

# Optimizing Hydroxide-Functionalized Carbon Dioxide Adsorbents: Impact of Pore Structure on Adsorption Performance<sup>#</sup>

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## ABSTRACT

In the development of adsorbents for direct air capture of carbon dioxide, a novel charged-sorbents, enabled by electrochemically inserting hydroxide ions into activated carbon electrodes, has demonstrated enhanced carbon dioxide uptake at low pressures due to chemisorption to form (bi)carbonates. However, the further application of charged-sorbents is limited due to a lack of quantitative studies to material properties of absorption performance, particularly those prepared from inexpensive and readily available commercial activated carbon cloth. In this work, we employed a combined experimental and numerical method to investigate how the carbon dioxide adsorption performance of charged-sorbents is related to structural properties of carbon-based porous absorbent, i.e., charge capacity per unit mass, average pore size, pore volume, and specific surface area. We identified that the average pore size and the mass charging capacity are the two most influential factors. Higher mass charging capacity and smaller pore sizes, in general, lead to higher sorption performance. We observed that a commercial carbon cloth (AC-10-300) with a charging capacity of 1173 C/g and an average pore size of 0.933 nm showed an excellent sorption performance of 0.213 mmol/g with 400 ppm CO<sub>2</sub>. Our study provides valuable insights into the development and optimization of hydroxide-functionalized adsorbents for direct air capture using commercial activated carbon cloth substrates.

**Keywords:** direct air capture, activated carbon cloth, pore structure, hydroxide-functionalized adsorbents

## NONMENCLATURE

### Abbreviations

CCUS	Carbon Capture Utilization and Storage
DAC	Direct Air Capture

NLDFT	Non-Local Density Functional Theory
IUPAC	International Union of Pure and Applied Chemistry
GCMC	Grand Canonical Monte Carlo
<i>Symbols</i>	
$C_m$	Mass charging capacity (C/g)
$d$	Average pore size (nm)
$V$	Pore volume (ml/g)
$S_{BET1}$	Specific surface area before load (m <sup>2</sup> /g)
$S_{BET2}$	Specific surface area after load (m <sup>2</sup> /g)

## 1. INTRODUCTION

CCUS is considered as an emerging technology to effectively mitigate CO<sub>2</sub> emissions and its concentration in ambient air<sup>[1]</sup>. Traditional carbon capture technologies, namely pre-combustion, oxy-fuel combustion, and post-combustion carbon capture, aim to separate carbon dioxide from large, centralized sources, such as flue gas from coal-fired power plants<sup>[2, 3]</sup>. Compared to the centralized carbon sources associated with traditional carbon capture technologies<sup>[4]</sup>, approximately half of annual CO<sub>2</sub> emissions are derived from distributed carbon sources in residences, stores and buildings, especially in ambient air<sup>[5]</sup>. Therefore, there is an urgent need for DAC technology to be employed to remove greenhouse gases from the atmosphere, thus achieving net-zero emissions and limiting climate change<sup>[6]</sup>. Hydroxide-based scrubbers are considered one of the most promising methods for DAC of carbon dioxide<sup>[7, 8]</sup>. Industrially mature methods use potassium hydroxide aqueous solution<sup>[9]</sup> or solid calcium hydroxide<sup>[10]</sup> as adsorbents, but they typically require natural gas for regeneration at high temperatures of 900°C<sup>[9]</sup>. These high regeneration temperatures arise from the significant lattice energy of the formed carbonate materials and contribute greatly

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to the costs of running a DAC process<sup>[11]</sup>. Another method by which the regeneration temperature can be significantly reduced is by dispersing hydroxides in porous materials or polymer matrices<sup>[12, 13]</sup>. However, these materials suffer from limited stabilities and high sorbent costs<sup>[14, 15]</sup>. A. Forse et al.<sup>[16]</sup> present a new class of quinone-functionalized electrodes for electrochemical CO<sub>2</sub> capture, using the diazonium radical reaction to graft quinone molecules to a porous carbon surface, paves the way for the design and discovery of improved electrode materials for electrochemical CO<sub>2</sub> capture. Li et al.<sup>[17]</sup> recently proposed a charged-sorbents that inserts hydroxide ions into inexpensive carbon cloth through double-layer charging. Based on this method, CO<sub>2</sub> from the air can be captured and regenerated at low temperatures (90-100°C), significantly reducing the regeneration temperature. Due to the wide variety of activated carbon cloths with different structures, there is a lack of systematic studies on charged-sorbents supported by carbon cloths, especially regarding the structure-performance relationship between the physical properties of different activated carbon cloths and the hydroxide ion charge density. Additionally, adsorption rate and cyclic stability are also important evaluation criteria to charged-sorbents. Therefore, a multidimensional comprehensive assessment of charged-sorbents is necessary to effectively promote the industrial application.

In this work, eight different types of activated carbon cloths were selected to investigate the structure-performance relationship between the CO<sub>2</sub> adsorption performance of charged-sorbents and the substrate structures. Applying the method proposed by Li et al.<sup>[17]</sup>, hydroxide ions were loaded onto the activated carbon cloths through double-layer charging at the corresponding voltages. The effects of various factors of the activated carbon cloths (including charge capacity per unit mass, average pore size, pore volume, and specific surface area) on CO<sub>2</sub> adsorption performance were analyzed to obtain the adsorbent with the optimal adsorption performance. Our research provides a more comprehensive insight into the development and optimization of charged-sorbents.

## 2. EXPERIMENTAL SECTION

### 2.1 Chemicals and materials

Activated carbon cloth ACC-5092-10 was purchased from Kynol. ACC-5092-10 was activated at 300°C, 500°C, and 700°C for 1 hour, respectively, to obtain ACC-10-300, ACC-10-500, and ACC-10-700. Activated carbon cloth

STC-1000-70G, STC-1000-100G, STC-1300, and STC-1800 were purchased from the Sutong Carbon Fiber Co., Ltd. (Jiangsu, China). All cloths were activated for 1 h at 100 °C in a vacuum oven before use. Potassium hydroxide (99%) was purchased from Sigma-Aldrich. Chemical was of analytical grade and directly used as received without further purification. N<sub>2</sub> (99.99%) and 400ppm CO<sub>2</sub> (nitrogen balance) were purchased from Guangqi gas Co., Ltd. (guangzhou, China).

### 2.2 Preparation of charged-sorbents

The preparation of charged-sorbents is based on the charging of an electrochemical energy storage device. The charged sorbents were prepared in a three-electrode configuration with a homemade cell. The experimental setup is shown in the figure 1 and mainly includes the following components: an electrochemical workstation (CHI660e, CH Instruments, China), an electrolytic cell, a Hg/HgO (in 0.1 M KOH) reference electrode, a platinum sheet electrode (LEDONLAB), and a platinum wire electrode (CHI115, YUECHI, China). The activated carbon fabric was charged with a constant potential for 4 hours (0.565 V vs SHE for the PCS-OH, PCS-300-OH, PCS-500-OH and PCS-700-OH, 0.715 V vs SHE for 70G-OH, 100G-OH and 1800-OH, and 1.165 V vs SHE for 1300-OH, respectively) in 40 mL of 6 M KOH (aq.) via chronoamperometry (CA). After completing the charging process, the charged cloth was removed and held by plastic tweezers and rinsed with deionized water for 5 minutes in total on both sides. 500 mL deionized water in total was used to wash off the residual KOH solution. The rinsed cloth was then placed in the vacuum oven at 75 °C for 24 h to remove the remaining water. Finally, it was activated in a vacuum oven at 120°C for 12h.

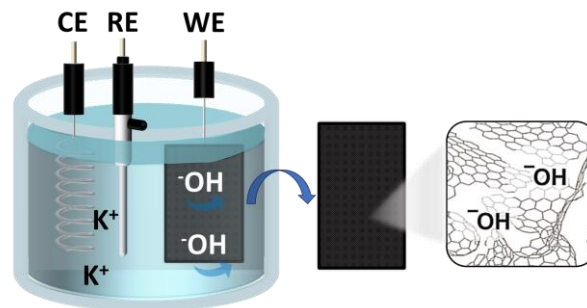


Fig. 1 Scheme of charging activated carbon cloth in 6 M KOH via a three-electrode configuration

### 2.3 Characterization

N<sub>2</sub> adsorption-desorption isotherms were measured by Advanced Specific Surface Area and Micropore Analyzer (BSD-PM2, BSD Instrument, China) at 77 K. The following parameters were calculated based on N<sub>2</sub>

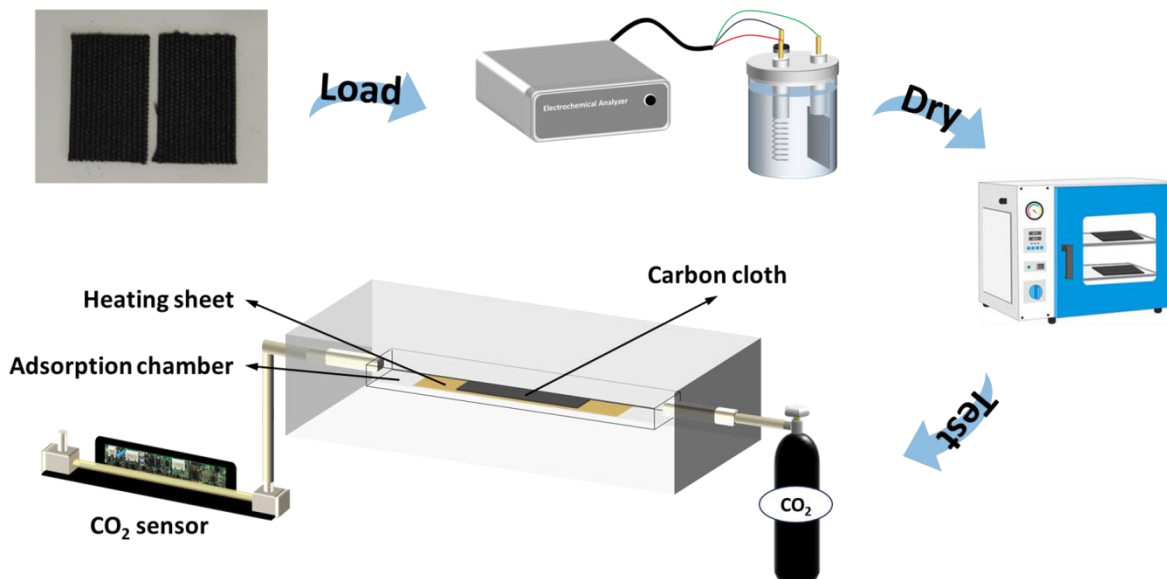


Fig. 2 Preparation and testing process of charged-sorbents

adsorption–desorption isotherm data: (a) the specific surface areas of the samples were obtained by BET Multi-point Specific Surface Area method, (b) the pore size distributions of the samples were determined by the Dubinin-Astakhov (D-R) Micropore method and the NLDFT Pore Size and Pore Volume method, respectively. The porosity of all activated carbon cloths were characterized by Automatic True Density Analyzer (BSD-TD, BSD Instrument, China).

#### 2.4 CO<sub>2</sub> adsorption performance measurement

The CO<sub>2</sub> adsorption performance of the adsorbents was evaluated in an adsorption chamber, as shown in figure 2. The activated carbon cloth was heated using a polyimide heating sheet placed in the adsorption chamber for auxiliary heating. The temperature of the material was controlled using a thermocouple, and the adsorption and desorption of CO<sub>2</sub> were measured using the Gas Chromatograph (GC9790PLUS, FULI Instruments, China). Real-time changes in CO<sub>2</sub> concentration were recorded using a CO<sub>2</sub> sensor (N-CO<sub>2</sub>, Sangbay Gas Sensor, China). First, the charged-sorbents underwent pretreatment before CO<sub>2</sub> adsorption. The hydroxide-functionalized activated carbon cloth (1.5 cm x 2 cm) was placed in the adsorption chamber and purged at 110 °C with N<sub>2</sub> flow of 100 mL/min for 60 minutes. Then, the temperature was cooled to 30°C, and the atmosphere was switched to 60 mL/min of 400 ppm CO<sub>2</sub> (with N<sub>2</sub> as the balance gas) for 20 minutes to equilibrate, during which the adsorption curve was recorded. After the adsorption process, the carbon cloth was heated to 120°C for desorption, and the desorption curve was recorded. Subsequently, the next adsorption-desorption

cycle was performed to complete the cycle performance test.

### 3. RESULTS AND DISCUSSION

To study the effects of substrates with various structures on the sorption performance under low partial pressure of CO<sub>2</sub>, 8 carbon cloth substrates are utilized and tested. The sorption performance under 400 ppm CO<sub>2</sub> of charged-sorbents on 8 substrates are shown in figure 3. As seen, the best case, i.e., ACC-10-300 achieved a CO<sub>2</sub> uptake of 0.213 mmol/g after activation under 300 °C for 4 hours. Note that STC series samples are in general showed inferior performance compared the AC series samples, possibly due to the small average pore size of AC series samples. Table 1 summarizes the mass charging capacity, average pore size after load, pore volume after load, and specific surface area (SSA) before and after charging.

Table 1: Textural properties of each substrate

Sample	$C_m$ (C/g)	$d$ (nm)	$V$ (ml/g)	$S_{BET1}$ (m <sup>2</sup> /g)	$S_{BET2}$ (m <sup>2</sup> /g)
STC-1000-70G	841	1.047	0.32	694	611
STC-1000-100G	622	1.119	0.45	859	820
STC-1300	690	1.114	0.50	959	945
STC-1800	676	1.066	0.39	1391	1305
ACC-10	1326	0.944	0.42	811	573
ACC-10-300	1173	0.933	0.42	814	592
ACC-10-500	1328	0.986	0.42	797	540
ACC-10-700	1268	0.965	0.46	874	671

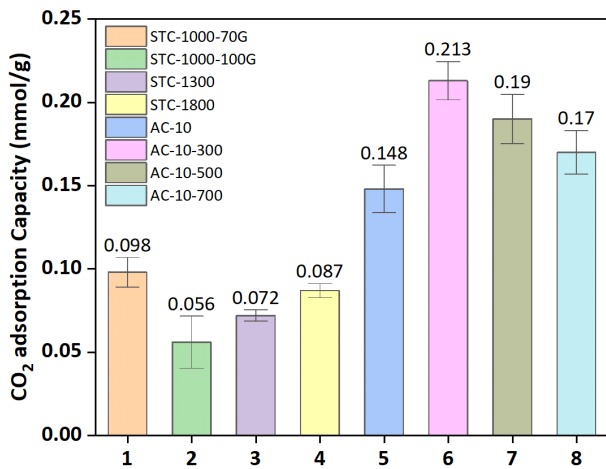


Fig. 3 CO<sub>2</sub> adsorption capacity of charged-sorbents on different substrates

The N<sub>2</sub> adsorption isotherms are shown in figure 4 for all samples after charging. The isotherms exhibit nearly vertical adsorption at low relative pressure ( $P/P_0 < 0.1$ ) and lack a significant hysteresis loop in the pressure range of 0.20–0.99, indicating that all activated carbon cloth samples exhibit strong chemical adsorption selectivity, do not react with N<sub>2</sub>, and contain a large amount of micropores and a very small amount of mesopores.

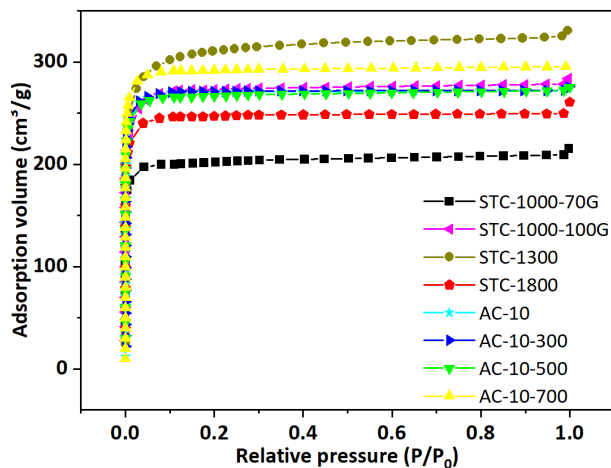


Fig. 4 N<sub>2</sub> adsorption isotherm of activated carbon cloth

### 3.1 Mass charging capacity and conductivity

Mass charging capacity can be calculated out using equation 1:

$$C_m = \frac{Q}{m} \quad (1)$$

where Q represents the total charge obtained by integrating the chronoamperometry curve, and m denotes the mass of the activated carbon cloth. The relationship between the mass charging capacity and the adsorption capacity for different substrate structures is shown in Figure 5. The adsorption capacity increases

with the rise in mass charging capacity. The greater the mass charging capacity of the activated carbon cloth, the more charges are stored in the double layer between the materials. Consequently, more anions (specifically hydroxide ions) are loaded onto the carbon cloth from the solution. At very low partial pressures, e.g., 400 ppm, the hydroxide ions chemically react with carbon dioxide, thereby capturing more CO<sub>2</sub>.

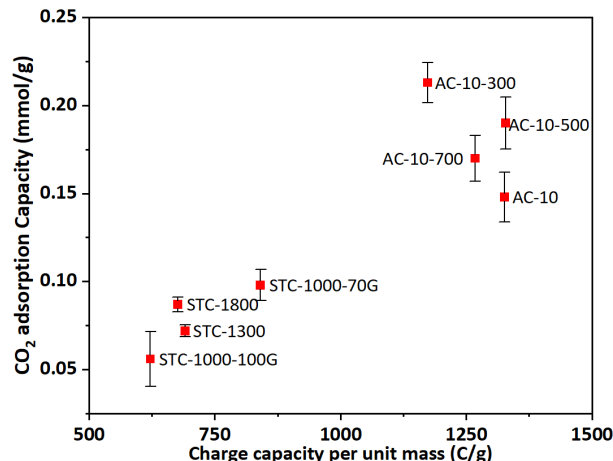


Fig. 5 CO<sub>2</sub> adsorption capacity and mass charging capacity relationship diagram

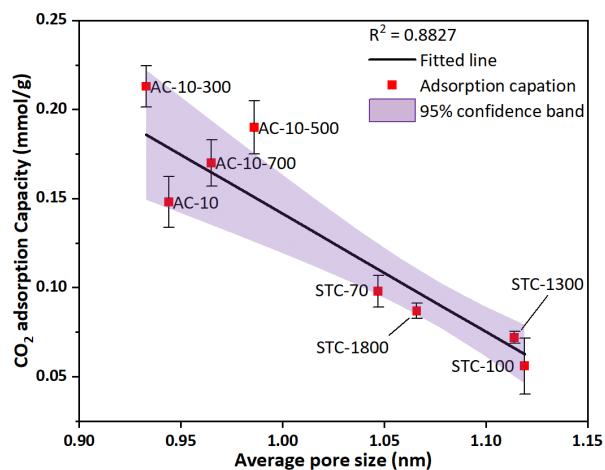


Fig. 6 CO<sub>2</sub> adsorption capacity and average pore size relationship diagram

### 3.2 Average pore size and pore volume

The relationship between the average pore size of different activated carbon cloths after loading and the adsorption capacity is shown in Figure 6. The average pore size of the eight activated carbon cloths is less than 2 nm, indicating that all the carbon cloths are microporous materials. Additionally, as the average pore size of the eight activated carbon cloths increases from 0.933 nm to 1.119 nm, the adsorption capacity decreases from 0.213 mmol/g to 0.056 mmol/g. A linear fit of the data in Figure 6 yields an R<sup>2</sup> value of 0.8827, indicating

that the adsorption capacity tends to increase as the average pore size of the activated carbon cloth decreases. This trend aligns with the concept that smaller pores provide higher adsorption potential for CO<sub>2</sub>. This is consistent with the GCMC simulations by Chen et al.<sup>[18]</sup>, which showed that the adsorption density of CO<sub>2</sub> is highest at 0.4 nm and decreases exponentially as the pore size increases.

At a CO<sub>2</sub> partial pressure of 400 ppm, using the liquid density of CO<sub>2</sub> ( $\rho_{\text{liq}}(\text{CO}_2)$ : 1.044 g/ml<sup>[19]</sup>), the volume occupied by the adsorbed CO<sub>2</sub> molecules is calculated to range from  $2.36 \times 10^{-3}$  ml to  $8.98 \times 10^{-3}$  ml. This is much lower than the pore volume calculated using the NLDFT method (Table 1). Therefore, at a CO<sub>2</sub> partial pressure of 400 ppm, the CO<sub>2</sub> adsorption capacity of all studied samples is independent of the pore volume.

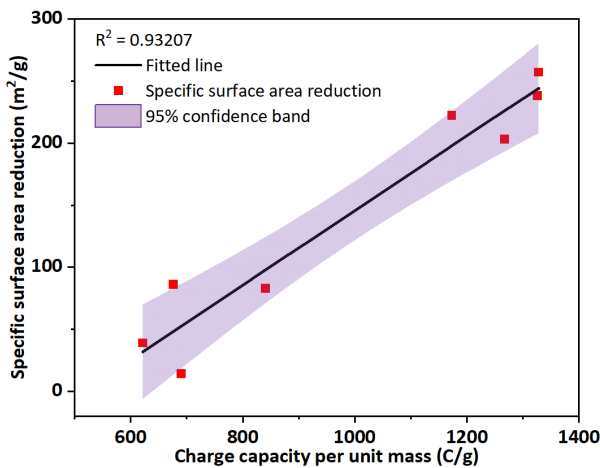


Fig. 7 Specific surface area reduction and mass charging capacity relationship diagram

### 3.3 Specific surface area

The specific surface areas of different activated carbon cloths decrease to varying degrees after hydroxide ion loading. Among them, the STC series carbon cloths show a relatively smaller reduction in specific surface area, with decreases of less than 100 m<sup>2</sup>/g after loading. In contrast, the AC series carbon cloths experience a reduction in specific surface area close to 25% of their original value, with decreases exceeding 200 m<sup>2</sup>/g. As shown in Figure 7, a linear fit between the reduction in specific surface area before and after loading and the mass charging capacity yields an R<sup>2</sup> value of 0.9327, indicating that the greater the mass charging capacity, the larger the reduction in specific surface area after loading. Figure 8 presents linear fits between the specific surface area before and after loading and the CO<sub>2</sub> adsorption capacity. The correlation coefficient between the pre-loading specific surface area and CO<sub>2</sub> adsorption capacity is 0.0668, and the correlation coefficient

between the post-loading specific surface area and CO<sub>2</sub> adsorption capacity is 0.3043, indicating that the fits are not ideal. Therefore, despite the slight reduction in specific surface area before and after loading, the adsorption performance is independent of the specific surface area.

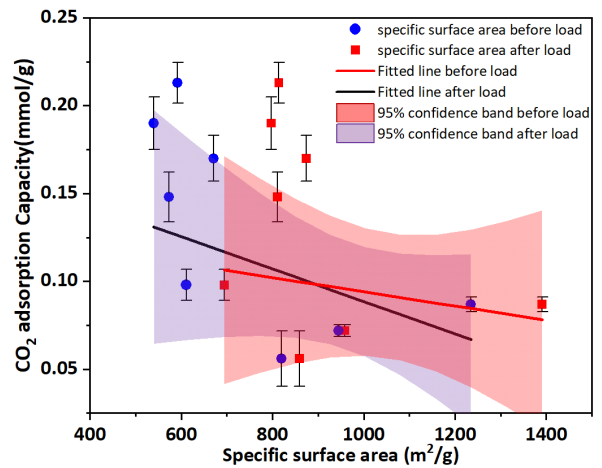


Fig. 8 CO<sub>2</sub> adsorption capacity and specific surface area relationship diagram

## 4. CONCLUSIONS

In summary, the mass charging capacity and the average pore size significantly impact the adsorption performance of charged adsorbents using activated carbon cloth as the substrate. The mass charging capacity is positively correlated with adsorption performance, while the average pore size is negatively correlated. Additionally, it found that at the tested CO<sub>2</sub> partial pressure of 400 ppm, adsorption is not limited by the available pore volume due to the relatively low adsorption amount. Although the specific surface area of the activated carbon cloth slightly decreases after loading, its correlation with adsorption performance is minimal. This comprehensive assessment provides valuable insights for optimizing the application of commercial activated carbon cloth as charged adsorbents for direct air capture. The findings suggest that enhancing the mass charging capacity and controlling average pore size are crucial for improving CO<sub>2</sub> adsorption performance. These insights could guide the future development of more efficient adsorbents for industrial applications.

## ACKNOWLEDGEMENT

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