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Moisture swing frequency response method for characterization of ion-transport kinetics of CO₂ adsorption

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ABSTRACT

Direct air capture of CO_2 (DAC) sufficiently mitigates atmospheric CO_2 to prevent the impacts of global warming of 1.5 °C above preindustrial levels. To overcome the challenges of the kinetics of sorbent under the ultra-low partial pressure (40 Pa) of DAC, the underlying mechanisms need to be constructed for better designs, simulations, and developments of the separation processes of carbon dioxide. Herein, a transient model based on the diffusion-reaction of ions at the molecular scale is developed for the moisture swing adsorption (MSA) process, disclosing the mechanism of mass transfer of multi-ions of sorbents. To compare the model with the experiment quantitatively, Fourier-transformed moisture-swing frequency response is applied to accurately measure the H₂O—CO₂ concentration response, ensuring a systematic approach for unknown kinetic parameters for the model. The results reveal that the gradient of water vapor causes a counter gradient of CO₂ concentration, generating the spontaneous transportation of CO₂ of the MSA membrane from one side to another. Specifically, the diffusion coefficient of HCO₃ drives the CO₂ adsorption process predominantly, where the diffusion coefficient of HCO₃ increases about ten times, leading to a nearly 12 times enhanced CO₂ separation rate accordingly. Notably, CO₂ adsorption kinetics can be stimulated by controlling specific ion conductivity in the moisture swing sorbent. With the enhancement of adsorption kinetics and low capital cost, the progress of CO₂ mitigation using Moisture Swing Adsorption can be achieved for direct air capture of CO₂.

1. Introduction

The continuously increasing anthropogenic activities account for a severe rise in CO₂ levels in the atmosphere [1,2]. In response to creating a sustainable development society, CO₂ Capture Utilization and Storage (CCUS) has been recognized with significant impacts on controlling global warming and leading to progressive transitions in the global sustainable energy scenarios. Complimenting emissions reductions, the emerging array of Negative Emission Technologies (NETs) at large scale can reach the target amount to be removed, i.e., at least 10 Gt of CO₂ removal by midcentury, according to the Intergovernmental Panel on Climate Change (IPCC) report [3–5].

Direct air capture (DAC) has been declared promising among the NETs by IPCC 1.5 °C special report [4,6,7]. Through decades of solid sorbents development ranging from alkaline metals to solid amines sorbents [8–11], the progress of the solid adsorbents facilitates the

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diffusion of molecules for functionalization and CO2 adsorption [12–15]. However, the porous structures inside DAC adsorbents limit the complete filling of pore channels, causing inhomogeneous surroundings, thereby impeding the diffusivity of molecules [16,17]. The adsorbents with homogeneous micropore structures, like bicarbonate and carbonate ions, have been exclusively caught attention. Given the fact that the CO2 capture capacity is reversely correlated with the temperature required for sorbent regeneration, T_{re} (temperature-swing): the inevitable demand of Tre over 100 °C restricts the flexibility of location for DAC deployments [18-20]. Quaternary ammonium (QA)-based materials step forward to solve energy and degradation issues using the moisture swing adsorption (MSA) regeneration method [21-24]. Driven by water evaporation energy, the quaternary ammonium-based ion exchange resin (QAER) can capture and release atmospheric CO₂ without external heat input. That's to say, QAER, as a moisture swing sorbent, can absorb CO_2 when it is dry and release CO_2 when wet [23,25]. On the basis of the moisture swing properties, a material capable of pumping

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Nomenclature		k _C Pi	the Henry constant of CO_2 the partial pressure of species <i>i</i>
	the one dimensional system given surface of the one dimensional system the discretize the spatial derivative the discretize the time derivative the discretization step of space the discretization step of time the amount of the species <i>i</i> per unit volume the nondimensionalized amount of species <i>i</i> the molar amount of carbon nondimensionalized molar amount of carbon total current applied to the <i>i</i> moving particle the diffusion current applied to the <i>i</i> moving particle the drift current applied to the <i>i</i> moving particle the charge of species <i>i</i> the equilibrium constant of reaction on the surface the equilibrium constant of reaction inside the sorbent the Henry constant of H ₂ O	$\begin{array}{c} \Pi_i \\ \Pi_i \\ k_p \\ p \\ D_i \\ C_i \\ \mu_i \\ \mathcal{F} \\ N_B \\ V \\ T \\ \lambda \\ Q_i \\ k_B \\ R \end{array}$	nondimensionalized partial pressure of species i the equilibrium constant of reaction inside the sorbent the power constant of reaction inside the sorbent the diffusion coefficient of the species i nondimensionalized diffusion coefficient of the species i the ion's mobility of the species i the Faraday constant the electrical force inside the material the number of sorbent particles in the chamber the potential of the electric field inside the material temperature the solution of the volume of the beads divided volume of the air the charge of the i moving particle the Boltzmann constant the gas constant

 CO_2 without any resource except water is established [25,26]. Therefore, optimizing the kinetics of sorbent for the efficient MSA process can facilitate the cost- and energy-effective deployment of DAC of CO_2 .

The ultra-dilute partial pressure of CO_2 (400 ppm) in ambient air obstacles high efficiency and rapid kinetics of DAC [25]. The adsorption kinetics research consists of physical relations of diffusion-reaction, mass transfer, and ions transport process, in which the intrinsic transport coefficients include experimental measurements and data analysis process. By using amine-loaded materials [27,28] and ionic functionalized polymers [29,30] for the mass transfer process in sorbents, significant development is reported in the quasi-steady-state CO2 adsorption kinetics models, such as the shrinkage core model (SCM) [31, 32], progressive conversion model (PCM) [33] and homogeneous solid diffusion models (HSDM) [34]. These models have a significant role in revealing the limiting step for adsorption and characterizing the parameters of mass transfer, such as diffusion coefficients in the bulk environment, chemical reaction rate constants, and activation energies of each reaction. The quasi-steady-state kinetic model requires control of the boundary conditions, parameters in the environmental experiment, and the restriction of mass transfer of multiple components in moisture swing adsorption of CO₂, such as CO₂, H₂O, and multi-ions [1,25,35]. Thus, a transient model based on the kinetic relationships for each ion transfer can better describe the coupling mass transfer process with multiple components [36-38]. Developing a transient mass transfer model with partial differential equations (PDEs) can function the coupled mass transfer mechanism [39,40] associated with Fourier-Transform, which transforms the second-order time-domain PDEs into the frequency-domain ordinary differential equations (ODEs) [41,42]. The analysis of its series value facilitates the preliminary results, such as phase difference and amplitude in the frequency domain, and thus, simultaneously acquires the parameters of mass transfer and equilibrium, leading to fast searching, high precision, and easy operation processing.

Herein, we have developed a novel moisture-swing frequency response method from the atomic scale to the continuum scale to characterize the transportation of ions, water, and CO_2 inside a quaternary ammonium-based resin for CO_2 adsorption. Specifically, a transient model of the mass transfer process with the diffusion-reaction of ions in a polymer is established in the manuscript. At the same time, a homogeneous membrane model is transformed from it to an infinite surface made of quaternary ammonium-based ion exchange resin. To ensure the accuracy of the developed theoretical model, a Fouriertransformed moisture-swing frequency response (MSFR) experimental setup is established to collect the experimental data, which is further compared to the model using the deep learning algorithms. The periodic fluctuations in water vapor determined the working range for the model. By combing the numerical and experimental methods, we reveal the inhibited mechanism of multi-ion transport inside the CO₂ sorption process for moisture swing sorbents.

2. Materials and methods

2.1. Multi-ion transport model with a single particle sorbent

To present the general equations which describe the behavior of the multi-ion transport process for CO_2 adsorption, we consider the process that happened inside a single particle CO_2 sorbent with a given shape and a given surface $\partial \phi$ as shown in Fig. 1. Hence, the model illustrates the function of the CO_2 sorbent, which is assumed as a homogeneous spherical and symmetrical bead, capturing and releasing CO_2 through



stand for the one-dimensional system

Fig. 1. Illustration of the multi-ion transport process. Inside the sorbent, the species of H_2O , CO_2 , HCO_3^- , and CO_3^{2-} follow the diffusion-reaction.

the MSA process. The backbone of the polymer sorbent is polystyrene, which the quaternary ammonium cation is attached to it by a covalent bond. The counter anion $\text{CO}_3^{2^-}$ interacts with the cation through an ionic bond, which is mobile in the polymer. On the interface, the water and CO_2 molecules dissolve into the MSA sorbent, reacting with $\text{CO}_3^{2^-}$ to produce HCO_3^{-} .

A one-dimensional system ϕ is considered in the *R* coordinates with the given direction $\partial \phi$. The surface of the bead divides the space into two distinct regions: (1) Constant moisture air with a flux condition (Neumann condition), in which the flux-CO₂ adsorption at the center of the bead is null; (2) Wet air with constant moisture (Dirichlet condition). The system is at chemical equilibrium at any time, i.e., reactions occur extremely fast than any other transports phenomenon. As the surface is in contact with the outside environments and inner side of the material, resulting in two reactions:

On the surface :
$$OH^- + CO_2 \stackrel{\kappa_1}{\leftrightarrow} HCO_3^-$$
 (1)

Inside the sorbent :
$$HCO_3^- + OH^- \stackrel{K_2}{\leftrightarrow} + CO_3^{2-} + H_2O$$
 (2)

where K_1 and K_2 as the equilibrium constant of reactions on the surface and inside the sorbent, respectively.

The system undergoes continuous pressure and temperature, making it uniform, spherical, independent, and indistinguishable at any time. In addition, the system with a multi-ion charge follows the electroneutrality rule as follows:

$$2n_{\rm CO_2^{2-}} + n_{\rm HCO_3^{-}} + n_{\rm OH^{-}} = n_+ = \text{constant}$$
(3)

where n_i refers to the number of ions inside the sorbent.

Gas-solid interface: The relation between the partial pressure of CO_2 and H_2O from outside environments and the concentration on the surface $\partial \phi$ is verified through Henry's law. The equations can be written as,

$$P_{\rm H_2O}(t) = k_H(n_{\rm CO_2}(R_{\partial\Omega}, t)) \cdot n_{\rm H_2O}(R_{\partial\Omega}, t)$$
(4)

$$P_{\rm CO_2}(t) = k_C(n_{\rm H_2O}(R_{\partial\Omega}, t)) \cdot n_{\rm CO_2}(R_{\partial\Omega}, t)$$
(5)

where $\forall (R_{\partial\Omega}, t) \in \partial\Phi \times \mathbb{R}_+$ refers to the space of the sorbent; k_H and P_{H_2O} refer to the Henry constant and partial pressure of H₂O, k_C and P_{CO_2} refer to the Henry constant and partial pressure of CO₂.

Chemical reactions: The main chemical reactions in the system occur either at or out of equilibrium. On the surface of the single particle, hydroxide reacts with CO_2 in the surrounding atmosphere and forms a bicarbonate ion; it transforms into anions through HCO_3^- and CO_3^{2-} in the interior of the membrane. The equilibrium constant of the second reaction K_2 depends on the local humidity. At equilibrium, it can be written as:

$$K_{1} = \frac{k_{1}}{k_{-1}} = \frac{n_{\text{HCO}_{3}}}{n_{\text{OH}^{-}} \cdot P_{\text{CO}_{2}}}$$
(6)

$$K_2(n_{\rm H_2O}) = \frac{k_2}{k_{-2}} = \frac{n_{\rm CO_3^2} \cdot n_{\rm H_2O}}{n_{\rm OH} \cdot n_{\rm HCO_3^-}} = k_{\rm p} \cdot (n_{\rm H_2O})^{\rm p}$$
(7)

where k_p and p are the forward and reverse rate coefficients, respectively. All the n_i depend on $(r, t) \in \Phi \times \mathbb{R}_+$.

Mass diffusion: The migration process creates diffusive fluxes of the moving species, resulting in two components: the diffusion current and the drift current. Fick's first law relates the diffusive flux to the concentration. The drift current can be transformed using the Einstein Relation [40]:

$$D_i = \mu_i k_B T \tag{8}$$

where *i* refers to any of the four species, D_i is the diffusion coefficient (depends on quantities and time), μ_i refers to *i* ion's mobility, k_B refers to the Boltzmann constant, and *T* is temperature.

Hence, the drift current can be written as,

$$J_{i}^{drif} = n_{i}\mu_{i}F = -n_{i}\frac{D_{i}\mathscr{T}z_{i}}{RT}\nabla V$$
⁽⁹⁾

where the electrical force F equals the charge of the ion times the electric field, \mathcal{T} refers to the Faraday constant, R is the gas constant, and V is the potential of the electric field.

The Nernst-Planck equation expresses the diffusive fluxes of the moving species, which can be written as,

$$J_i = J_i^{diffusion} + J_i^{drift} = -D_i \nabla n_i - \frac{z_i \mathscr{F}}{RT} D_i n_i \nabla \mathbf{V}$$
(10)

where *i* refers to any of the four species, J_i is the total diffusive flux for multi-species, $J_i^{\text{diffusion}}$ refers to the diffusion current, J_i^{drift} refers to the drift current, and z_i is the charge of species.

Under the electroneutrality condition, the Nernst-Planck equation can be transformed by multiplying \mathscr{F}_{z_i} and sum for all species *i*. Hence, we get the electrical current due to the charged-species diffusion as follows:

$$J_{tot} = -F \sum_{i=1}^{4} z_i D_i \nabla n_i - \frac{F^2}{RT} \sum_{i=1}^{4} z_i^2 D_i n_i \nabla V = 0$$
(11)

where J_{tot} refers to the electrical current due to the diffusion currents for the charged-species, which is OH⁻, HCO₃⁻, CO₃²⁻, and H₂O.

3. Methodology of multi-ion transport model

3.1. Numerical analysis method

Nondimensionalization: In order to simplify and clarify the theoretical model, the numerical analysis method is shown in Fig. 2. With the nondimensionalization of the model, apparent parameters, which are linked to others, are eliminated to allow intrinsic quantities and scales to emerge. Independent from units, this can be analyzed as a set of PDEs coupled by a non-linear term [43]. Considering the differential equations are parabolic, it gives the uniqueness and stability of the solutions.



Fig. 2. Theoretical analysis of MSA homogeneous membrane.

However, the involvement of four species makes the problem far more complicated. The temporary and steady regimes in spatially discretized grids can be written as follows:

$$\frac{\partial n_i}{\partial t} = D_i \frac{\partial^2 n_i}{\partial x^2} - c \frac{\partial n_i}{\partial x} - f(n_1, n_2, n_3, n_4)$$
(12)

where $D_i \frac{\partial^2 N_i}{\partial \gamma^2}$ represents diffusion term, $c \frac{\partial n_i}{\partial x}$ is the drift term, and $\pm f(n_1, n_2, n_3, n_4)$ is the chemical term. In drift terms, c is a constant even though the electrical field depends on n_i .

Discretization: In order to compute all the parameters of the model, a discretization method is applied, specifically for all the spatial and temporal derivative terms. With a finite difference approximation to discretize the spatial and time derivatives, initially, the whole experimental domain (*R*-radius membrane & t_{tot} -time experiments) is divided into finite grids, as shown in Fig. 3. In this scheme, the first derivative of time is approximated by:

$$\frac{\partial N_i}{\partial t}(r_k, t_m) = \frac{N_i(r_k, t_{m+1}) - N_i(r_k, t_m)}{\Delta t}$$
(13)

The space derivatives are described as follows:

$$\frac{\partial N_i}{\partial r}(r_k, t_m) = \frac{N_i(r_{k+1}, t_m) - N_i(r_{k-1}, t_m)}{2\Delta r}$$
(14)

$$\frac{\partial N_i}{\partial r^2}(r_k, t_m) = \frac{N_i(r_{k+1}, t_m) - 2N_i(r_k, t_m) + N_i(r_{k-1}, t_m)}{\Delta r^2}$$
(15)

Nevertheless, the stability condition of Forward Time Centered Space (FTCS) method is conditionally given by the Courant–Friedrichs–Lewy condition, i.e., $D\frac{\Delta T}{\Delta \gamma^2} \leq \frac{1}{2}$ [44]. As the described scheme is not a simple diffusion equation, a similar condition with the water's diffusion coefficient is needed, which is the biggest to obtain stable solutions [45].

This model is undoable analytically; the parameters are calibrated to compare $P_{CO_2}^{th}$ (theoretical pressure from the model) with $P_{CO_2}^{exp}$ (actual pressure from the experiments) by imposing a periodic water vapor signal $P_{H_2O}(t)$ and then varying the parameters until the theoretical results are equivalent to experimental ones. In fact, the ions' concentrations inside the beads are unattainable by experimental mapping in real-time. The data accessed by experiments are P_{H_2O} , P_{CO_2} , P_{system} , and



Fig. 3. The space-time grid discretized using the FTCS method. This grid represents a finite discretization of this model where space is divided into $K\Delta r$ and time into $M\Delta t$.

potentially the weight of the sample. The relevant partial pressures require to be measured in a closed system, leading to implementation in the computer model.

During the experiments, the total amount of carbon in the system, $n_{molar}^{carbon}(t)$, remains constant. To start with, working back with the dimensionalized units and with first-order approximations, the total amount of carbon in the system can be written as follows:

$$n_{carbon}^{molar}(t) = \sum_{k=1}^{K} \left(\left(\frac{n_{HCO_{3}^{-}}(r_{k+1},t) + n_{HCO_{3}^{-}}(r_{k},t)}{2} + \frac{n_{CO_{3}^{2-}}(r_{k+1},t) + n_{CO_{3}^{2-}}(r_{k},t)}{2} \right) \cdot 4\pi N_{B} r_{k}^{2} \Delta r \right) + \infty \frac{P_{CO_{2}}}{RT}(t) \cdot V_{air}$$
(16)

In the meantime, define λ as the solution of the volume of the beads V_{beads} divided volume of the air in the chamber V_{air} . Therefore, using the carbon conservation between the times t and $t + \Delta t$, the CO_2 partial pressure, Π_{CO_2} , can be calculated as follows:

$$\Pi_{CO_{2}}(t + \Delta t) = \Pi_{CO_{2}}(t) - 3\lambda \cdot \Delta r \cdot \sum_{k=1}^{K} \left(\left(\frac{\Delta N_{HCO_{3}^{-}}(r_{k+1}, t_{m}) + \Delta N_{HCO_{3}^{-}}(r_{k}, t_{m})}{2} + \frac{\Delta N_{CO_{3}^{2-}}(r_{k+1}, t_{m}) + \Delta N_{CO_{3}^{2-}}(r_{k}, t_{m})}{2} \right) \cdot r_{k}^{2} \right)$$
(17)

$$\Delta N_{HCO_{3}^{-}}(r_{k}, t_{m}) = N_{HCO_{3}^{-}}(r_{k}, t_{m} + \Delta t) - N_{HCO_{3}^{-}}(r_{k}, t_{m})$$
(18)

$$\Delta N_{CO_3^{2-}}(r_k, t_m) = N_{CO_3^{2-}}(r_k, t_m + \Delta t) - N_{CO_3^{2-}}(r_k, t_m)$$
(19)

where *r* and *t* refer to the discretize the spatial and time derivatives, *k* and *m* refer to the discretization step of space and time, Π_{CO_2} refers to the CO_2 partial pressure, λ refers to the solution of the volume of the beads divided volume of the air.

3.2. Data analysis by fast Fourier transform

The objective is to compute $P_{CO2}(r,t)$ and compare its evolution to a similar actual experiment, implying that the parameters are adjusted to obtain the best fit experimental data. Some fixed parameters can be experimentally estimated, while others are optimized according to the simulation results.

Using a Fast Fourier Transform (FFT), the amplitude and phase of the output P_{CO2} signal are compared at relevant frequencies. The comparison of the phase at the fundamental frequency and the first harmonic gives similar results. Indeed, both experimental and simulated results have a phase around. It provides sinusoidal waves of P_{H2O} and P_{CO2} in the temporal domain, then FFT is applied to transform the data to the frequency domain. For a linear system stimulated by a single driver, $\Delta P_{\text{H2O}} = A \sin(\omega t)$, and thus, the concentration of CO₂ can be represented by the following equation:

$$\Delta P_{CO_2} = A\sin(\omega t) + B\cos(\omega t) \tag{20}$$

where ωt is the phase of the signal.

The values of *A* and *B* depend on the peaks obtained from FFT. If the output of FFT exhibits noise, it is essential to smooth them out using a Gaussian. It is given by the formula:

$$v(n) = e^{\left((-1/2)\left(a_{\overline{(N-1)/2}}^{n}\right)\right)} = e^{\left(-n^{2}/2\sigma^{2}\right)}$$
(21)

3.3. Conjugate gradient with random walk method for global optimization algorithm

The conjugate gradient optimization method is employed for the numerical value of PDEs. The algorithm finds the minimum of a function through a number of variables. The steepest-descent method is a minimization algorithm, which is generally used to optimize a sparse range of data; the conjugate gradient is more efficient than the steepestdescent method. These optimization algorithms mentioned before are iterative methods to solve an extensive system of linear equations.

Considering an N-dimensional point P with the value of a function f (P) and its gradient of, the conjugate gradient of the function is given by the quadratic equations:

$$f(\vec{x}) = \frac{1}{2}\vec{x}^{T}A\vec{x} - \vec{b}^{T}\vec{x} + c$$
(22)

$$\nabla f(\vec{x}) = A\vec{x} - \vec{b} \tag{23}$$

Hence,

$$\vec{d_k} = -\nabla f\left(\vec{x}_{k-1}\right) = \vec{b} - A\vec{x}_{k-1}$$
(24)

$$\alpha_{k} = \frac{\overrightarrow{d_{k}}^{T} \overrightarrow{d_{k}}}{\overrightarrow{d_{k}}^{T} A \overrightarrow{d_{k}}}, \quad \overrightarrow{x}_{k} = \overrightarrow{x}_{k-1} + \alpha_{k} \overrightarrow{d_{k}}$$
(25)

Therefore, the convergence property of the conjugate gradient method is typically an iterative method, where the CG method monotonically improves approximations \vec{x}_k to the exact solution and may reach the required tolerance after a relatively small number of iterations. Thus, the convergence preconditioning is commonly used as $\vec{u}^T A \vec{v} = 0$, and the calculating time step is limited to less than 10^4 time in the employed algorithms.

In order to find the minimum of the function, a random walk gradient-descent method is suitable for the initial value. The initial value x is known in the early stage; however, the gradient descent search range is small; the range of x in each dimension can infer that the function is likely to fluctuate sharply and have multiple minimum points. By the gradient-descent method, a function is expected to fall into the local optimum. Thus, to change the initial value, the random numbers are introduced with two requirements. First, the random number cannot be too small, which too small lies in the local optimal range; second, the random number cannot be too large, where the range may cross the boundary. Thus, it needs to double the difference to select the random number range: the final value and initial value of the gradient-descent. Therefore, the objective function undergoes iteration until the optimal solution is obtained.

4. Experimental

4.1. Experimental setup for moisture-swing frequency method

The frequency response (FR) experiment employs a periodic (typically sinusoidal) perturbation of a system [31], and the frequency of perturbation is introduced as an additional degree of freedom to distinguish similar mass transfer mechanisms [46]. Since the adsorption capacity is directly correlated with the partial pressure of adsorbate, the pressure-swing frequency response (PSFR) and concentration-swing frequency response (CSFR) techniques have been widely adopted to measure gas diffusion in the sorbent. In contrast, a novel MSFR technique is developed in this paper if the adsorption capacity of a specific sorbent is strongly affected by other factors. The experimental schematic diagram of MSFR is shown in Fig. 4.

The experimental setup consists of a closed-loop system in which P_{H2O} is controlled and can be precisely measured along with P_{CO2} . The obtained results are compared with the numerical simulation. The experimental setup includes a sample chamber, infrared gas analyzer (IRGA, LI-COR840A), pump, Peltier element, and an airflow controller. The QA-based resin [25] with a diameter range of 0.3–0.6 nm for IER and charge density of 1.3 mmol g^{-1} is contained in the sample chamber and is arranged in such a way that the individual beads are all independent and do not touch each other. The exchange capacity of QA resin is about 1.17 mmol g^{-1} . The IRGA is used to analyze the concentration of CO₂, H₂O, and pressure inside the system. The pump forces air to circulate/counterbalance the pressure drops inside the entire system. The Peltier element is a device that controls the moisture in the sample chamber and imposes the correct value for P_{H2O} in the system. Its function is basically based on the thermoelectric effect (Peltier effect), which is a chamber with a water reservoir that is either cooled or heated according to the voltage sign. The airflow controller controls the flow of air into the chamber. In order to monitor our system along with control over every parameter, the loop is connected to a computer to manage through LabVIEW by a visual programming interface.

4.2. Water diffusion coefficient measurement

In order to temporally link our model with MSFR experiments, the



Fig. 4. Experimental schematic diagram of MSFR. The apparatus mainly contained a sample chamber, infrared gas analyzer, humidity swing controller, PID controller, airflow controller, valves, and pumps.



Fig. 5. Weight evolution of the particles with change in $P_{\rm H2O}$.

 $\rm P_{H2O}$ of the sample chamber is controlled by using a Proportional-Integral-Derivative (PID) controller to measure any error between $P_{\rm H2O}$ measured and $P_{\rm H2O}^{\rm setpoint}$. The Peltier element received this correction and transformed to the current, which drives the temperature to optimize the moisture in the system. Thus, it is achieved to impose periodic setpoint values for humidity inside the system. In addition, it is necessary to know the model time scale given by $D_{\rm H2O}$ with conducting a water adsorption experiment to obtain the diffusivity of water. With a step in $P_{\rm H2O}$ and the corresponding characteristic time of the weight, the response can evaluate $D_{\rm H2O}$ by data fitting. As shown in Fig. 5, the blue dots are the experimental data points. The black line is the first exponential approximation, and the red one is the numerical simulation of the diffusion model. By calculating, the value of $D_{\rm H2O}$ is $4.2 \times 10^{-11} \, {\rm m}^2/{\rm S}$.

4.3. Multi-ion transport model calibration with experiment

The comparison of the shape and amplitude between the actual experiments and the corresponding numerical simulations is presented in Fig. 6, as obtained by four sine functions with nearly close frequencies. It presents the system with a single frequency at a time and lets the system reach its equilibrium in between.

By observing from Fig. 6, an apparent offset, which is almost similar between the simulation and experiment, at amplified modeled signal is noticed with high frequencies, as previously mentioned. The input signal for $P_{\rm H2O}$ starts with 20 min-period sine. Every six periods, it switches to a new signal whose period is calculated by adding additional minutes with respect to the previous period. Starting at $P_{\rm CO2} = 400$ ppm, an offset is observed due to the non-linear behavior of the beads. Indeed, both responses oscillate around a higher value, which is 700 ppm for the experimental response and 650 ppm for the numerical response. In addition, a low-frequency oscillation was noticed in both cases, even though it is emphasized in simulated results. Thus, the theoretical amplitude could be more perfectly relevant, especially at relatively high or low frequencies.



Fig. 6. P_{H2O} excitation signal and corresponding experimental and modeled P_{CO2} response. P_{H2O} signal consists of four different wave trains with different frequencies. The numerical response (blue line) lies in the middle, and the experimental response (red line) displays at the top of the figure.

Table 1

Fitting values of unknown parameters.

Parameters	Initial values employed in the model	Best fitting values with experiments
D _{H2O}	4.20×10^{-11}	4.20×10^{-11}
$D_{\rm OH-}$	3.20×10^{-12}	$3.10 imes10^{-12}$
$D_{ m HCO3-}$	$6.30 imes10^{-12}$	$6.60 imes10^{-12}$
$D_{\rm CO32-}$	$5.10 imes10^{-12}$	4.90×10^{-12}
Ka	$2.10 imes10^{-5}$	$2.10 imes10^{-5}$
K _C	$8.70 imes10^{-3}$	$8.60 imes10^{-3}$
K_1	$4.00 imes 10^8$	$4.10 imes 10^8$
$k_{ m p}$	$5.10 imes10^{-12}$	$5.30 imes10^{-12}$
р	9.50	9.50

5. Results and discussions

5.1. Parameters fitting by Fourier analysis

As shown in Table 1, humidity impacts the kinetic parameters of CO_2 adsorption. As humidity increases, more water is dissolved into the polymer, blocking the gas diffusion of CO_2 in a porous structure. The diffusion coefficient of CO_2 (D_{CO2}) decreases with high humidity around the polymer. Meanwhile, the increased water vapor weakens the interactions between cation and counter anions, accelerating the transfer process of counter anions. Consequently, the value of diffusion

coefficients of carbonate and bicarbonate (D_{CO3}^{2-} and D_{HCO3}^{-}) is stimulated with increasing humidity in the environment. The difference between experimental data and 1D numerical result is represented by the delay time, which can be calculated by the phase difference of P_{CO2} based on the variance formula, as shown in Fig. 7b, in which the error is calculated by dividing the difference between experimental data and numerical result by experimental data:

$$S^{2} = \frac{\sum_{i=1}^{i=4} (x_{i} - \bar{x})^{2}}{n-1}$$
(26)

Table 2

Fitting results of unknown parameters in the simulation of the membrane under different absolute humidity.

Parameters	10 ppt*	15 ppt	20 ppt
D_{H2O} D_{OH} D_{HCO3} D_{CO3}^{2} K_{H} K_{C}	$\begin{array}{c} 4.2 \times 10^{-11} \text{ m}^2/\text{s} \\ 4.9 \times 10^{-11} \text{ m}^2/\text{s} \\ 4.1 \times 10^{-12} \text{ m}^2/\text{s} \\ 4.0 \times 10^{-12} \text{ m}^2/\text{s} \\ 2.1 \times 10^{-5} \\ 4.7 \times 10^{-3} \\ 5.9 \times 10^{-12} \end{array}$	$\begin{array}{c} 4.2 \times 10^{-11} \text{ m}^2/\text{s} \\ 4.4 \times 10^{-11} \text{ m}^2/\text{s} \\ 6.6 \times 10^{-12} \text{ m}^2/\text{s} \\ 5.0 \times 10^{-12} \text{ m}^2/\text{s} \\ 2.1 \times 10^{-5} \\ 8.6 \times 10^{-3} \\ 6.1 \times 10^{-12} \end{array}$	$\begin{array}{c} 4.2 \times 10^{-11} \text{ m}^2/\text{s} \\ 4.1 \times 10^{-11} \text{ m}^2/\text{s} \\ 8.2 \times 10^{-12} \text{ m}^2/\text{s} \\ 6.4 \times 10^{-12} \text{ m}^2/\text{s} \\ 2.1 \times 10^{-5} \\ 1.2 \times 10^{-2} \\ 5.0 \times 10^{-12} \end{array}$
κ_p p	5.3 × 10 9.5	9.5	5.2 × 10 9.5

* ppt shorts for parts per thousand, which defines the amount of water vapor in the air.



Fig. 7. Optimization of experiment and simulation with algorithms. (a) FFT analysis of P_{CO2} phase spectrum: Top—experimental response, Bottom—simulation response, (b) Delay time of P_{CO2} phase difference for experiment and simulation, (c) Algorithm by conjugate gradient with random walk method, and (d) Optimization minimum results by Global Optimization Algorithm. The direction of x, y, and z represents the diffusion coefficient of the three anions (OH⁻/HCO₃⁻/CO₃²⁻), and the color represents the value of the objective function to be sought: more red color means closer to the experimental value.



Fig. 8. Scheme of CO₂ pump with multi-ion transport inside the membrane.

Where S^2 represents the variance value of the difference between experimental data and numerical result, x_i each represent the experimental data from the four periods, \bar{x} is the numerical result. From Fig. 7d, it represents the four-dimensional data point and the path of gradient descent. Since the hydrophilicity of CO_3^{2-} is greater than that of HCO₃, the variation of the diffusion coefficient of carbonate D_{CO3}^2 is higher than that of bicarbonate D_{HCO3}^- . Table 2 indicates that the amount of CO₂ dissolved in the polymer decreases as the humidity increases. Generally, high humidity accelerates the CO₂ adsorption process¹⁸, as most carbon inside the particles is diffused as ions instead of CO₂.

5.2. Multi-ion transport model of the homogeneous membrane sorbent

On the basis of moisture swing properties, a membrane capable of pumping CO₂ without any resource except water is established. The hypothesis and physicochemical behavior of the model consisting of homogeneous membrane sorbent is similar to a single particle sorbent, as the cations inside the beads, being quaternary ammonium ions, are immobile. The anions in the forms of OH⁻/HCO₃⁻/CO₃²⁻ groups are mobile and responsible for the transport of CO₂ in and out of the system. The membrane creates a CO₂ gradient due to the H₂O gradient, which is indeed opposed. The degree field can generate a stable carbon flux, and the humidity gradient is used to collect CO₂, named "CO₂ pump", as shown in Fig. 8.

The diffusion-reaction model of the membrane is simplified into a two-step process by considering a mass balance on an infinitesimal volume. The first step is the diffusion phase of ions and then an instantaneous readjustment of every concentration in order to meet the chemical equilibria at any time. The equations can be explained as follows:

$$\frac{\partial n_i}{\partial t} = \frac{\partial n_i}{\partial t}\Big|_{\text{current}} + \frac{\partial n_i}{\partial t}\Big|_{\text{chemical}}$$
(27)



Fig. 9. Scheme of CO_2 pump with multi-ion transport inside the membrane. A stable carbon flux of (a) OH^- , (b) CO_3^{-} , and (c) HCO_3^{-} concentration generated the degree field; (d) Elucidation of specific ion effects, such as HCO_3^{-} , CO_3^{2-} , and OH^- , in CO_2 sorbent during the water gradient inside the membrane.



Fig. 10. Material optimization and ion diffusion profile inside the membrane with the effect of humidity, different ions, membrane thickness, and ion diffusion efficiency on CO₂ adsorption rate.

Consequently, the diffusion-reaction equations are given as,

$$\frac{\partial n_i}{\partial t} = \nabla \cdot \left(\sum_{k=1}^4 D_{ik} \nabla n_k\right) + r_i, i = 1, \dots, 4$$
(28)

where D_{ik} is the diffusion coefficient of species *i* in the concentration gradient of species *k*:

$$D_{ik} = D_i \delta_{ik} - \frac{z_i z_k D_i D_k n_i}{\sum_{k=1}^{4} z_k^2 D_k n_k}, \text{ where } \delta_{ik} \begin{cases} 1, \text{ if } i = k\\ 0, \text{ otherwise} \end{cases}$$
(29)

As depicted in the model, the membrane creates a CO₂ gradient contributed by the H₂O gradient (in the opposite direction), and then the water vapor transfers. It is observed from the experiment that water diffuses faster than HCO_3^- and CO_3^{2-} ions. In addition, the carbon diffusion profile is more curved than previously predicted, which may be ascribed to the diffusion velocity of CO2. For quaternary amine-based polymers, the functional, active sites assist the humidification regeneration characteristics, generating an inorganic carbon flux related to the humidity gradient field during the moisture swing adsorption of CO₂, where $P_{CO2,1} > P_{CO2,2}$ and $RH_1 > RH_2$, as shown in Fig. 9d. The water gradient field can generate a stable inorganic carbon flux of OH^- , CO_3^{2-} , and HCO_3^- concentration (Fig. 9a–c). Thus, the humidity gradient performed adsorbing/desorbing CO₂, i.e., CO₂ pump. By maintaining the continuous water vapor and, in consequence, the humidity gradient inside and outside the polymer is maintained. The quaternary ammonium functionalized polymers generate a CO₂ gradient in the opposite direction of water vapor transfer. Therefore, by diffusing water from the inside of the polymer to the outside, CO_2 diffuses in the opposite direction, forming steam of CO_2 enrichment.

5.3. Design optimization for dynamical behavior

Humidity exhibits a significant effect on the dynamic characteristics of CO₂ adsorption by quaternary amine-based particles. The higher the humidity is, the greater the adsorption rate is. The bound water not only affects the thermodynamic equilibrium of CO₂ adsorption by quaternary amine-based particles but also influences the kinetics of the adsorption reaction, and the influence on the thermodynamic equilibrium is dominant. As shown in Fig. 10a, the diffusion coefficient of HCO₃ shows the most impact on the CO2 adsorption process, i.e., lower humidity causes a greater apparent adsorption rate constant. It is attributed to the diffusion of CO2 gas molecules, which is the predominant way for the diffusion of inorganic carbon, but the proportion of gas-phase CO2 molecules in the particles to the total inorganic carbon is deficient. The effect of CO₂ concentration on the dynamic characteristics of CO₂ adsorption by quaternary amine-based particles is not noticeable. At higher CO₂ concentrations, the apparent desorption rate constant is slightly larger.

As the humidity increases, more water is dissolved into the particles, which blocks the diffusion of CO₂. Therefore, D_{CO2} decreases as the humidity increases. The added water causes weak interactions between cations and counter-anions, accelerating the movement of counter-anions. Therefore, D_{CO3}^2 and D_{HCO3}^2 increase as the humidity increases.

Since the hydrophilicity of CO_3^{--} is higher than that of HCO_3^{-} , the variation of $D_{\text{CO}3}^{--}$ is more significant than that of $D_{\text{HCO}3}^{--}$ for a change in humidity. Table 2 summarizes that the amount of CO_2 dissolved into the particles decreases as the humidity increases. Generally, high humidity accelerates the CO_2 adsorption process, as most carbon inside the particles is diffused as ions instead of CO_2 . This result shows that the diffusion coefficient of HCO_3^- has the most impact on the CO_2 adsorption process. In terms of improvement of efficiency, if the diffusion coefficient of HCO_3^- increases about ten times, the CO_2 separation rate improves about 12 times, respectively.

The above discussion confirmed the reliability of the simulated results. However, the amplitude of the simulated results shows a smaller range of variation than that of experimental results, especially at high or low frequencies. This may originate from the assumption that the diffusion coefficients are constant. Indeed, the diffusion coefficients depend on water concentration. Here, we conducted a series of experiments with a slight swing size of $P_{\rm H2O}$ under different humidity values, as shown in Table 2.

In Fig. 10b, a type of ion-membrane in the electrodialysis process exhibits the diffusion coefficients of ions in the range of 10^{-12} – 10^{-8} mol $m^{-2} s^{-1}$, which is much higher than the polymer (we used in experiments) [47]. The results illustrate that with the thickness of the membrane around 100 μ m, the CO₂ adsorption rate improves about 10³ times. The hydroxide ion can transport across the membrane more quickly than either carbonate or bicarbonate ions. If the material is replaced, the intermediate ion rate can increase, and the related change of CO₂ diffusion flux in the membrane is shown in Fig. 10. With the membrane being put in the carbonate/bicarbonate form, the reduced CO₂ concentration in the performance of humidity change is seen by both the model and the experimental results. The fitting results are shown in Fig. 10c. The low ionic conductivity agrees with the trend observed for the ion-membrane diffusion coefficients. If an ion has a lower diffusion coefficient, then its ionic conductivity would be lower as well. This model enabled the performance of the MSA process in the hydroxide form and found compatible experimental results. The specific ion diffusion efficiency changes CO2 adsorption rate, such as HCO3, $\mathrm{CO}_3^{2-}\!,$ and $\mathrm{OH}^-\!,$ in CO_2 sorbent: the diffusion coefficient of ions has a significant improvement of about 10² times for different membrane materials.

6. Conclusions

In summary, we developed a mesoscopic model to describe the physicochemical behavior of the moisture swing membrane. The model combined particle diffusion, electrical fields, thermodynamics, and chemical equilibria with respective parameters: diffusion coefficients, electrical mobilities, Henry's constant, and chemical equilibrium constant. A theoretical study was conducted with parameters used in the experimental data to further calibrate the model. To confront a theoretical model with experiment quantitatively, Fourier-transformed moisture-swing frequency response is applied to accurately measure H₂O-CO₂ concentration response, ensuring a systematic approach for unknown kinetic parameters for the model. In this paper, the results show that the gradient of water vapor causes a counter gradient of CO2 concentration, resulting in the spontaneous transportation of CO₂ from one side of the MSA membrane to another side. Specifically, the diffusion coefficient of HCO3 drives the CO2 adsorption process predominately, and the diffusion coefficient of HCO₃⁻ increases about ten times, leading to a nearly 12 times enhanced CO₂ separation rate accordingly. Notably, CO₂ adsorption kinetics can be stimulated by controlling specific ion conductivity in the sorbent. With the enhancement of adsorption kinetics and low capital cost, real progress in MSA can be achieved for direct air capture of CO₂.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Tao Wang: Conceptualization, Supervision, Funding acquisition, Writing – review & editing. **Xinru Wang:** Conceptualization, Methodology, Data curation, Writing – review & editing. **Hao Dong:** . **Kun Ge:** Conceptualization, Supervision. **Klaus Lackner:** Conceptualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- C. Breyer, M. Fasihi, C. Bajamundi, F. Creutzig, Direct air capture of CO₂: a key technology for ambitious climate change mitigation, Joule 3 (2019) 2053–2057, https://doi.org/10.1016/j.joule.2019.08.010.
- [2] P. Arias, N. Bellouin, E. Coppola, R. Jones, G. Krinner, J. Marotzke, N. Vaishali, P. Matthew, G. Plattner, R. Joeri, IPCC climate change 2021: the physical science basis. contribution of working group I to the sixth assessment report of the intergovernmental panel on climate change, (2021).
- [3] R. Millar, M. Allen, Chapter 2. Understanding the role of CCS deployment in meeting ambitious climate goals, RSC Energy Environ. Ser. (2019) 8–35, https:// doi.org/10.1039/9781788012744-00008.
- [4] J.C. Minx, W.F. Lamb, M.W. Callaghan, S. Fuss, J. Hilaire, F. Creutzig, T. Amann, T. Beringer, W. De Oliveira Garcia, J. Hartmann, T. Khanna, D. Lenzi, G. Luderer, G.F. Nemet, J. Rogelj, P. Smith, J.L. Vicente Vicente, J. Wilcox, M. Del Mar Zamora Dominguez, Negative emissions - Part 1: research landscape and synthesis, Environ. Res. Lett. 13 (2018), https://doi.org/10.1088/1748-9326/aabf9b.
- [5] K. Hennessy, J. Lawrence, B. Mackey, IPCC sixth assessment report (AR6): climate change 2022-impacts, adaptation and vulnerability: regional factsheet Australasia, (2022).
- [6] M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, H.J. Herzog, G. Jackson, J. Kemper, S. Krevor, G.C. Maitland, M. Matuszewski, I.S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D.M. Reiner, E.S. Rubin, S.A. Scott, N. Shah, B. Smit, J.P.M. Trusler, P. Webley, J. Wilcox, N.M. Dowell, Carbon capture and storage (CCS): the way forward, Energy Environ. Sci. 11 (2018) 1062–1176, https://doi.org/10.1039/ c7ee02342a.
- [7] K. Lackner, Is direct air capture nature-inspired?, (2019).
- [8] S.M. Kim, G. Léonard, Performance and sensitivity analysis of direct air capture (DAC) model using solid amine sorbents for CO2 capture, in: 2022.
- [9] M. Wang, R. Shaw, E. Gencer, T.A. Hatton, Technoeconomic analysis of the electrochemically mediated amine regeneration CO₂ capture process, Ind. Eng. Chem. Res. 59 (2020) 14085–14095, https://doi.org/10.1021/acs.iecr.0c02166.
- [10] Y. Miao, Z. He, X. Zhu, D. Izikowitz, J. Li, Operating temperatures affect direct air capture of CO₂ in polyamine-loaded mesoporous silica, Chem. Eng. J. 426 (2021), 131875, https://doi.org/10.1016/j.cej.2021.131875.
- [11] C. Halliday, T.A. Hatton, Sorbents for the capture of CO₂ and other acid gases: a review, Ind. Eng. Chem. Res. 60 (2021) 9313–9346, https://doi.org/10.1021/acs. iecr.1c00597.
- [12] K.S. Lackner, Capture of carbon dioxide from ambient air, Eur. Phys. J. Spec. Top. 176 (2009) 93–106, https://doi.org/10.1140/epjst/e2009-01150-3.
- [13] I.A. Digdaya, I. Sullivan, M. Lin, L. Han, W.H. Cheng, H.A. Atwater, C. Xiang, A direct coupled electrochemical system for capture and conversion of CO₂ from oceanwater, Nat. Commun. 11 (2020) 4412, https://doi.org/10.1038/s41467-020-18232-y.

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- [14] Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, Amine-bearing mesoporous silica for CO₂ removal from dry and humid air, Chem. Eng. Sci. 65 (2010) 3695–3698, https://doi.org/10.1016/j.ces.2010.02.044.
- [15] A. Hemmatifar, J.S. Kang, N. Ozbek, K. Tan, T.A. Hatton, Electrochemically mediated direct CO₂ capture by a stackable bipolar cell, ChemSusChem 15 (2022), https://doi.org/10.1002/cssc.202102533.
- [16] J. Wang, R. Fu, S. Wen, P. Ning, M.H. Helal, M.A. Salem, B.B. Xu, Z.M. El-Bahy, M. Huang, Z. Guo, L. Huang, Q. Wang, Progress and current challenges for CO₂ capture materials from ambient air, Adv. Compos. Hybrid Mater. 5 (2022) 2721–2759, https://doi.org/10.1007/s42114-022-00567-3.
- [17] C. Lu, X. Zhang, X. Chen, advanced materials and technologies toward carbon neutrality, Acc. Mater. Res. 3 (2022) 913–921, https://doi.org/10.1021/ accountsmr.2c00084.
- [18] L.A. Darunte, K.S. Walton, D.S. Sholl, C.W. Jones, CO₂ capture via adsorption in amine-functionalized sorbents, Curr. Opin. Chem. Eng. 12 (2016) 82–90, https:// doi.org/10.1016/j.coche.2016.03.002.
- [19] X. Zhu, T. Ge, F. Yang, R. Wang, Design of steam-assisted temperature vacuumswing adsorption processes for efficient CO₂ capture from ambient air, Renew. Sustain. Energy Rev. 137 (2021), 110651.
- [20] B. Dinakar, A.C. Forse, H.Z. Jiang, Z. Zhu, J.-H. Lee, E.J. Kim, S.T. Parker, C. J. Pollak, R.L. Siegelman, P.J. Milner, Overcoming metastable CO₂ adsorption in a bulky diamine-appended metal-organic framework, J. Am. Chem. Soc. 143 (2021) 15258–15270.
- [21] C. Hou, D.R. Kumar, Y. Jin, Y. Wu, J.J. Lee, C.W. Jones, T. Wang, Porosity and hydrophilicity modulated quaternary ammonium-based sorbents for CO₂ capture, Chem. Eng. J. 413 (2021), 127532.
- [22] X. Shi, H. Xiao, H. Azarabadi, J. Song, X. Wu, X. Chen, K.S. Lackner, Sorbents for the direct capture of CO₂ from ambient air, Angew. Chem. Int. Ed. 59 (2020) 6984–7006.
- [23] Y. Kaneko, K.S. Lackner, Isotherm model for moisture-controlled CO₂ sorption, Phys. Chem. Chem. Phys. (2022).
- [24] H. Dong, T. Wang, X. Wang, F. Liu, C. Hou, Z. Wang, W. Liu, L. Fu, X. Gao, Humidity sensitivity reducing of moisture swing adsorbents by hydrophobic carrier doping for CO₂ direct air capture, Chem. Eng. J. 466 (2023), 143343.
- [25] T. Wang, X. Wang, C. Hou, J. Liu, Quaternary functionalized mesoporous adsorbents for ultra-high kinetics of CO₂ capture from air, Sci. Rep. 10 (2020) 21429, https://doi.org/10.1038/s41598-020-77477-1.
- [26] C. Lu, X. Shi, Y. Liu, H. Xiao, J. Li, X. Chen, Nanomaterials for adsorption and conversion of CO₂ under gentle conditions, Mater. Today 50 (2021) 385–399.
- [27] S. Choi, J.H. Drese, P.M. Eisenberger, C.W. Jones, Application of amine-tethered solid sorbents for direct CO₂ capture from the ambient air, Environ. Sci. Technol. 45 (2011) 2420–2427, https://doi.org/10.1021/es102797w.
- [28] C. Hou, Y. Wu, T. Wang, X. Wang, X. Gao, Preparation of quaternized bamboo cellulose and its implication in direct air capture of CO₂, Energy Fuels 33 (2019) 1745–1752, https://doi.org/10.1021/acs.energyfuels.8b02821.
- [29] H. He, M. Zhong, D. Konkolewicz, K. Yacatto, T. Rappold, G. Sugar, N.E. David, K. Matyjaszewski, Carbon black functionalized with hyperbranched polymers: synthesis, characterization, and application in reversible CO₂ capture, J. Mater. Chem. A 1 (2013) 6810, https://doi.org/10.1039/c3ta10699c.
- [30] H. He, W. Li, M. Zhong, D. Konkolewicz, D. Wu, K. Yaccato, T. Rappold, G. Sugar, N.E. David, K. Matyjaszewski, Reversible CO₂ capture with porous polymers using the humidity swing, Energy Env. Sci. 6 (2013) 488–493, https://doi.org/10.1039/ C2EE24139K.
- [31] M.J. Mitchell, O.E. Jensen, K.A. Cliffe, M.M. Maroto-Valer, A model of carbon dioxide dissolution and mineral carbonation kinetics, Proc. R. Soc. Math. Phys. Eng. Sci. 466 (2010) 1265–1290, https://doi.org/10.1098/rspa.2009.0349.

- [32] T. Wang, J. Liu, H. Huang, M. Fang, Z. Luo, Preparation and kinetics of a heterogeneous sorbent for CO₂ capture from the atmosphere, Chem. Eng. J. 284 (2016) 679–686.
- [33] V. Nikulshina, M.E. Gálvez, A. Steinfeld, Kinetic analysis of the carbonation reactions for the capture of CO₂ from air via the Ca(OH)₂–CaCO₃–CaO solar thermochemical cycle, Chem. Eng. J. 129 (2007) 75–83, https://doi.org/10.1016/ j.cej.2006.11.003.
- [34] L.A. Darunte, T. Sen, C. Bhawanani, K.S. Walton, D.S. Sholl, M.J. Realff, C. W. Jones, Moving beyond adsorption capacity in design of adsorbents for CO₂ capture from ultradilute feeds: kinetics of CO₂ adsorption in materials with stepped isotherms, Ind. Eng. Chem. Res. 58 (2019) 366–377, https://doi.org/10.1021/acs.iecr.8b05042.
- [35] H. Azarabadi, K.S. Lackner, A sorbent-focused techno-economic analysis of direct air capture, Appl. Energy 250 (2019) 959–975, https://doi.org/10.1016/j. apenergy.2019.04.012.
- [36] S. Fang, X. Zhou, Y. Rong, X. Zhi, K. Wang, L. Qiu, Multi-stage internally-cooled membrane-based liquid desiccant dehumidifiers: driving-force based insights into structural improvement, Int. J. Heat Mass Transf. 171 (2021), 121068, https://doi. org/10.1016/j.ijheatmasstransfer.2021.121068.
- [37] A. Mareev, E. Kirichenko, K. Kirichenko, Mathematical Modelling of Transport of Single and Double Charged Ions Through Layered Ion Exchange Membranes, IOP Publishing, 2020, 012059.
- [38] J. Cai, L. Zhang, W. Wei, Chapter 1 a brief introduction to flow and transport in fractal porous media, J. Cai, L. Zhang, W. Wei. Model. Flow Transp. Fractal Porous Media, Elsevier, 2021, pp. 1–10, https://doi.org/10.1016/B978-0-12-817797-6.00009-9.
- [39] I. Tosun, 11 unsteady-state microscopic balances with generation, I. Tosun (ed.). Modelling Transparent Phenomenon, 2nd ed., Elsevier Science B.V., Amsterdam, 2007, pp. 483–522, https://doi.org/10.1016/B978-044453021-9/50012-9.
- [40] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, 2nd ed., John Wiley & Sons, Inc., New York, 2007. Revised.
- [41] W. Wei, Y. Xia, J. Cai, Chapter 3 tortuosity in two-dimensional and threedimensional fractal porous media: a numerical analysis, J. Cai, L. Zhang, W. Wei. Modelling Flow Transparent Fractal Porous Media, Elsevier, 2021, pp. 25–36, https://doi.org/10.1016/B978-0-12-817797-6.00007-5.
- [42] L. Zhang, Chapter 9 application of fractal theory in transient pressure properties of hydrocarbon reservoir, J. Cai, L. Zhang, W. Wei. Modelling Flow Transparent Fractal Porous Media, Elsevier, 2021, pp. 193–249, https://doi.org/10.1016/B978-0-12-817797-6.00008-7.
- [43] I. Tosun, 7 unsteady-state macroscopic balances, I. Tosun, Modelling Transparent Phenomenon (2007) 161–211, https://doi.org/10.1016/B978-044453021-9/ 50008-7.
- [44] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical recipes. The Art of Scientific Computing, 3rd ed., Cambridge university press, 2007.
- [45] J.C. Foster, I. Akar, M.C. Grocott, A.K. Pearce, R.T. Mathers, R.K. O'Reilly, 100th anniversary of macromolecular science viewpoint: the role of hydrophobicity in polymer phenomena, ACS Macro Lett. 9 (2020) 1700–1707.
- [46] İ. Tosun, Chapter 11 unsteady-state microscopic balances with generation, İ. Tosun. Modelling Transparent Phenomenon, 2nd ed., Elsevier Science B.V., Amsterdam, 2002, pp. 473–490, https://doi.org/10.1016/B978-044451052-5/ 50011-9.
- [47] A.M. Kiss, T.D. Myles, K.N. Grew, A.A. Peracchio, G.J. Nelson, W.K.S. Chiu, Carbonate and bicarbonate ion transport in alkaline anion exchange membranes, J. Electrochem. Soc. 160 (2013) F994, https://doi.org/10.1149/2.037309jes.