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Supercapacitor-based CO₂ capture enhanced by electrolyte pH control

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Supercapacitive swing adsorption (SSA) is emerging as an energy-efficient alternative to traditional thermally-driven CO₂ capture technologies. While a range of operational factors have been actively explored to increase understanding of this technology, SSA is currently constrained by low CO₂ capture rates. In this work, we investigate how electrochemical CO₂ capture responds to changes in electrolyte pH by combining galvanostatic CO₂ adsorption measurements with quantitative solid-state ¹³C-NMR spectroscopy. Our measurements show 30% higher adsorption rates for basic electrolytes than for neutral electrolytes. In contrast, in an acidic electrolyte, we see substantially lower adsorption rates and capacities. To probe the origin of these observations, we use ¹³C NMR spectroscopy on uncharged electrolyte-soaked electrodes to examine CO₂ speciation. While dissolved CO₂ is detected across all electrolytes, bicarbonate concentrations increase with increasing initial electrolyte pH (*i.e.* the pH), before any reaction-induced pH changes occur, suggesting a bicarbonate- or pH-swing driven mechanism. Overall, our study provides additional insights into the factors governing CO₂ capture in SSA by highlighting the role of CO₂ speciation and electrolyte pH in optimising device performance.

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Introduction

Climate change, driven by excessive CO₂ emissions from fossil fuels and industrial activities, poses a critical threat to ecosystems and societies worldwide.¹ While global efforts like the Paris Agreement aim to limit warming to below 1.5 °C compared to pre-industrial levels and reach net-zero emissions by 2050, many sectors remain dependent on fossil fuels.^{2,3} The situation has even escalated further: in 2024, a 1.6 °C rise in global temperature (12 month average) was reported compared to the beginning of the last century.⁴ Consequently, carbon capture technologies, including point-source capture from industrial flue gas and direct air capture (DAC) from the atmosphere, are crucial for complementing emission reduction strategies and achieving climate goals.⁵

Amine scrubbing, a mature carbon capture technology, involves amines reacting with CO₂ to form carbamates. This technology benefits from fast absorption and high CO₂ selectivity.⁶ To release the CO₂, however, a large amount of energy is required to reverse the process, typically through temperature- or pressure-swing.⁶ In this context, the advent of electrochemical CO₂ capture technologies has demonstrated the

potential for increased efficiency, stability, and safety over the state-of-the-art amine capture approach.^{7,8} Examples for electrochemical carbon capture methods use redox-active molecules like quinones that reversibly bind CO₂^{9,10} or employ electrochemically-mediated pH swings using phenazine-based molecules.¹¹ By integrating electrochemical carbon capture technologies with renewable energy sources, it is possible to create a sustainable, closed-loop system that captures CO₂ while minimising the environmental footprint of the technologies.¹²

Supercapacitive swing adsorption (SSA) is a particularly promising electrochemical carbon capture technology.¹³ In SSA, CO₂ is adsorbed when charging an electric double-layer capacitor (EDLC), and is subsequently desorbed when discharging the device. Typically, in SSA setups, the working electrode is preferentially exposed to a gas reservoir (Fig. 1a). A key advantage of SSA lies in its utilisation of low-cost, earth-abundant carbon electrode materials and environmentally friendly aqueous electrolytes.¹³ Furthermore, as charge storage takes place electrostatically in EDLCs, the devices exhibit high cyclability, capable of undergoing over 10 000 charge-discharge cycles without significant degradation.¹⁴ However, SSA is limited by its low CO₂ adsorption rate (100–500 mmol kg⁻¹ h⁻¹), which is outperformed by other electrochemical CO₂ capture processes.^{15,16} This is partly due to its low capacity (typically around 100 mmol kg⁻¹, normalised to the mass of the working electrode when using commercial activated carbon electrodes)¹⁷ compared with amine-based capture

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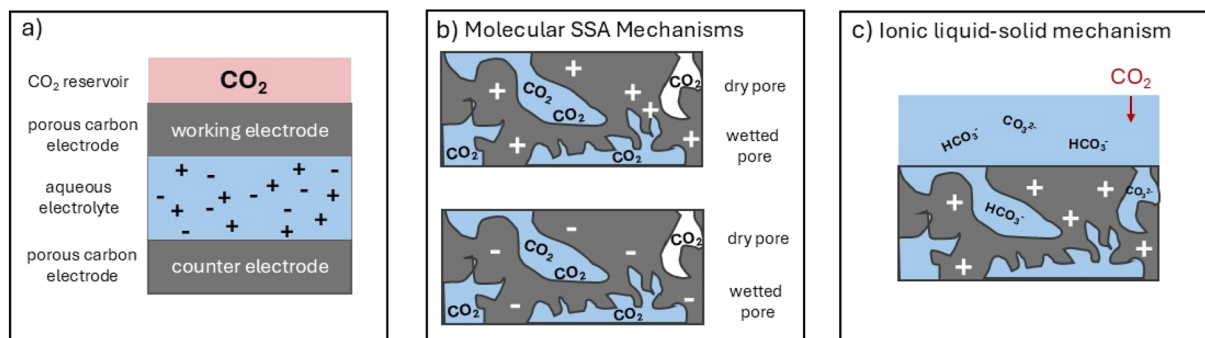


Fig. 1 (a) Typical setup of a supercapacitor used for supercapacitive swing adsorption. The working electrode is exposed to a CO₂-containing reservoir and can be charged negatively (negative charging mode) or positively (positive charging mode). (b) Molecular mechanisms of CO₂ capture visualised for the carbon electrode only. Adsorption of CO₂ within dry or wetted pores of the porous carbon electrode; mechanisms are polarity-independent and can occur at both the negatively and positively charged electrode. (c) Ionic mechanism of CO₂ capture: CO₂ from the reservoir dissolves in the aqueous electrolyte, creating bicarbonate and carbonate ions. Adsorption of CO₂-derived ionic species (HCO₃⁻ or CO₃²⁻) at the positively charged electrode.

technologies (800 mmol kg⁻¹), but may also be limited by other factors, such as gas-liquid mass transfer. Additionally, the underlying adsorption mechanism is poorly understood, hindering the rational design of SSA devices with improved CO₂ adsorption capacities.¹⁵

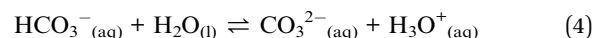
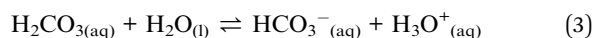
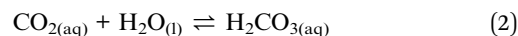
To increase the CO₂ adsorption capacities of the devices, the electrolyte composition,¹⁸ the electrolyte concentration,¹⁹ the physicochemical properties of the activated carbon electrodes,^{20–22} the operating voltage windows,²³ the charging protocols,²⁴ the use of different materials for the counter electrode,²⁵ and the polarity of the gas-exposed electrode¹⁷ have been investigated. All these studies have shown that tuning specific system parameters can lead to higher adsorption capacities; however, more rational process optimisation is limited by a poor understanding of the mechanism of action.^{20,26}

Zhu *et al.* originally proposed three CO₂ capture mechanisms, differentiated by the species involved in capture – molecular CO₂ *versus* CO₂-derived ions such as bicarbonate and carbonate.¹⁹ Fig. 1 introduces the molecular and ionic mechanisms of capture. The molecular mechanism suggests that neutral CO₂ molecules are captured in electrolyte-filled (or non-infiltrated) pores of the activated carbon electrode during charging of the supercapacitor (Fig. 1b). As the CO₂ molecule is neutral, capture can happen at the counter electrode regardless of its polarity.

A recent study demonstrated the feasibility of this mechanism, showing that the presence of CO₂ in the EDL formed on gold electrodes immersed in aqueous electrolytes decreases capacitance.²⁷ However, these molecular mechanisms do not fully account for the experimental observations reported by Binford *et al.* for activated carbon electrodes, where CO₂ capture and release depend on electrode polarity.¹⁷ While it is possible in principle for a molecular mechanism to exhibit polarity dependence, the specific mechanism illustrated in Fig. 1b would be expected to lead to CO₂ adsorption irrespective of electrode polarity. The experimentally observed polarity-dependent behaviour therefore suggests that additional

factors beyond this molecular mechanism must be contributing to the observed behaviour.

In the ionic liquid–solid mechanism (Fig. 1c), bicarbonate (or carbonate) plays a major role in CO₂ capture and release, as CO₂ capture and release are driven by the electro-sorption of CO₂-derived ionic species into the electrical double layer, which influences the underlying chemical equilibria shown in eqn (1)–(4).^{17,19,20}



Previous studies based on electrochemical CO₂ capture measurements and COMSOL modelling proposed that charging the gas-facing electrode negatively results in local depletion of HCO₃⁻, promoting CO₂ capture; the reverse effect occurs upon positive charging.^{17,20,26} Recently, two preprints have also proposed a pH swing-driven mechanism of CO₂ capture, with one showing that use of a cation-exchange membrane may enhance SSA by stabilising a high-pH region at the gas-facing electrode.^{28,29} This emerging pH-swing hypothesis likely involves pH changes bulk of the electrolyte upon charging and discharging of the supercapacitor and requires further experimental proof involving *in operando* pH monitoring.

It has also been hypothesised that both the molecular and the ionic liquid–solid mechanism can occur and that the degree to which each of them contributes to CO₂ storage depends on the characteristics of the system, including electrolyte properties (*e.g.*, pH, ionic species, concentration) and electrode structures (*e.g.*, porosity, disorder, functionality).²⁷

Overall, electrolyte pH emerges as a central factor linking CO₂ speciation, adsorption behaviour, and capture performance. Motivated by this, we investigate the electrochemical CO₂ adsorption behaviour of activated carbon electrodes in a 1 M Na₂SO₄ electrolyte across a range of pH values, including



strongly acidic, neutral, and alkaline conditions. The reported pH values correspond to the initial pH measured prior to electrochemical testing, as the final pH during and after electrochemical testing could not be reliably determined. We combine this with quantitative solid-state nuclear magnetic resonance (ss-NMR) measurements of the electrode/electrolyte/ $^{13}\text{CO}_2$ system³⁰ (without charging) to probe CO_2 speciation within the electrolyte at varying pH. These results reveal that increasing the electrolyte pH results in higher rates of SSA capture, correlating with increased bicarbonate formation; in contrast, decreasing pH results in lower capacities and rates of SSA capture, as well as the absence of bicarbonate formation. Our results, therefore, reveal clear pH-dependent changes in speciation that influence capture performance, supporting the view that SSA is governed by ionic pathways or a pH-swing-driven mechanism.

Results

Effects of different electrolyte pH on CO_2 capture performance

To investigate the impacts of electrolyte pH on electrochemical CO_2 capture performance, we employed an activated carbon electrode (YP80F) and 1 M Na_2SO_4 electrolyte with different pH values as benchmark materials. We prepared acidic ($\text{pH}_{\text{initial}}$ 1.1), neutral ($\text{pH}_{\text{initial}}$ 7.0), and basic ($\text{pH}_{\text{initial}}$ 13.4) electrolytes, assembled a symmetric coin-cell supercapacitor (meaning mass-identical carbon electrodes) with a meshed top case. Starting from the initial electrolyte pH ($\text{pH}_{\text{initial}}$), the electrolyte pH inside the coin cell is expected to change as the system equilibrates (*e.g.* exposed to the experimental conditions of the SSA measurements). First, interactions between the electrolyte and the porous carbon electrodes modify $\text{pH}_{\text{initial}}$ as the electrolyte equilibrates with surface functional groups of the porous activated carbon and its point of zero charge (Fig. S9a).³¹ In addition, diffusion of CO_2 from a fixed reservoir into the electrolyte results in further acidification. Because the coin cell supercapacitors are a sealed system for the purpose of our CO_2 uptake measurements, direct *in situ* measurement of the final electrolyte pH (pH_{final}) is challenging. Instead, the pH was measured after opening coin cells after their exposure to experimental SSA conditions. Based on these measurements, the initially acidic electrolyte is estimated to be approximately 1.3, the initially neutral electrolyte 8.4, and the initially basic electrolyte 9.6. As this work focuses on the overall influence of electrolyte pH on SSA, pH values are reported with respect to the initial electrolyte pH ($\text{pH}_{\text{initial}}$) throughout the manuscript unless stated otherwise. The coin-cell type supercapacitor was introduced into a “gas cell” (Fig. 2a), which was custom-designed in our laboratory for the SSA work.^{17,20,25,26} Within the “gas cell”, the meshed coin-cell type supercapacitor is exposed to a pure CO_2 headspace, and any changes in pressure (from adsorption or desorption) are monitored using in-built pressure transducers. This setup allows simultaneous pressure recording while charging and discharging the supercapacitor at constant current (galvanostatic charge and discharge). In this work, we employ two different charging protocols, the negative and the positive charging mode. In the

negative charging mode, the gas-exposed electrode is charged negatively to -0.8 V, followed by a 5 minute voltage hold at -0.8 V before discharging the cell to 0.0 V. In the positive charging mode, the gas-facing electrode is charged to $+0.8$ V, held at $+0.8$ V for 5 minutes, and subsequently discharged to 0.0 V again. The negative or positive charging modes, therefore, refer to the polarisation of the gas-exposed electrode, identified as negative or positive, respectively. As the pressure transducers are not selective for monitoring CO_2 (over other gases), the overall pressure development inside the gas cells was carefully monitored to account for any continuous and irreversible pressure changes during charging and discharging of the supercapacitor. Parasitic side reactions (*e.g.*, water splitting) that would increase pressure are ruled out by the overall high coulombic efficiency (Fig. S1) and the lack of an irreversibly increasing baseline pressure (Fig. S2). In our systems, continuous pressure changes have been previously attributed to corrosion within the coin cells, especially at low current densities ($10\text{--}50\text{ mA g}^{-1}$).^{25,26} At higher current densities, the pressure baseline stabilises, enabling reliable determination of CO_2 uptake. Therefore, this work investigates the CO_2 uptake at high current densities (100, 150 and 300 mA g^{-1}).

To test the impact of different electrolyte pH on electrochemical CO_2 capture behaviour, we employed the negative charging mode to the assembled supercapacitor cells containing different electrolyte pH and exposed them to a pure CO_2 gas headspace. For all three electrolyte pH values, CO_2 capture is observed upon negative charging, visible by a decrease in pressure (Fig. 2b–d). In the positive charging mode, supercapacitors release CO_2 during charging, as indicated by an increase in pressure (Fig. S3). In essence, the supercapacitor cell captures CO_2 when the gas-exposed electrode receives electrons across all tested pH values of the electrolyte. These observations agree with previously conducted experiments employing different activated carbons as electrodes^{20,26} or other electrolytes.¹⁷

Excitingly, the pH of the electrolyte affects the magnitude of pressure changes observed across all measured pH values when the negative charging mode is employed. When we compare the acidic system (Fig. 2c) to the neutral benchmark system (Fig. 2b, $\Delta p \sim 5$ mbar), we see that the acidic system exhibits a smaller change in pressure ($\Delta p < 5$ mbar), suggesting that less CO_2 is captured. In contrast, the basic system (Fig. 2d) displays a higher pressure change ($\Delta p \sim 10$ mbar) than the neutral reference. To confirm this initially observed qualitative change, a comprehensive quantitative analysis of CO_2 capture and the involved speciation using ss-NMR spectroscopy will be presented in the following section of this work.

Quantitative ss-NMR reveals CO_2 -derived speciation within electrolyte-soaked electrodes

While the effects of solution pH on CO_2 uptake and speciation in bulk solution are very well-established, these properties are much more complex in electrode/electrolyte systems due to the possibility of nanoconfinement-induced oversolubility and changes to reactivity.^{30,32}



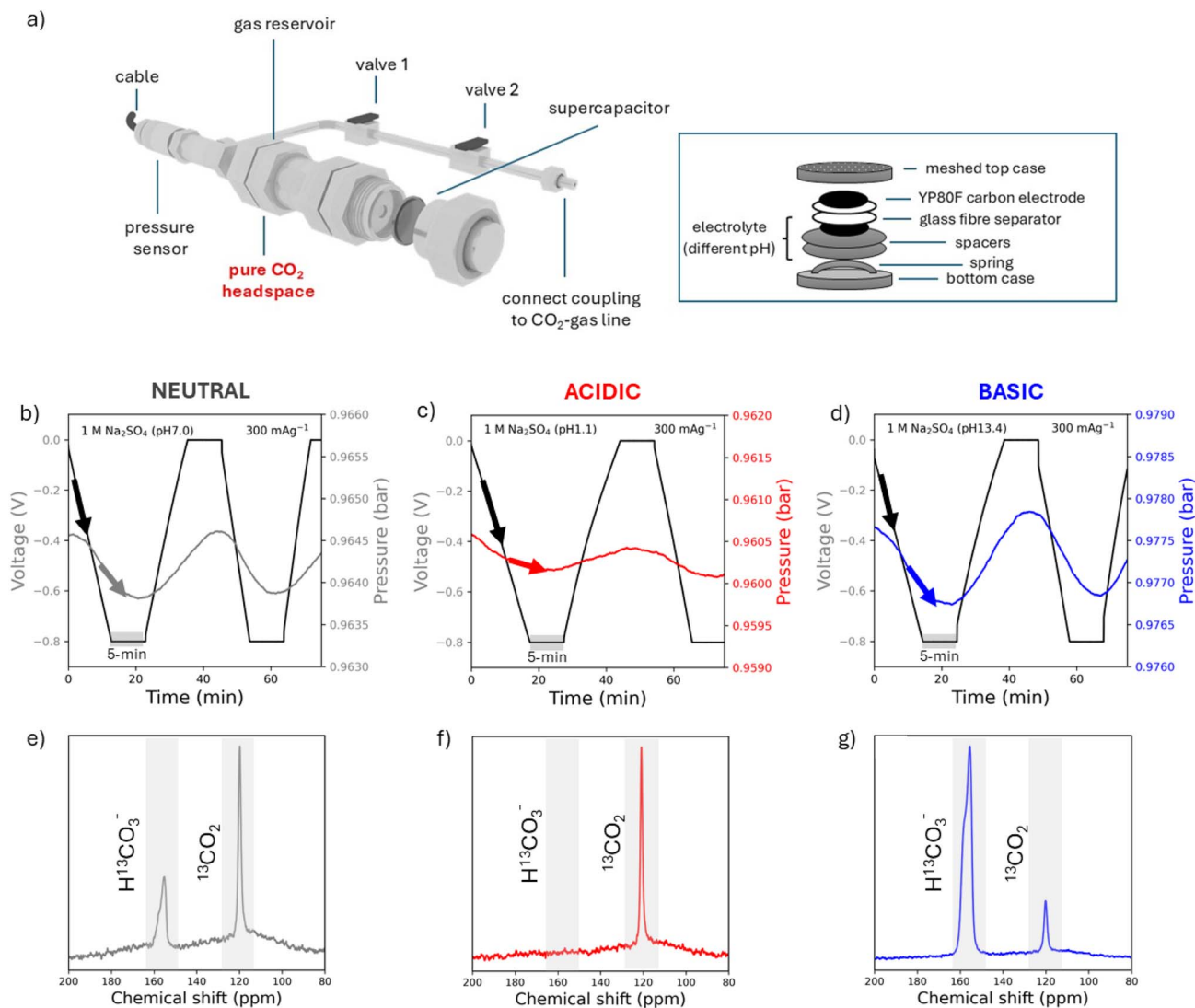


Fig. 2 CO₂ capture behaviour during negative charging mode for all measured electrolyte pH. (a) Experimental gas cell setup for electrochemical CO₂ sorption measurements and supercapacitor coin cell stacking sequence with meshed top case. Voltage-pressure curves for (b) neutral $pH_{\text{initial}} = 7.0$ (grey), (c) acidic $pH_{\text{initial}} = 1.1$ (red) and (d) basic $pH_{\text{initial}} = 13.4$ (blue) Na₂SO₄ electrolyte, with cells using YP80F electrodes and a pure CO₂ gas headspace. The coin-cell type supercapacitors were inserted into the gas cell and charged to -0.8 V, followed by a 5 min voltage hold and subsequent discharge to 0.0 V. ¹³C ss-NMR (9.4 T, 5 kHz MAS) measurements on electrolyte/electrode/¹³CO₂ systems to investigate the CO₂-derived speciation inside the (e) acidic (f) neutral and (g) basic electrolyte.

As stated previously, it is challenging to determine the pH_{final} of the electrolyte *in situ* without disassembly of the experimental setup. To explore how the change in electrolyte pH affects the CO₂ speciation in the activated carbon/electrolyte system, we therefore performed quantitative ss-NMR measurements of the electrolyte-soaked YP80F activated carbon thin film in a ¹³CO_{2(g)} dosed NMR-rotor, modelling the state of an SSA module without charging the cell. Our NMR experiment circumvents the challenges of direct pH_{final} measurements in the carbon-electrolyte system and allows us to directly probe the effects of pH_{initial} on SSA performance. In the ¹³C NMR spectrum of the neutral benchmark system (Fig. 2e), NMR resonances are observed for both CO₂ (at 120 ppm) and HCO₃⁻ (at 155 ppm). The 120 ppm peak was assigned to CO_{2(aq)} inside the activated carbon pores, which is shifted to a lower frequency from the literature value of

125–126 ppm for CO_{2(aq)}^{33–35} due to a nucleus-independent chemical shift (NICS) effect driven by confinement inside the activated carbon's pores.^{31,36} In-pore CO_{2(g)} is not believed to be present, based on comparison to a reference spectrum of dry YP80F dosed with ¹³CO_{2(g)} showing higher uptake and a different chemical shift in the dry sample (Fig. S4). Similarly, the peak at 155 ppm corresponds to HCO₃⁻(aq) inside the activated carbon pores, again shifted to a lower frequency from the literature value of 160–161 ppm by the NICS effect.^{35,37} Estimating the HCO₃⁻(aq):CO₃²⁻(aq) equilibrium *via* the chemical shift (after accounting for the NICS effect) indicates that there is negligible CO₃²⁻(aq) in the system.^{37,38} An additional shoulder peak is observed at 158 ppm, which likely reflects a HCO₃⁻(aq) exchange environment between the surface of the activated



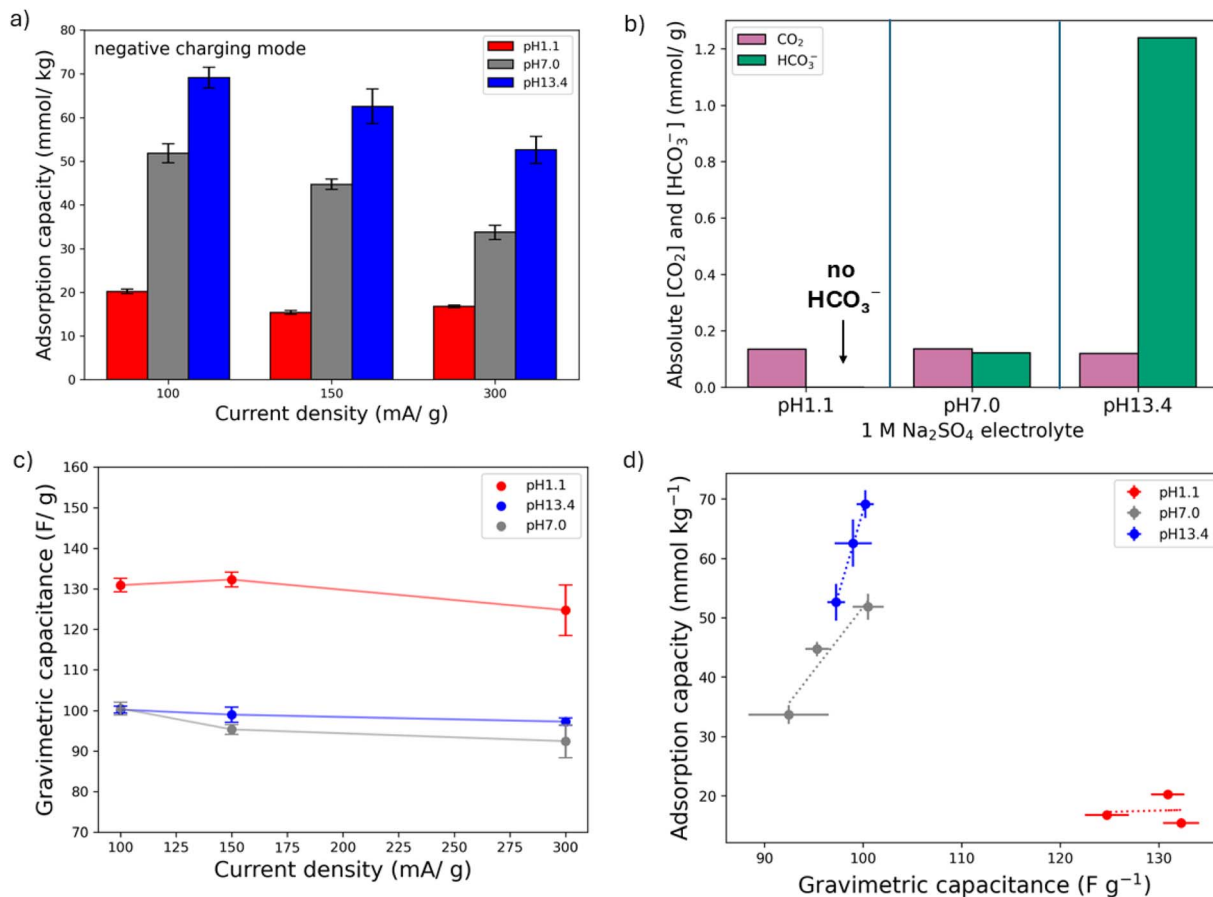


Fig. 3 (a) Adsorption capacities at different current densities for the YP80F/Na₂SO₄ system (acidic, neutral and basic electrolyte pH) in the negative charging mode. In these experiments, the supercapacitor was charged to -0.8 V, followed by a 5 min voltage hold and a discharge step to 0 V. Measured for three current densities (100, 150, 300 mA g⁻¹). Error bar calculated as the standard deviation from 5 cycles measured for every current density. For reproducibility purposes, two independent coin cells were assembled by the same researcher and measured in different gas cell setups (Fig. S5). (b) Gravimetric uptake of CO₂ and HCO₃⁻ in model uncharged SSA systems, calculated from NMR integrations. Uptake is normalised to the mass of activated carbon. The standard deviation divided by the mean was 5.6% for moles of CO₂ and 7.2% for moles of HCO₃⁻. (c) Gravimetric capacitances calculated from the discharge step of constant current measurements, excluding the voltage drops. (d) Correlations and linear fits between the gravimetric capacitance (F g⁻¹) and adsorption capacity (mmol kg⁻¹) for acidic, neutral, and basic electrolytes.

carbon and the electrolyte bulk.³⁹ Further discussion of peak assignment is contained inside the SI.

In the ¹³C NMR spectrum of the acidic electrolyte system (Fig. 2f), only the CO_{2(aq)} peak at 120 ppm is observed, indicating that HCO₃⁻ formation has been suppressed. Meanwhile, in the basic electrolyte system (Fig. 2g), formation of significantly more HCO₃⁻(aq) is observed compared to the neutral system. No change is observed in the HCO₃⁻(aq) peak's chemical shift, indicating that CO₃²⁻(aq) content remains negligible. In a bulk system, this corresponds to a pH below 10, compared to our starting point of 13.4 (based on CO₂ in pure water, Fig. S5). We attribute this to a combination of two effects: first, the activated carbon/1 M Na₂SO_{4(aq)} system has a pH_{pzc} of 9.1 (Fig. S9), indicating that contact with the carbon reduces the pH of the basic electrolyte; and second, dissolution of CO₂ further acidifies the solution.

Overall, quantitative ss-NMR experiments indicate that altering the electrolyte pH primarily affects HCO₃⁻ in the electrode/electrolyte system: acidic electrolyte suppresses

bicarbonate formation, while basic electrolyte favours it. In contrast, CO₂ uptake is less affected by pH.

In order to assess how the initial CO₂ speciation and uptake might explain the observed changes in SSA performance, we compared the “electrochemical CO₂ capacity” (Fig. 3a) and the “initial CO₂ and HCO₃⁻ uptake” in our uncharged model SSA electrodes (Fig. 3b), which were calculated from NMR peak integrations through comparison to quantitative ¹³C NMR of samples with known CO₂ uptake (see SI calculations). A large increase in electrochemical CO₂ capture capacity is observed as the electrolyte pH is increased, regardless of the current density (Fig. 3a). At the same time, electrolyte pH increases are accompanied by significant changes in initial CO₂ speciation and uptake measured by NMR spectroscopy (Fig. 3b). From NMR we observe that the initial amount of CO_{2(aq)} present is consistently 0.11–0.13 mmol g⁻¹ across all three systems, while the amount of bicarbonate varies from 0 mmol g⁻¹ in the acidic system to 1.2 mmol g⁻¹ in the basic system. The increase in “electrochemical CO₂ capacity” with increasing initial



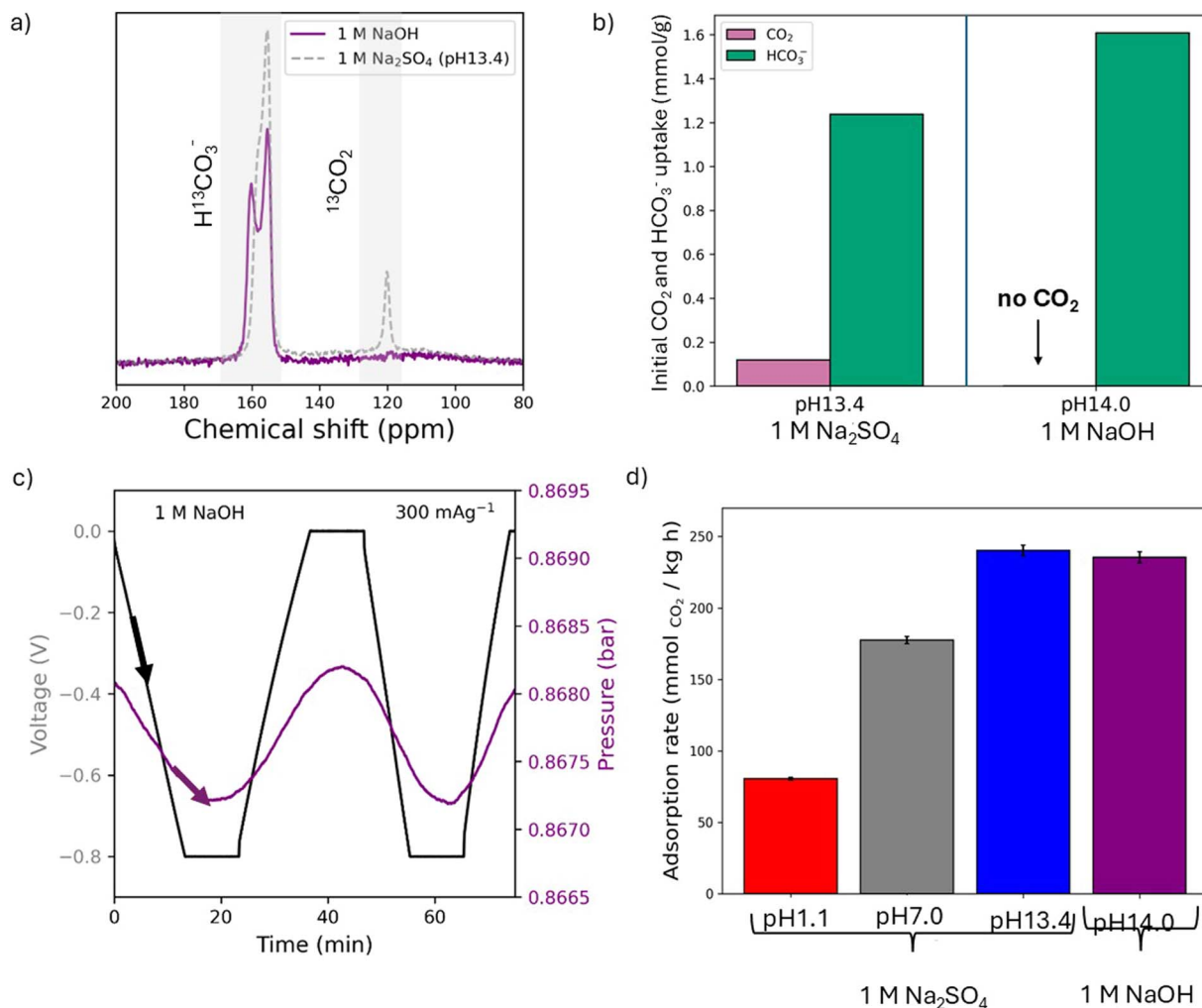


Fig. 4 (a) ^{13}C ss-NMR measurement on the YP80F/NaOH/ $^{13}\text{CO}_2$ system (dosed at 10 psi), with the analogous spectrum for basic (pH initial 13.4) 1 M $\text{Na}_2\text{SO}_{4(\text{aq})}$ electrolyte plotted for comparison in grey. (9.4 T ssNMR, 5 kHz MAS) (b) pressure voltage curves of SSA in 1 M NaOH in the negative charging mode. (c) Comparison between CO_2 and bicarbonate concentration for basic 1 M Na_2SO_4 and 1 M NaOH electrolyte. (d) Overall adsorption rates ($\text{mmol}_{\text{CO}_2} \text{ kg}^{-1} \text{ h}^{-1}$) for all the measured electrolyte systems in this work at 300 mA g^{-1} .

bicarbonate concentration suggests that bicarbonate plays a key role in CO_2 capture in aqueous based supercapacitors. With regards to the proposed mechanisms within the literature, the ionic liquid–solid mechanism as well as a pH-swing dominated mechanism become more likely as they are directly or indirectly influenced by bicarbonate concentration. Work is ongoing to further demonstrate this effect, and identify a mechanistic explanation of how increasing bicarbonate concentration leads to enhanced CO_2 capture in SSA systems. Interestingly, when performing an SSA experiment in 1 M NaHCO_3 (Fig. S10), similar CO_2 adsorption capacities were obtained compared to measurements obtained with basic 1 M Na_2SO_4 ($\text{pH}_{\text{initial}} = 13.4$) (Fig. S10). Both electrolytes exhibit comparable CO_2 adsorption performance, with no significant difference observed between them. This result indicates that the presence of bicarbonate ions plays a key role in the SSA mechanism, while variations in pH primarily influence the ionic speciation and concentration rather than fundamentally altering the adsorption behaviour. The similarity in performance between the two electrolytes

therefore supports the conclusion that bicarbonate-related equilibria, rather than pH alone, govern the observed CO_2 uptake behaviour.

Enhanced SSA uptake in basic systems is not explained by changes in capacitance

Throughout the literature, a positive correlation between the electrochemical capacitance of the activated carbon electrodes and adsorption capacity has been reported.^{21,22} However, in this work, the acidic system shows the highest electrochemical capacitance ($132.3 \pm 1.8 \text{ F g}^{-1}$ at 150 mA g^{-1}) while the basic and neutral systems show a similar capacitance around 100 F g^{-1} (Fig. 3c). The enhanced capacitance of the acidic system can be attributed to the activation of functional groups (e.g., quinones) on the activated carbon's surface at low pH, which facilitates faradaic charge storage. In contrast, higher pH levels diminish this effect and reduce capacitance.^{40–42} Our results do not follow the trend of higher electrochemical CO_2 capture for



electrodes with increased capacitance,^{21,22} as the acidic system shows the highest electrochemical capacitance but the smallest electrochemical CO₂ adsorption capacity (Fig. 3d). To further investigate this relationship, electrochemical CO₂ capacities were plotted against the gravimetric capacitances (Fig. 3d). Indeed, there is no linear correlation among the acidic, neutral, and basic systems visible, suggesting that the relationship between electrochemical CO₂ capacity and capacitance is not straightforward and is further influenced by CO₂ speciation within the electrolyte. In particular, recent studies have shown that the presence of molecular CO₂ in the electrolyte/the electric double layer can indeed modify electrochemical capacitance.^{27,43,44} Additionally, the presence of carbonate/bicarbonate may also contribute to a change in EDL structure/charge storage. Some supercapacitors using mixed ion electrolytes have been shown to have an increased capacitance due to a change in packing arrangements within the EDL.⁴⁵ Our results highlight the significant role of electrolyte speciation in influencing both the charge storage behaviour of supercapacitors and the capacity for CO₂ adsorption. Additionally, the overall similar charge storage kinetics observed for all electrolytes suggest that other physicochemical properties (*e.g.*, ionic conductivity) do not play a dominant role in the charging behaviour under the conditions studied. Further research is necessary to clarify the relationships between these parameters.

Basic electrolytes show higher CO₂ uptake rates

To further probe the role of electrolyte pH on SSA modules, and to control for potential competition between HCO₃⁻ and SO₄²⁻ electrosorption during charging, we also examined 1 M NaOH (pH_{initial} 14.0, pH_{final} 12.3) electrolyte. NMR measurements revealed that in the ¹³C₂O₂/YP80F/1 M NaOH system, bicarbonate is the sole CO₂-derived species present in the electrolyte (Fig. 4a), with no CO_{2(aq)} and minimal CO₃²⁻_(aq) present. Fig. 4b compares NMR-derived uptake and speciation inside the basic Na₂SO₄ and the 1 M NaOH electrolyte/electrode systems. Integration indicates the formation of approximately 30% more bicarbonate in the NaOH (pH_{initial} 14) system compared to the basic (pH_{initial} 13.4) Na₂SO₄ electrolyte, which is likely driven by the higher OH⁻ concentration prior to contact with CO₂. Across all current densities and charging modes, the CO₂ adsorption capacities for the NaOH electrolyte are slightly lower than those measured for the basic Na₂SO₄ electrolyte (pH_{initial} 13.4) (Fig. 3a). It is evident that the higher bicarbonate concentration does not further increase adsorption capacity, indicating the limitations of increasing the system's adsorption capacity and suggesting that the presence or absence of SO₄²⁻ has little effect on SSA activity.

Achieving high adsorption capacities during SSA is an important goal, but ultimately, high CO₂ adsorption rates are more relevant for the development and industrial scaling of SSA technology. Generally, higher adsorption rates can be achieved by applying current densities above 100 mA g⁻¹, and we therefore prioritised such current densities in our study. Previous research indicates that the SSA adsorption capacity significantly declines at higher current densities, primarily due to kinetic

limitations.^{20,24,26} Amongst all the investigated electrolytes in this study, the basic Na₂SO₄ electrolyte (pH_{initial} 13.4) shows the highest adsorption rates at the current density of 300 mA g⁻¹ (Fig. 4d). With 240 mmol_{CO₂} kg⁻¹ h⁻¹, the adsorption rate is 35% higher in comparison to the neutral electrolyte (177 mmol_{CO₂} kg⁻¹ h⁻¹, pH initial 7.0) and approximately three times higher than the acidic electrolyte (80 mmol_{CO₂} kg⁻¹ h⁻¹, pH_{initial} 1.1). It becomes evident that the basic electrolyte systems (1 M NaOH and pH_{initial} 13.4 Na₂SO₄) examined here demonstrate particularly strong performance at elevated current densities, suggesting that basic electrolytes (where bicarbonate species dominate) show improved kinetics.

Conclusion

By performing CO₂ capture in electrolytes with variable pH levels, we investigated the effects of pH on supercapacitive swing adsorption (SSA). Using quantitative NMR spectroscopy, we demonstrated that electrolyte pH influences CO₂ speciation in electrolyte-soaked electrodes. The NMR methodology allowed us to directly quantify CO₂-speciation within electrolyte-soaked electrodes and provides experimental confirmation of how these equilibria manifest in porous carbon environments across a range of different electrolyte pH values. We find that electrochemical CO₂ uptake occurs in both strongly basic and strongly acidic electrolytes (pH_{initial}), even in environments where certain dissolved CO₂ species are expected to be less prevalent. Basic systems containing only bicarbonate showed higher electrochemical adsorption rates than acidic systems that lacked bicarbonate. However, the presence of molecular CO₂ may also play a role in the mechanism, as the highest adsorption capacities were observed in a system containing both CO₂ and bicarbonate (specifically, a basic Na₂SO₄ electrolyte), rather than in the system with the highest bicarbonate concentration (1 M NaOH). These results suggest that electrochemical CO₂ capture by supercapacitors involves mixed contributions from both ionic and molecular liquid–solid mechanisms and can also be explained by a “pH-swing” mechanism.^{28,29} Additionally, we found that electrochemical CO₂ adsorption capacity does not correlate with electrochemical capacitance, highlighting the importance of CO₂ speciation in the electrolyte for better understanding the mechanisms of SSA. This study emphasises the critical role of CO₂ speciation in both the mechanism and the performance of SSA. Taken together, our observations suggest that the balance of CO₂-related species and the electrolyte pH can strongly influence electrochemical CO₂ capture performance in aqueous supercapacitor systems. Our work highlights the central role of electrolyte pH in SSA. While further studies are needed to resolve the underlying processes, this work provides new experimental evidence to guide the design of improved capture devices.

Materials and methods

Carbon electrode fabrication

Electrodes were prepared by mixing commercially available activated carbon YP80F (200 mg, Kuraray) with



polytetrafluoroethylene (PTFE) binder (17.5 mg, 60 wt% dispersion in H₂O, Sigma-Aldrich) in a 95 : 5 weight ratio. The carbon and the PTFE were dispersed in ethanol (*ca.* 5 mL, VWR Chemicals) and stirred by hand on a watch glass for 20 min until a jelly-like consistency was achieved. The resulting black material was kneaded with a spatula for 5 min, with ethanol droplets added from time to time to prevent it from drying out. The solid was placed on a glass sheet and rolled out to produce a free-standing carbon electrode (0.25 mm thickness). The electrode thin film was transferred onto aluminium foil and dried in a vacuum oven at 90 °C for 48 hours.

Electrolyte preparation

After initial preparation of neutral (pH_{initial} 7.0) 1 M Na₂SO₄ electrolyte, an acidic (pH_{initial} 1.1) electrolyte was prepared by the combination of 0.17 mL of 1 M H₂SO₄ with 0.2 mL of 1 M Na₂SO₄ electrolyte, and a basic (pH_{initial} 13.4) electrolyte was prepared by combination of 0.07 mL of 1 M NaOH with 0.2 mL of 1 M Na₂SO₄ electrolyte. Electrolyte pH was measured using a pH probe, calibrated using commercial buffers.

10 mL of 1 M NaHCO₃ electrolyte was prepared by dissolving 0.84 g of NaHCO₃ in a 10 mL volumetric flask and filling the flask to the mark with DI water. For the experiments, 0.2 mL of electrolyte was used to prepare the coin cell.

Meshed coin cell assembly

Two mass-identical carbon electrodes (0.5 inch diameter, 12–15 mg mass range) and glass fibre separators (5/8 inch diameter, GF/A Whatman) were cut with a steel punch. The meshed coin cell was assembled as follows from bottom to top: bottom case, conical spring, spacers (0.5 mm), bottom electrode, separators, 100 μL of electrolyte, gas-exposed electrode and meshed top case (SS316, CR2032, Cambridge Energy Solutions). The coin cell was sealed in a Compact Hydraulic Coin Cell Crimper (Cambridge Energy Solutions) at 80 kg cm⁻². The assembled coin cell was then placed inside the gas cell with the meshed side facing the gas reservoir (Fig. 1a).

Meshed coin cell disassembly and pH_{final} estimations

To estimate the pH_{final} of the electrolyte in our gas cells a new set of symmetric coin cell type supercapacitors were assembled using the electrolytes with different pH_{initials}. The mass of the carbon electrodes ranged between 10–12 mg and a total of 0.2 mL of electrolyte was added. The cells were sealed and exposed to a pure CO₂ gas reservoir (partial pressure between 0.9–1.1 bar) within the custom made gas cells for 12 h to establish the conditions of SSA measurements. The coin cells were then opened using a coin cell decrimping unit (Cambridge Energy Solutions), the electrolyte was collected from the separator and activated carbon electrodes and the pH_{final} was measured using a pH probe.

Carbon dioxide dosing

To dose the gas reservoir with CO₂ (99.80% purity, BOC), a custom gas manifold was used. The cell was exposed to a static

vacuum to avoid evaporation of the electrolyte by opening the two valves on the gas cell. The gas cell pressure dropped to approximately 0.4 bar. In a next step, the valve closest to the cell was closed and the gas manifold was dosed with CO₂ at 1.3 bar. Upon opening the valve to the cell, the CO₂ in the gas manifold mixes with the gas in the reservoir due to the reduced pressure in the gas cell. The valve was closed again and the manifold put back under dynamic vacuum. The dosing process was repeated for a total of 5 cycles to give a 98.7% CO₂ headspace assuming ideal gas mixing.

Pressure measurement

The gas adsorption and desorption was measured with a pressure transducer (PX309-030A5V, Omega). The noise of the pressure transducer is at the level of 0.1 mbar, with a signal to noise ratio of over 5, indicating a reasonable sensitivity of the pressure sensor. For both, the negative and the positive charging protocol, the pressure data was smoothed over 100 seconds. For gas uptake calculations from the pressure data, sudden pressure increases from opening the incubator ovens (temperature drop) were excluded from the analysis.

Electrochemical measurement

A potentiostat (VSP-3e and VMP-3e, Biologic) was used to measure galvanostatic charge and discharge (GCD) and cyclic voltammetry. The gas cell was allowed to reach 30 °C in an incubator oven (SciQuip Incu-80S) to maintain a constant temperature during the measurement. Then the supercapacitor was precycled by conducting 20 cyclic voltammetry cycles at a scan speed of 1 mVs⁻¹ within the voltage range of –0.8 V to +0.8 V to activate the electrode–electrolyte interface. In this work, negative and positive charging protocols were applied to conduct the SSA experiments. The supercapacitors were charged to –0.8 V at constant current, the cell voltage was held at –0.8 V for 5 min, then the supercapacitor was discharged back to 0 V again, and the cell voltage was held for another 5 min at 0 V. This protocol was also applied for the positive charging mode.

ss-NMR measurements

Solid-state NMR sample preparation and measurement was carried out per the method described previously in Coady *et al.* (2025),³⁰ with minor adjustments detailed below.

Activated carbon films were cut into small pieces, then an approximately 10 mg sample was weighed and placed in a vial. Electrolyte (either pH initial 1.1, pH initial 7.0, or pH initial 13.4 1 M Na₂SO_{4(aq)}, or 1 M NaOH_(aq)) was then added to achieve a 2 : 3 mass/volume ratio of activated carbon and electrolyte. The vial was sealed and left for 5 minutes to allow electrolyte to saturate the sample. Then, the electrolyte-soaked electrode was packed into a 3.2 mm rotor as quickly as possible to minimize evaporation of the solvent. Samples and vessels were weighed before and after addition of solvent and packing to quantify any loss of solvent due to evaporation.

Each sample was briefly evacuated for 1 minute under a static vacuum in a home-built gas manifold, as described



previously in Forse *et al.* 2018.⁴⁶ Samples were then dosed with ¹³CO_{2(g)} at a pressure of 0.7 bar for 30 minutes, before rotors were sealed while inside the gas manifold using a mechanical plunger.

The NMR experiments were carried out using a Bruker Avance Neo spectrometer in a Bruker 3.2 mm HXY triple resonance probe. For the measurements, a magnetic field strength of 9.4 T was applied, corresponding to a ¹H Larmor frequency of 400.1 MHz. All spectra were acquired with a 90° pulse-acquire sequence at an MAS speed of 5 kHz, at which speed we observe resolved spectra while avoiding excess frictional heating or centrifugation.^{47,48} The 90° pulse length was optimised for every sample. Recycle delays were set to >5 T₁ for the CO₂ and the HCO₃⁻ peaks for each sample to guarantee a quantitative measurement. T₁ was measured through inversion recovery experiments. The ¹³C NMR spectra were referenced relative to the ¹³C CH resonance of adamantane at 37.78 ppm as a secondary reference to TMS. NMR spectra were processed and integrated using the Topspin software and Python code. A full description of the data analysis procedure is described in the SI.

Point of zero charge measurements (PZC)

The point of zero charge (PZC) was performed using the pH drift method. For the measurement, 60 mg of cut activated carbon thin film was added to 500 μL of aqueous Na₂SO₄ electrolyte at different pH values. The carbon suspension was left overnight to reach equilibrium. The electrolyte pH was measured using a calibrated pH meter (Mettler Toledo). The PZC was determined graphically by the intercept between the pH sorption plateau and the line through the origin with a slope of 1 (equivalent to no ion adsorption).

Author contributions

A. C. F., Z. C. and Z. X. supervised and guided the project. All authors designed the research. S. E. W. prepared the electrode and electrolyte fabrication, device assembly, electrochemical CO₂ capture testing and data analysis. Z. C. conducted the solid-state NMR experiments and analysed the results. S. E. W. and Z. C. drafted the manuscript and all authors contributed to the manuscript revision.

Conflicts of interest

The authors declare no competing interests.

Data availability

All raw experimental data files are available in the Cambridge Research Repository, Apollo, with the identifier: <https://doi.org/10.17863/CAM.129151>.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ta10332k>.

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