

DOI: 10.1002/aic.18018

RESEARCH ARTICLE

Separations: Materials, Devices and Processes

AICHE JOURNAL

Modeling salt adsorption in electrical double layer for capacitive deionization

Yu-Jeng Lin¹ | Chau-Chyun Chen²

¹Department of Chemical Engineering, National Tsing Hua University, HsinChu City, Taiwan

²Department of Chemical Engineering, Texas Tech University, Lubbock, Texas, USA

Correspondence

Chau-Chyun Chen, Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, USA. Email: chauchyun.chen@ttu.edu

Funding information

J.F Maddox Foundation; Office of Energy Efficiency and Renewable Energy, Grant/Award Number: DE-EE0007888

Abstract

This work presents an electrical double layer (EDL) model for capacitive deionization (CDI) by intercorrelating the salt adsorption, the electrode voltage, and the surface charge density. The counterion condensation is considered a crucial contribution to salt adsorption because of the high surface charge density in the charged micropores. The counterions condense when the surface charge density exceeds a critical value, which is predicted by the counterion condensation theory. The EDL model accurately correlates the NaCl salt adsorption and electrode voltage with various surface charge densities and well predicts the salt adsorption in a wide range of external salt concentrations. The EDL model reproduces the non-monotonic relationship between the salt adsorption and the specific surface area observed in experiments and provides an explanation from the modeling perspective. Exhibiting superior accuracy and predictability for salt adsorption, the EDL model could serve as an enabling tool contributing to the development of CDI processes.

KEYWORDS

desalination, electrochemical process, thermodynamic modeling

1 | INTRODUCTION

Capacitive deionization (CDI) is a promising technology to remove salts from saline water with low or moderate salt concentration.¹ In the CDI processes shown in Figure 1, the saline water containing at least 5 mM sodium chloride (NaCI) flows through a spacer channel between a cell consisting of an anode and a cathode. As the charges on the electrode surface are polarized by the applied voltage using an external power supply, the cations and anions are attracted by the cathode and the anode, respectively through electrostatic force.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Desalinated water is obtained from the effluent as the salts are adsorbed by the electrodes. Porous activated carbon electrodes with nanometer micropores are commonly employed for CDI because of the high specific surface area. A regeneration step is later performed by reversing the voltage, releasing the salts previously adsorbed. Without Faradaic reactions, the salts are adsorbed solely by capacitive storage in the electrical double layer (EDL) at the electrode-solution interface, where the ion concentrations and the electrical potential are perturbed from the bulk solution. The net charges in the EDL due to the excess counterions counterbalance the electrode charges. The counterions and coions are defined as the ions that have opposite and same signs to the electrode charges, respectively.

The electrode charges, salt adsorption capacity, and applied voltage are the key properties of interest as they determine the desalination efficiency and energy consumption. A CDI model that can represent the EDL structure with accurate descriptions of how the electrode charges and the salt adsorption capacity vary in response to the applied voltage is essential to designing and scaling up the CDI



FIGURE 1 Schematic capacitive deionization process for desalination and electrical double layer structure in micropores

AIChE 2 of 11

15475905, 2023, 5, Downloaded from https doi/10.1002/aic. 18018 by Texas Tech University Libraries, Wiley Online Library on [28/08/2023]. See the Terms and Conditions s (http: on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons

process. The Langmuir and Freundlich adsorption isotherms have been employed to model the salt adsorption in CDI processes assuming the electrosorption is comparable to the gas adsorption.²⁻⁵ However, the isotherm-based models are purely empirical, lacking direct relations with the applied voltage and the electrode charges. The modified Donnan model has been used to calculate the salt adsorption using the Donnan potential.⁶⁻⁹ To fit the salt adsorption data, the model hypothesized strong attractive physical interactions between the ions and the electrode.⁹ As a result, at zero applied voltage the salt concentration in the micropores is as high as 120 mM when the external salt concentration is 5 mM, contributing to significant physical salt adsorption with 2 mg NaCl/g electrode. However, the physical adsorption of NaCl in several activated carbon electrodes reported in experimental studies is less significant.¹⁰⁻¹² The concentration of potassium fluoride in the pore phase without applied voltage was in the same order of magnitude as that in the external solution.¹³ Prior molecular dynamics (MD) simulations also indicated that at zero applied voltage the ions preferentially stay outside the carbon micropores and result in a lower ion concentration in the micropores than in the bulk solution.^{14–17} A better model that can describe the EDL structure is needed.

The counterion condensation phenomenon has been well recognized experimentally in polyelectrolyte and colloidal solutions containing highly charged polyions and macroions, respectively.^{18–20} The invariant effective surface charge densities of polyions and macroions suggest that counterions "condense" on the charged surface and reduce the surface charges to a critical value. The polyion/macroion and the condensed counterions are intimately associated through strong electrostatic attraction and can be seen as an entity moving through the solution. It is suggested that the counterion condensation effect on thermodynamic properties should be considered especially for the systems containing highly-charged species.²¹ The counterion condensation is expected to play a crucial role for charged electrodes in CDI processes because of its high surface charge density.²² The counterion condensation phenomenon was also observed in MD simulations that modeled NaCl aqueous solution in charged micropores.¹⁴ A high-density distribution of counterions was found near the charged graphene surface.

The counterion condensation theory developed by Manning provides a theoretical approach to determining the effective charge density and has been a success in describing the thermodynamic properties of aqueous polyelectrolyte solutions and ion-exchange membranes over the past decades.^{23,24} The counterion condensation theory has been subsequently extended from rod-like polyions to plane geometry, which resembles the charged plate electrodes.²⁵

The present work aims to develop an EDL model for CDI processes that accurately intercorrelates salt adsorption with electrode voltage and surface charge density. The micropores of carbon electrodes are modeled as two parallel charged plates with equal charge densities on each plate. Figure 1 shows the schematic EDL structure including the Stern layer and the diffuse layer. The counterions are present as the condensed counterions at the interface of the Stern layer and diffuse layer and as the uncondensed free counterions in the diffuse layer. The salt adsorption due to the counterion



FIGURE 2 The absolute critical charge density (σ^{crit}) calculated by condensation theory for single-plate and two-parallel-plate electrodes at various plate distances; T = 298.15 K; $\varepsilon_r = 78$; $|z_{ct}| = 1$; d^{pr} : distance between two parallel charged plates

condensation is to be calculated by extending the counterion condensation theory. The electrode voltage is also correlated with the surface charge density by considering the potential differences in the Stern layer and the diffuse layer. The resulting EDL model accurately represents the experimental CDI performance at various surface charge densities, the specific surface area of electrodes, and external salt concentrations.

2 | COUNTERION CONDENSATION THEORY FOR EDL

Counterion condensation is the key contributor to salt adsorption in the EDL model developed in this work. Manning's counterion condensation theory determined the critical charge density σ^{crit} for the single-plate geometry by minimizing the Gibbs free energy for the system which includes the contributions from the electrostatic interaction energy and the transfer entropy due to counterion condensation.²⁵ If the operating surface charge density σ exceeds σ^{crit} , counterions condense until σ is reduced to σ^{crit} . The number of condensed counterions can be calculated by the difference between σ and σ^{crit} .

In this work, the counterion condensation theory is extended from the single-plate geometry to the two-parallel-plate geometry that resembles micropores. Applying two-parallel-plate geometry to model micropores is considered adequate since the pore sizes are typically in nanometers, an order of magnitude larger than ion sizes. The use of two-parallel-plate geometry will need care when the pores have sizes similar to ions or are highly tortuous. The derivation of extending the condensation theory to two-parallel-plate geometry can be found in the Supplementary Information (Data S1). The resulted σ^{crit} is:

$$\sigma^{crit} = \frac{q_e \kappa \ln(\kappa \lambda_B)}{2\pi z_{ct} \lambda_B} \tanh\left(\frac{\kappa d^{pr}}{2}\right), \qquad (1)$$

where q_e is the elementary charge; κ is the Debye parameter; λ_B is the Bjerrum length; z is the signed charge number; subscript ct represents counterion; d^{pr} is the pore size.

 κ and λ_B are defined as:

$$\kappa = \sqrt{\frac{q_e^2}{\varepsilon_s \varepsilon_0 k_B T} \sum_i z_i^{2} C_i^{bk}}, \qquad (2$$

$$\lambda_{\rm B} = \frac{q_e^2}{4\pi\varepsilon_{\rm s}\varepsilon_{\rm O}k_{\rm B}\mathsf{T}},\tag{3}$$

where k_B is the Boltzmann constant; T is the system absolute temperature; ε_0 is the dielectric constant of vacuum; ε_s is the relative permittivity of solvent; z_i is the signed charge number of ion i; C_i^{bk} is the bulk concentration of ion i.

Figure 2 compares the calculated σ^{crit} for the single-plate and the two-parallel-plate electrodes. The σ^{crit} approaching zero suggests that all the counterions condense at infinite dilution. The two-parallel-plate electrode needs a lower σ^{crit} than the single-plate electrode to condense counterions because of the strong electric field intensified by the two charged plates. The σ^{crit} reduces when the distance between charged plates decreases, suggesting the counterions condense at a lower surface charge density in narrow pores. It should be noted that the use of σ^{crit} was suggested to be limited to dilute solutions up to the concentration at where $|\sigma^{crit}|$ reaches a maximum.²⁶ For instance, the σ^{crit} of the single-plate electrode in aqueous solution at 298.15 K is applicable up to 25 mM.

3 | MODELING FRAMEWORK

In the CDI experiments for desalination, the salt adsorption and the electrode charge are obtained by integrating the effluent salt concentration and the electrical current with time, respectively. At each electrode voltage (*E*), the salt adsorption (N_{solt}^{ad}) and the specific electrode charge (*Q*) were reported after being normalized by the total weight of the electrode pair. The specific surface areas (A^{sp}) of the porous carbon electrodes were measured by Brunauer–Emmett–Teller (BET) method. The specific volumes (V^{sp}) were calculated by nonlocal density functional theory (NLDFT) or quenched solid density functional theory (QSDFT) models. To have a consistent basis with the reported N_{solt}^{ad} and *Q*, this work uses the A^{pr} and V^{pr} , which are defined as the area and volume of one electrode (cathode or anode) per weight of the electrode pair. The A^{pr} and V^{pr} are converted from A^{sp} and V^{sp} assuming an equal weight of anode and cathode as follows.

$$A^{pr} = \frac{A^{sp}}{2},\tag{4}$$

$$V^{pr} = \frac{V^{sp}}{2}.$$
 (5)

The salt adsorption data measured from eight porous carbon electrodes are studied in this work.^{7–9,27} The electrode systems were synthesized with various methods and materials. The electrode materials are activated carbon-based (CR-B, AC-1, and AC-2) and carbidederived carbon-based (CDC-1, CDC-2, TiC-CDC, HIPE SiC-CDC, and OM SiC-CDC). The specific surface area of electrodes is across a wide range from 1130 to 2720 m²/g.

3.1 | Modeling salt adsorption

The salt is assumed to be fully dissociated in aqueous solutions as follows:

$$CN_{\nu_{cn}}AN_{\nu_{an}} \longrightarrow \nu_{cn}CN^{z_{cn}} + \nu_{an}AN^{z_{an}}, \qquad (6)$$

where CN and AN are cation and anion, respectively; ν is the stoichiometric coefficient; the subscripts *cn* and *an* represent cation and anion, respectively.

The total salt adsorption (N_{salt}^{ad}) is contributed by the counterion condensation (N_{salt}^{cond}) and the diffuse layer sorption (N_{salt}^{df}) . The physical adsorption is assumed negligible compared to electrosorption as suggested by prior experiments.¹⁰⁻¹²

$$N_{salt}^{ad} = N_{salt}^{cond} + N_{salt}^{df}.$$
 (7)

Surface charge density (σ) is the key variable determining the electrostatic force and the effectiveness of salt adsorption. The operating σ can be calculated using the measured Q and the A^{pr} assuming that the electrode charges are spread uniformly on the surface.

$$\sigma = \frac{\mathsf{Q}}{\mathsf{A}^{pr}}.\tag{8}$$

The σ^{eff} is the effective surface charge density after being partially screened by the condensed counterions and "seen" by the free ions in the diffuse layer. If the σ exceeds the σ^{crit} , the counterions condense and reduce the σ to σ^{crit} ; otherwise, the surface charge density stays at σ .

$$\sigma^{\text{eff}} = \begin{cases} \sigma^{\text{crit}}, |\sigma| \ge |\sigma^{\text{crit}}| \\ \sigma, |\sigma| < |\sigma^{\text{crit}}| \end{cases}$$

$$\tag{9}$$

The salt adsorption from the counterion condensation can be calculated as:

$$N_{salt}^{cond} = -\frac{(\sigma - \sigma^{eff})A^{pr}}{\nu_{ct} z_{ct} q_{e}}.$$
 (10)

Using the A^{pr} to calculate the salt adsorption from the counterion condensation assumes the surface areas measured by BET method

are accessible for counterion condensation when $> \sigma^{crit}$. This assumption is supported by the findings of prior MD simulations that suggest the counterions enter the micropores only when the σ reaches a threshold value.¹⁵ The reported threshold σ at $0-2 \,\mu\text{C/cm}^2$ is consistent with the σ^{crit} predicted by the counterion consternation theory in this work. In the other words, increasing the surface charge density not only provides the driving force for electrosorption but also helps the ions overcome the energy barrier required to access the micropores.

After counterion condensation, the partially screened surface charge density on the electrode attracts the counterions in the diffuse layer. The net charge density in the solution counterbalances the effective charge density as shown below.

$$\sigma^{eff} = -q_e \left(z_{ct} C_{ct}^{pr} + z_{co} C_{co}^{pr} \right) \frac{V}{A} = -q_e \left(z_{ct} C_{ct}^{pr} + z_{co} C_{co}^{pr} \right) \frac{d^{pr}}{2}, \tag{11}$$

where the C^{pr} is the average concentration of uncondensed ions in the diffuse layer; the subscript *ct* and *co* represent counterion and coion, respectively; the *V* and *A* are the solution volume and the electrode surface area for diffuse layer sorption, respectively.

The A^{pr} is not used in Equation (11) as it is assumed that the micropores might not be fully accessible when the effective surface charge density is below σ^{crit} and is not high enough to overcome the energy barrier for ions to enter. Instead, the ratio of V/A is adjustable and is replaced by $d^{pr}/2$ to be consistent with the two-parallelplate geometry. The d^{pr} is determined by fitting the salt adsorption data.

The Donnan equilibrium between the pore phase and the bulk phase also needs to be satisfied.

$$\left(\mathbf{C}_{ct}^{pr}\right)^{\nu_{ct}}\left(\mathbf{C}_{co}^{pr}\right)^{\nu_{co}} = \left(\mathbf{C}_{ct}^{bk}\right)^{\nu_{ct}}\left(\mathbf{C}_{ct}^{bk}\right)^{\nu_{co}},\tag{12}$$

where the C^{bk} is the concentration of ions in the bulk.

Combining Equations (11) and (12), the counterion and coion concentrations in the diffuse layer can be solved. Finally, the salt adsorption by the diffuse layer can be calculated either from cations or anions.

$$N_{salt}^{df} = \frac{V^{pr}}{\nu_{cn}} \left(C_{cn}^{pr,cathode} - C_{cn}^{bk} \right) + \frac{V^{pr}}{\nu_{cn}} \left(C_{cn}^{pr,anode} - C_{cn}^{bk} \right) \\ = \frac{V^{pr}}{\nu_{an}} \left(C_{an}^{pr,cathode} - C_{an}^{bk} \right) + \frac{V^{pr}}{\nu_{an}} \left(C_{an}^{pr,anode} - C_{an}^{bk} \right), \qquad (13)$$

where the superscripts *cathode* and *anode* represent cathode and anode, respectively.

For symmetric electrolytes with stoichiometric coefficient ν , Equation (13) is simplified to:

$$N_{salt}^{df} = \frac{V^{pr}}{\nu} \left(C_{ct}^{pr} - C_{ct}^{bk} \right) + \frac{V^{pr}}{\nu} \left(C_{co}^{pr} - C_{co}^{bk} \right).$$
(14)

3.2 | Modeling electrical potential

The measured electrode voltage (*E*) consists of the electrical potential differences across the Stern layer ($\Delta \phi^{st}$) and the diffuse layer ($\Delta \phi^{df}$) as shown in Figure 3.

$$\mathsf{E} = 2 \left(\Delta \phi^{\mathsf{st}} + \Delta \phi^{\mathsf{df}} \right). \tag{15}$$

The factor of 2 accounts for the anode and cathode as the $\Delta \phi^{st}$ and $\Delta \phi^{df}$ are defined as unsigned (i.e., positive for both anode and cathode). The $\Delta \phi^{df}$ is the potential difference between the diffuse layer and the bulk solution and is calculated from the linearized Possion–Boltzmann theory for two charged plates with an equal surface charge density.²⁸

$$\Delta \phi^{df} = \frac{|\sigma^{eff}|}{\varepsilon_s \varepsilon_{0\kappa}} \operatorname{coth}\left(\frac{\kappa d^{pr}}{2}\right). \tag{16}$$

The σ^{eff} is used because the uncondensed free ions in the diffuse layer only experience the surface density that is partially screened by the condensed counterions.

The charge-free Stern layer can be seen as a parallel-plate capacitor that lies between the electrode and the solution carrying opposite surface charge densities σ and $-\sigma$. The potential difference of an infinitely large parallel-plate capacitor is expressed as²⁹:

$$\Delta \phi^{\rm st} = \frac{|\sigma|}{\varepsilon_{\rm st} \varepsilon_0} d^{\rm st},\tag{17}$$

where d^{st} is the thickness of the Stern layer; ε_{st} is the relative permittivity in the Stern layer.

The ε_{st} depends on the dielectric media determined by the composition of the Stern layer. The compression of the Stern layer under a high electric field has been suggested.³⁰ The d^{st} is reduced due to the electrostatic force exerted by the attracted counterions. An empirical expression has been employed to model the compressed d^{st} .³⁰



FIGURE 3 Schematic electrical potential profile between two parallel charged plates with positive charges

$$\frac{d^{\rm st}}{d^{\rm st}_{\sigma=0}} = \frac{1}{1+\beta\sigma^2}.$$
 (18)

The Stern layer thickness at zero surface charge density $(d_{\sigma=0}^{st})$ is used as a reference thickness. The β is the compression factor characterizing the change of d^{st} as the σ increases. Unknown parameters $d_{\sigma=0}^{st}$ and the ε_{st} are combined into α and is determined together with β by fitting the electrode voltage data at various surface charge density.

$$\alpha = \frac{d_{\sigma=0}^{\rm st}}{\varepsilon_{\rm st}}.$$
 (19)

The $\Delta \phi^{st}$ becomes:

$$\Delta \phi^{\rm st} = \frac{|\sigma|\alpha}{\varepsilon_0 (1 + \beta \sigma^2)}.$$
 (20)

4 | RESULTS AND DISCUSSIONS

4.1 | Salt adsorption and electrode voltage

Table 1 summarizes the modeling results of the salt adsorption and electrode voltage for the eight CDI systems studied in this work. The root-mean-square error (RMSE) is defined as:

$$\mathsf{RMSE} = \sqrt{\frac{\sum\limits_{k=1}^{n} \left(\mathsf{Y}_{k}^{model} - \mathsf{Y}_{k}^{exp} \right)^{2}}{n}}.$$
 (21)

Figure 4 shows the modeling results of the CR-B electrode system with 5 and 20 mM external NaCl concentration at 298.15 K. With the 5 mM NaCl solution, the salt adsorption data increases at a relatively smooth rate at 0–0.5 μ C/cm² but rising rapidly as the σ is above around 0.5 μ C/cm². Similarly, the electrode voltage data also has a slope change at around 0.5 μ C/cm². With the 20 mM NaCl solution, a slope change is also expected to be around 1 μ C/cm² since the extrapolation of data does not go through the origin.

The EDL model accurately correlates the salt adsorption and the electrode voltage data. The slope changes correspond to the σ^{crit} predicted by the counterion condensation theory, at 0.5 and 1.2 μ C/cm² for 5 and 20 mM salt solutions, respectively. At low σ below the σ^{crit} , the salt adsorption is solely attributed to the diffuse layer sorption. When the σ exceeds σ^{crit} , both the counterion condensation and the diffuse layer sorption contribute to the salt adsorption and result in a rapid change as σ increases.

Figure 5 shows the counterion and coion concentrations calculated by the EDL model at 5 mM external salt concentration. The counterion increases to 35 mM while the coion decreases to 0.7 mM in the diffuse layer at σ^{crit} . At $\sigma > \sigma^{crit}$, because the diffuse layer only experiences a constant surface charge density screened by the condensed counterions, the ion concentrations in the diffuse layer are

TABLE 1

A^{pr} Vpr d^{pr} RMSE of Salt β RMSE of N_{salt} Data α Electrode (m²/g) (mL/g) conc. (mM) (Å) (m^4/C^2) sources (nm) E (V) (mg/g) CDC-1 1130 0.50 5 5.1 1.3 120.8 0.010 0.763 7 CDC-2 1290 0.60 5 4.4 1.6 74.9 0.007 0.602 7 0.017 TIC-CDC 1309 0.52 5 3.1 1.8 213.8 0.606 8 CR-B 1330 0.55 5, 20 3.3 1.4 52.9 0.040 0.790 9,27 AC-1 1450 0.70 5 2.9 2.0 0.018 0.378 7 148.1 AC-2 1600 0.70 5 3.3 2.6 282.8 0.009 0.464 7 HIPE SiC-5 475.0 0.011 0.598 8 2351 1.14 2.5 2.8 CDC 0.018 0.702 OM SiC-CDC 2720 1.98 5 2.2 3.0 577.7 8

Summary of modeling results of capacitive deionization process for desalination using porous carbon electrodes; A^{pr} and V^{pr} are the



reported values from indicated data sources; d^{pr} , α , and β are the model fitting parameters.

FIGURE 4 Modeled and experimental salt adsorption and electrode voltage of CDI using CR-B electrode; 5 mM (red) and 20 mM (blue) NaCI aqueous solution; T = 298.15 K; points: measured data⁹; solid lines: EDL model in this work

2

3

σ (μC/cm²)

4

0

1

constant and independent of σ . The total salt adsorption is dominated by the counterion condensation at $\sigma > \sigma^{crit}$. Figures 6 and 7 show the modeling results of all the other electrode systems across a wide







FIGURE 6 Modeled and experimental salt adsorption in various porous carbon electrode systems; E = 0.6-1.4 V; T = 298.15 K; external NaCl concentration = 5 mM; points: measured data from various sources indicated in Table 1; lines: EDL model in this work

6 of 11

AICHE



FIGURE 7 Modeled and experimental electrode voltage in various porous carbon electrode systems; T = 298.15 K; external NaCl concentration = 5 mM; points: measured data from various sources indicated in Table 1; lines: EDL model in this work



FIGURE 8 Predicted electrode charge and salt adsorption by the EDL model for CR-B electrode compared to experimental data; external NaCl concentration: 2–100 mM; E = 1.2 V; T = 298.15 K; points: experimental data⁹; solid lines: modeled results with calculated σ^{crit} ; dotted lines: modeled results with a constant σ^{crit} at 45 mM

range of surface areas from 1130 to 2720 m^2/g with 5 mM external salt concentration. Similar to the CR-B electrode system, the slope changes are predicted between 0 and 1 $\mu C/cm^2$. The EDL model accurately correlates the salt adsorption and electrode voltage data for all the electrode systems with the RMSE at 0.3–0.8 mg/g and 0.01–0.04 V, respectively.

4.2 | Model predictions with various salt concentrations

The model parameters of the CR-B electrode system obtained by fitting the data at 5 and 20 mM salt concentrations are used to predict



FIGURE 9 Modeled pore size (d^{pr}) and Stern layer parameters α and β correlated with specific surface area (A^{sp}) ; points: parameters obtained from this work; lines: trend lines using Equations (22) and (23)

the salt adsorption and electrode charge in a wide range of concentrations from 2 to 100 mM at a constant electrode voltage of 1.2 V. As mentioned in Section 2, the condensation theory is only applicable to dilute solution before the predicted σ^{crit} reaches a maximum. The CR-B electrode with a pore size of 3.3 nm has the maximum σ^{crit} of 1.4 μ C/cm² at 45 mM. The σ^{crit} above 45 mM is assumed to be a constant value of 1.4 μ C/cm². Figure 8 shows that the modeling results well capture the salt adsorption and electrode charge data in a wide range of external NaCl concentrations from 2 to 100 mM. The model prediction is satisfactory considering the standard deviations of experimental data to be around 1 mg/g for salt adsorption and 5 C/g for electrode charge. The EDL model also predicts the maximum salt adsorption at around 5 mM suggested by the data. From the modeling point of view, the maximum salt adsorption is resulted from the tradeoffs between the electrode charge and the critical charge density. At a constant applied voltage, the electrical potential model predicts that the electrode charge increases with increasing salt concentration. On the other hand, the counterion condensation theory calculates a higher critical charge density as the salt concentration increases, reducing the salt adsorption by counterion condensation. The results

are governed by the applicable Creative Commons.

successfully demonstrate the predictability of the EDL model developed in this work.

4.3 | Interpretations of model parameters

Figure 9 shows that the model parameters d^{pr} , α , and β are highly correlated to the specific surface area. It was reported that the AC-1, AC-2, CDC-1, and CDC-2 electrodes have pore sizes at 0.7- 2 nm^7 and the TiC-CDC, HIPE SiC-CDC, and OM SiC-CDC electrodes have pore sizes at 0.7-4 nm.⁸ The d^{pr} identified to be 2–5 nm is consistent with the pore size distributions reported in literature. The pore sizes obtained in this work also well follow the expected trend that smaller pores generally provide higher specific surface areas.

The Stern layer model parameters α and β obtained are indicative of the Stern layer structure. The effective relative permittivity can be used to quantify the composition of the dielectric media on the surface of porous materials.³¹ The Stern layer is expected to be a mixture of vacuum/air and water molecules, which have a relative permittivity of 1 and 6, respectively at 298.15 K. The relative permittivity of water under a strong electric field reduces from 78 to 6 due to the dielectric saturation effect.²⁹ Therefore, the ε_{st} is expected to be in between 1 and 6 when the Stern layer is not fully covered with water molecules.

The ε_{st} can be calculated from α assuming the $d_{\alpha=0}^{st}$ is the thickness of a single-layer water molecule at 3 Å. The ε_{st} inferred from the modeling results in this work ranges from 1 to 2.5 as the specific surface area decreases from 2720 to 1130 m²/g. The fact that the ε_{st} is lower than 6 implies the Stern layer is not fully covered by water molecules. This is consistent with the results from prior MD simulations that the ions adsorbed in the micropores are not fully hydrated.¹⁴ The average hydration number per counterion in the micropores was found to decrease with increasing surface charge density as the counterions reside close to the charged surface at the expense of losing hydration shells. The dehydration is especially significant in the electrodes that have smaller pore sizes.¹⁶ The decreasing ε_{st} with increasing specific surface area (i.e., small size of pores) is also in line with MD simulation results.

The trend of the compression factor β further confirms the hypothesis above. A greater β implies the Stern layer can be compressed more easily as the σ increases because fewer water molecules lie between the counterions and the electrode.

4.4 | Effect of specific surface area

Prior experimental studies have compared the salt adsorption performance at different specific surface areas of the electrode. The inverse relationship was found between the NaCl adsorption (CDC-1 > CDC-2 > AC-1 > AC-2) and the specific surface area (AC-2 > AC-1 > CDC-2 > CDC-1) at a constant electrode voltage.⁷ The non-monotonic trend of NaCl adsorption with the specific surface area was reported, following the electrode type A7 (670 m²/g) > A5 (480 m²/g) > A10



FIGURE 10 Modeled salt adsorption and surface charge density with varied specific surface areas (A^{sp}) using generic EDL model; E = 1.2 V; T = 298.15 K; external salt concentration = 5 mM; $V^{pr} = 0.8 \text{ ml/g}$; $d^{pr} = 3 \text{ nm}$; α , and β are calculated by Equations (22) and (23), respectively.

 $(1050\ m^2/g)\approx A15\ (1890\ m^2/g)^3.$ Another study also showed the non-monotonic behavior that the Na_2SO_4 adsorption is at a minimum when the specific surface area is $1500\ m^2/g.^{32}$ The reported results contradict the common view that the salt adsorption capacity increases monotonically with the specific surface area and has not been well understood.

A generic model generalized from the eight CDI electrodes studied in this work is employed to investigate the effect of the specific surface area on salt adsorption. The α and β are correlated with the specific surface area using the empirical correlations with selected equation forms that give the best fittings.

$$\alpha = 1.97 \ln A^{sp} - 12.4, \tag{22}$$

$$\beta = 0.32 A^{sp} + 282,$$
 (23)

where the α is in Å; the β is in m⁴/C²; A^{sp} is in m²/g.

Other electrode characteristic parameters and CDI operating conditions are fixed as constant so that the effect of specific surface area can be isolated. The d^{pr} , V^{pr} , external salt concentration, and the electrode voltage are fixed at 3 nm, 0.8 ml/g, 5 mM, and 1.2 V, respectively. Figure 10 shows the salt adsorption and the surface charge density with varied specific surface areas from 1000 to 3000 m²/g.

The non-monotonic relationship suggested by prior data is also predicted by the generic EDL model. The tradeoff between the surface charge density and the surface area is the cause. At a constant applied voltage, the surface charge density decreases with increasing specific surface area, implying the electrodes with smaller pore sizes require a higher electrode voltage to polarize the surface charge. Following the hypothesis in Section 4.3, because the ions are adsorbed in the micropores with incomplete hydration shells, the lack of water molecules in the Stern layer that serve as dielectric buffer makes the surface charge polarization less effective especially for electrodes with

9 of 11 | AIChE JOURNAL

small pore sizes (i.e., high specific surface area). The dilution effect of the electrode charge by the high surface area is another contribution to the low surface charge density. As the specific surface area continues increasing (above 1800 m²/g), the high surface area eventually outweighs the decrease of the surface charge density and results in higher salt adsorption.

When below 1000 m²/g, it is expected that the increase of the salt adsorption levels out as the specific surface area continues to decrease because the α and β ultimately settle to constants as the Stern layer is fully covered by water molecules and does not contribute to the increase of the surface charge density anymore. The generic EDL model successfully reproduces the puzzling relationship between the salt adsorption and the specific surface areas observed in prior experimental results and gives insights into the optimal electrode design for CDI processes.

5 | CONCLUSIONS

A novel EDL model was developed to intercorrelate the salt adsorption, the electrode voltage, and the surface charge density in the CDI process for desalination. The EDL model calculates the salt adsorption by considering the contributions from the counterion condensation and the diffuse layer sorption. Manning's counterion condensation theory was extended to two-parallel plate geometry that resembles charged micropores. The electrode voltage is calculated by accounting for the potential differences in the Stern layer and diffuse layer.

The EDL model accurately correlates the experimental salt adsorption and electrode voltage data at the surface charge density of $0-5 \ \mu\text{C/cm}^2$ for eight porous carbon electrodes with specific surface areas from 1130 to 2720 m²/g. The counterion condensation dominates the salt adsorption as the operating surface charge density exceeds the critical charge density predicted as $0-1 \ \mu\text{C/cm}^2$ by the counterion condensation theory. The EDL model also well predicts the salt adsorption and electrode charge in a wide range of external NaCl salt concentrations from 2 to 100 mM at a constant electrode voltage of 1.2 V.

The physical significance of the model parameters was examined. The fact that the fitted micropore sizes decrease with increasing specific surface areas is qualitatively consistent with the expected trend. Interpreting the modeling parameters α and β suggests that the ions are adsorbed in the micropores with incomplete hydration shells, consistent with the findings from prior MD simulations. The generic EDL model successfully reproduces the non-monotonic relationship between the salt adsorption and the specific surface area at a constant electrode voltage observed in the experiments and provides the explanation from a modeling perspective. Having demonstrated superior accuracy and predictability, the new EDL model could be a useful tool contributing to CDI process development while giving insights into optimal electrode design. Upon the successful demonstration in the CDI system, the counterion

condensation theory has great potential to be applied to more electrochemical processes and facilitate process development.

NOTATION

Symbols

	-	
	А	electrode surface area for diffuse layer sorption (m^2)
	A ^{sp}	specific surface area (m^2/g)
	A ^{pr}	specific surface area of cathode or anode per weight of elec-
		trode pair (m^2/g)
	AN	anion
	CN	cation
	C_i^{bk}	concentration of ion <i>i</i> in the bulk $(1/m^3)$
	C_i^{pr}	the average concentration of uncondensed ion <i>i</i> in the dif-
	,	fuse layer $(1/m^3)$
	d st	the thickness of the Stern layer (m)
	d st	the thickness of the Stern layer at zero surface charge den-
	8-0	sity (m)
	d ^{pr}	pore size (m)
	Е	electrode voltage (V)
	kв	Boltzmann constant (J/K)
	Nad	total salt of adsorption per weight of electrode pair $(1/g)$
	Ncond	salt of adsorption by counterion condensation per weight of
	sun	electrode pair $(1/g)$
	N ^{df}	salt of adsorption by diffuse layer sorption per weight of
	Suit	electrode pair (1/g)
	n	number of data points
	Q	specific electrode charges in cathode or anode per weight of
		electrode pair (C/g)
	<i>q</i> _e	elementary charge (C)
	T	system temperature (K)
	V	solution volume for diffuse layer sorption (m^3)
	V ^{sp}	specific total volume (m^3/g)
	V ^{pr}	specific volume of cathode or anode per weight of electrode
		pair (m^3/g)
	Y ^{model}	modeled value of data point k
	Yexp	measured value of data point k
	Z _i	signed charge number of ionic species i
Greek letters		
	α	Stern layer modeling parameter (m)
	β	Stern layer compression factor (m^4/C^2)
	$\Delta \phi^{ m st}$	unsigned electrical potential difference in the Stern layer (V)
	$\Delta \phi^{df}$	unsigned electrical potential difference in the diffuse layer (V)
	£0	dielectric constant of vacuum $(C/V - m)$

 ϵ_s relative permittivity of solvent

 ε_{st} relative permittivity in the Stern layer

 κ Debye parameter (1/m)

 λ_B Bjerrum length (m)

u stoichiometric coefficient of electrolyte

 σ surface charge density on the electrode (C/m²)

 σ^{eff} effective surface charge density (C/m²)

 σ^{crit} critical surface charge density (C/m²)

Superscripts

anode anode *cathode* cathode

Subscripts

an anion

- cn cation
- co coion
- ct counterion

AUTHOR CONTRIBUTIONS

Yu-Jeng Lin: Conceptualization (equal); data curation (lead); formal analysis (lead); funding acquisition (supporting); investigation (lead); methodology (lead); project administration (equal); resources (supporting); software (lead); supervision (supporting); validation (lead); visualization (lead); writing – original draft (lead); writing – review and editing (supporting). **Chau-Chyun Chen:** Conceptualization (equal); data curation (supporting); formal analysis (supporting); funding acquisition (lead); investigation (supporting); methodology (supporting); project administration (equal); resources (lead); software (supporting); supervision (lead); validation (supporting); visualization (supporting); writing – original draft (supporting); writing – review and editing (lead).

ACKNOWLEDGMENTS

Funding support is provided by the U.S. Department of Energy under the grant DE-EE0007888. The authors gratefully acknowledge the financial support of the Jack Maddox Distinguished Engineering Chair Professorship in Sustainable Energy sponsored by the J.F Maddox Foundation.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

ORCID

Yu-Jeng Lin bhttps://orcid.org/0000-0002-9399-6390 Chau-Chyun Chen bhttps://orcid.org/0000-0003-0026-9176

REFERENCES

- Oren Y. Capacitive deionization (CDI) for desalination and water treatment-past, present and future (a review). *Desalination*. 2008; 228(1-3):10-29.
- Li HB, Pan LK, Zhang YP, et al. Kinetics and thermodynamics study for electrosorption of NaCl onto carbon nanotubes and carbon nanofibers electrodes. *Chem Phys Lett.* 2010;485(1–3):161-166.
- Huang ZH, Wang M, Wang L, Kang F. Relation between the charge efficiency of activated carbon fiber and its desalination performance. *Langmuir*. 2012;28(11):5079-5084.
- Han LC, Karthikeyan KG, Anderson MA, Wouters JJ, Gregory KB. Mechanistic insights into the use of oxide nanoparticles coated asymmetric electrodes for capacitive deionization. *Electrochim Acta*. 2013; 90:573-581.

- Nordstrand J, Dutta J. Dynamic Langmuir model: a simpler approach to modeling capacitive deionization. J Phys Chem C. 2019;123(26): 16479-16485.
- Porada S, Bryjak M, van der Wal A, Biesheuvel PM. Effect of electrode thickness variation on operation of capacitive deionization. *Electrochim Acta*. 2012;30(75):148-156.
- Porada S, Weinstein L, Dash R, et al. Water desalination using capacitive deionization with microporous carbon electrodes. ACS Appl Mater Interfaces. 2012;4(3):1194-1199.
- Porada S, Borchardt L, Oschatz M, et al. Direct prediction of the desalination performance of porous carbon electrodes for capacitive deionization. *Energy Environ Sci.* 2013;6(12):3700-3712.
- Biesheuvel PM, Porada S, Levi M, Bazant MZ. Attractive forces in microporous carbon electrodes for capacitive deionization. J Solid State Electrochem. 2014;18(5):1365-1376.
- Wang S, Wang DZ, Ji LJ, Gong QM, Zhu YF, Liang J. Equilibrium and kinetic studies on the removal of NaCl from aqueous solutions by electrosorption on carbon nanotube electrodes. *Sep Purif Technol.* 2007;58(1):12-16.
- Chen ZL, Song CY, Sun XW, Guo HF, Zhu GD. Kinetic and isotherm studies on the electrosorption of NaCl from aqueous solutions by activated carbon electrodes. *Desalination*. 2011;267(2–3):239-243.
- 12. Hou CH, Huang CY. A comparative study of electrosorption selectivity of ions by activated carbon electrodes in capacitive deionization. *Desalination*. 2013;314:124-129.
- Kastening B, Heins M. Properties of electrolytes in the micropores of activated carbon. *Electrochim Acta*. 2005;50(12):2487-2498.
- Kalluri RK, Konatham D, Striolo A. Aqueous NaCl solutions within charged carbon-slit pores: partition coefficients and density distributions from molecular dynamics simulations. J Phys Chem C. 2011; 115(28):13786-13795.
- Kalluri RK, Ho TA, Biener J, Biener MM, Striolo A. Partition and structure of aqueous NaCl and CaCl₂ electrolytes in carbon-slit electrodes. *J Phys Chem C*. 2013;117(26):13609-13619.
- Bo Z, Yang H, Zhang S, Yang J, Yan J, Cen K. Molecular insights into aqueous NaCl electrolytes confined within vertically-oriented graphenes. *Sci Rep.* 2015;5:14652.
- Mao Y, Ardham VR, Xu L, Cui P, Wu D. Insight into electrosorption behavior of monovalent ions and their selectivity in capacitive deionization: an atomic level study by molecular dynamics simulation. *Chem Eng J.* 2021;415:128920.
- Manning GS. The critical onset of counterion condensation: a survey of its experimental and theoretical basis. *Ber Bunsenges Phys Chem*. 1996;100(6):909-922.
- Huang QR, Dubin PL, Moorefield CN, Newkome GR. Counterion binding on charged spheres: effect of pH and ionic strength on the mobility of carboxyl-terminated dendrimers. J Phys Chem B. 2000;104(5):898-904.
- Guo X, Kirton GF, Dubin PL. Carboxylated ficolls: preparation, characterization, and electrophoretic behavior of model charged nanospheres. J Phys Chem B. 2006;110(42):20815-20822.
- Zhang H, Dubin PL, Kaplan J, Moorefield CN, Newkome GR. Dissociation of carboxyl-terminated cascade polymers: comparison with theory. J Phys Chem B. 1997;101(18):3494-3497.
- 22. Manning GS. The interaction between a charged wall and its counterions: a condensation theory. J Phys Chem B. 2010;114(16):5435-5440.
- Manning GS. Limiting laws and counterion condensation in polyelectrolyte solutions. I. Colligative properties. J Chem Phys. 1969;51(3):924-933.
- 24. Yu Y, Yan N, Freeman BD, Chen C-C. Mobile ion partitioning in ion exchange membranes immersed in saline solutions. *J Membr Sci.* 2021;620:118760.
- 25. Manning GS. Electrostatic free energies of spheres, cylinders, and planes in counterion condensation theory with some applications. *Macromolecules*. 2007;40(22):8071-8081.
- 26. Manning GS. Counterion condensation on charged spheres, cylinders, and planes. J Phys Chem B. 2007;111(29):8554-8559.

11 of 11 AIChE JOURNAL

- 27. Zhao R, Biesheuvel PM, Miedema H, Bruning H, van der Wal A. Charge efficiency: a functional tool to probe the double-layer structure inside of porous electrodes and application in the modeling of capacitive deionization. J Phys Chem Lett. 2010;1(1):205-210.
- Parsegian VA, Gingell D. On the electrostatic interaction across a salt solution between two bodies bearing unequal charges. *Biophys J*. 1972;12(9):1192-1204.
- 29. Bockris JOM, Reddy AKN, Gamboa-Aldeco M. *Modern Electrochemistry*. Vol 2A. 2nd ed. Kluwer Academic Publishers; 2002.
- Macdonald JR. Theory of the differential capacitance of the double layer in unadsorbed electrolytes. J Chem Phys. 1954;22(11):1857-1866.
- Chan CY, Knight RJ. Determining water content and saturation from dielectric measurements in layered materials. *Water Resour Res.* 1999; 35(1):85-93.

32. Oda H, Nakagawa Y. Removal of ionic substances from dilute solution using activated carbon electrodes. *Carbon*. 2003;41(5):1037-1047.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Lin Y-J, Chen C-C. Modeling salt adsorption in electrical double layer for capacitive deionization. *AIChE J.* 2023;69(5):e18018. doi:10.1002/aic.18018