsorption relative to N$_2$. Upon plasma functionalisation of the sample, while CO$_2$ shows a more pronounced adsorption now due to chemisorption via covalent bonding with the grafted amines as previously described, the increase in the adsorption of the other two gases is relatively much less. Specifically, the increase in the adsorption of CH$_4$ and N$_2$ are about 5 and 11 times lesser than that of CO$_2$, respectively. This is due to the chemical stability of these two gases which are unreactive towards amines. The slight improvement in the adsorption of CH$_4$ could be due to amines being more basic than any of the oxygen functionalities and thus, allowing for the weakly acidic CH$_4$ to form slightly stronger acid-base interactions with amines. However, for N$_2$, owing to its highly non-polar character, a negligible increase in the adsorption is observed. Ideal adsorption solution theory (IAST) fitting of the experimental results using the Toth isotherm (Fig. S7) revealed, in a typical biogas composition (40 % CO$_2$ and 60 % CH$_4$), a selectivity of 7.8 (purity 84 %) for the treated sample over 6.3 (purity 81 %) for the untreated sample which is considered very good for an activated carbon. In typical flue gas composition (20 % CO$_2$ and 80 % N$_2$), a selectivity of 31 (purity 89 %) for the treated sample over 26 (purity 86 %) for the untreated sample was obtained. See supplementary information for further details. Based on these results, ammonia plasma functionalisation of the AC shows a pronounced improvement only for the uptake of CO$_2$ owing to chemisorption. This selectivity of the plasma treated AC adsorbent towards CO$_2$ shows potential use in applications related to CO$_2$ separation.
4 Conclusions

N functionalisation of porous carbon materials by ammonia plasma was investigated for obtaining an improved CO$_2$ adsorbent. Successful N grafting was achieved at atmospheric pressures wherein the material was treated directly in its 3D monolithic form with a unique plasma reactor which could also be used for simultaneous CO$_2$ desorption and conversion. A higher N content and a more homogeneous modification was achieved with the low pressure plasma. Most AC materials treated at Pos I exhibited better N content compared to those treated at Pos II where excessive precursor fragmentation took place. However, some materials showed the opposite behaviour owing to a distinct difference in their pristine surface chemistry. These samples contained a high degree of sp$^3$ hybridised carbon and organic O groups which serve as preferential binding sites and thereby promote a more efficient N grafting at Pos II. Out of all the O-groups typically present on ACs, it was inferred that only aliphatic hydroxyls led to amine groups and other O groups upon reaction with excited NH species resulted in other N functionalities, primarily amides, nitriles and imines. Despite the challenges associated with functionalising microporous materials by plasma, a much lower but a still significant amount of N was found at depths of around 30 µm. Results suggested the existence of two populations of grafting species with a higher (80%) and lower (20%) sticking probability. Twice the amount of grafting species reached the surface at Pos I compared to at Pos II. This was further supported by a significant presence of N$_2^+$ species in the plasma at Pos II contributing to a stronger and thicker floating sheath potential and thus, inhibiting the transport of neutral N grafting species onto the surface. A slight decrease in the total microporosity was observed owing to partial pore blockage by the grafted N species. Some plasma treated samples with high N content exhibited an enhanced CO$_2$ adsorption capacity of up to 14% owing to chemisorption of CO$_2$ via reaction with the grafted amines. CH$_4$ and N$_2$ adsorption isotherms on these plasma treated ACs showed little to no significant increase in the adsorption suggesting that the effect of the plasma treatment was selective primarily towards the adsorption of CO$_2$ among the gases considered. Thus, provided the careful choice of process parameters, this work showed that ammonia plasma treatment...
can effectively functionalise microporous AC materials to enhance their CO₂ adsorption capacity.

**CRediT author statement**

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