Capacitive deionization (CDI) is an emerging desalination technology based on the same charge storage principles as in electrical double-layer supercapacitors (EDLC’s). In this study, electrodes of differing thicknesses were tested using constant current (CC-CDI) and constant voltage (CV-CDI) operational modes in order to study the best way of sequestering the highest amount of ions under different salt concentration scenarios. CV-CDI was used to calculate electrode time constants (RC) and thereby determine a suitable current density for desalinating the solution. Results showed that the voltage pulse produced a fast but heterogeneous layer of ion adsorption, presumably, on the most accessible part of the electrode surface. Thus, volumetric specific capacitance under CV-CDI mode might vary from 17–24 F cm⁻³ and 14–20 F cm⁻³ for 50 μm and 180 μm electrodes, respectively. Nevertheless, results demonstrated that, under the constant current mode, it is possible to increase charge storage by 30% for a CDI cell consisting of thin electrodes and as much as 80% for thicker electrodes simply by controlling current density and, therefore, the rate capability. Moreover, the analysis of the charge efficiency indicated that a proper selection of the current density can result in efficiencies above 80% regardless the salt concentration scenario.

The impact of water has on the production of energy and vice versa is unquestionable. Water is used to generate and transmit energy, and, at the same time, massive amounts of energy are needed to collect, clean, move and dispose of water. This link between water and energy production has been defined as the water-energy nexus. During the last decades, the relevance of the water-energy nexus has been expanded with the introduction of new energy and water production technologies affecting the demands of water and energy. In this context, brackish water desalination and treatment and reuse of effluents from different type of processes (municipal and industrial wastewater) for distinct applications (mainly agriculture, industrial wastewater) for distinct applications (mainly agriculture, and others like Singapore even human consumption) using energy-efficient technologies is becoming of increasing concern.

With the aim of facing these issues, Capacitive Deionization (CDI) technology has been proposed as an opportunity to produce clean water while at the same time storing energy. CDI is an electrochemically controlled desalination technology that removes ions from salt water by electrosorption via a two-step, non-faradaic process occurring in the electrical double layer region of porous electrodes. In a first stage (charging), the electrodes are polarized (either by applying a constant voltage or current) forcing in this way the ions present in the feed water to be electro-adsorbed. Subsequently, as soon as the water reaches the demanded quality, the salt desorption step (discharging) begins by switching the current/cell potential or short-circuiting the cell. This means that CDI mechanism is based on the same principle as EDLC’s which store energy in the double-layer formed at electrode/electrolyte interface. Thus, electric charges are accumulated on the electrode surface and ions of counter charge are arranged on the electrolyte side of that interface. This idea of storing energy while delivering water has drawn the interest of the CDI scientific community leading to recent studies focused on the energy recovery approach. Besides this advantage, CDI is also reported to have some other advantages over more established desalination methods. These include the operation at low voltages, in comparison with electrodialysis, or the lack of high pressures for water recovery, in contrast with membrane technologies. Therefore, the study of CDI technologies based on the knowledge obtained from research conducted in the field of EDLC could be considered a paradigm of the water-energy nexus.

Following this idea, since the electrode materials in EDLC’s are typically constructed using porous carbon materials with medium to high specific surface area (400–1100 m²·g⁻¹) and a very low electrical resistivity (less than 40 mΩ·cm⁻¹), they could be considered also suitable for the electrosorption of anions and cations. Thus, inexpensive activated carbons having a large surface area and an adequate pore size distribution strongly contributes to an increase in the gravimetric capacitance of these electrodes. In addition to the capacity of storing ions in the EDL, which is tied directly to salt adsorption capacity (SAC, mg·g⁻¹), another relevant parameter is the rate capability of EDLC or the rate of sequestering these ions in the porous electrodes. In this case, the rate capability would be linked to the average salt adsorption capacity (ASAR, mg·g⁻¹·min⁻¹), defined in the CDI literature as the amount of salt removed normalized by the mass of electrode/active material and duration of normalizing step or the entire CDI cycle. The rate capability of electrodes employed as EDLC is usually assessed evaluating the time constant that is defined by two components, its capacitance and its series resistance (ESR). Since these parameters constitute a highly relevant property of EDLC technology, the authors believe that this variable could be also used to tune electrode materials for optimizing the CDI process.

In this work, the behavior of the electrosorption – desorption processes using electrodes with different thickness were studied under differing values of water salinity and varying operational conditions employing constant voltage and constant current pulses. Thus, the main electrochemical parameters of CDI were evaluated in a flow cell assembled with electrodes prepared by a doctor-blading procedure that allowed us to control the film thickness of the carbon electrodes. In order to examine how the electrode thickness affects the rate of ion electrosorption into these porous carbon electrodes, the adsorption capacity of carbon film electrodes was theoretically derived from capacitance as a function of the film thickness. The adequate ion transport velocity through the pores of these materials was separately analyzed, from which a current density-dependence has been predicted.
Experimental

Preparation of electrodes.—The particular electrode design employed in our CDI system is shown in Fig. 1A. It consisted of carbon films coated on titanium foils. Activated carbon slurries were prepared using appropriate ratios (8:1:1) of activated carbon (Picactif BP 10, specific surface area = 2400 m²·g⁻¹), polyvinylidene fluoride (PVDF) from Sigma-Aldrich as a polymer binder, and Vulcan XC-72R (CABOT Corporation), respectively, in an n-methyl pyrrolidone solvent (NMP). These materials were mixed in a planetary ball mill before being spread by a doctor-blading technique onto a 0.025 mm thick titanium foil employed as a current collector. The casting knife gap between the knife blade and carrier determines the thickness of the carbon layer. The successful formation of defect free electrodes was achieved by gentle solvent evaporation, as cracking and peeling of the carbon films during drying can be caused by rapid solvent removal. Therefore, after doctor-blading, the electrodes were kept under vacuum initially for 30 minutes at 25 °C and subsequently heated inside at 140 °C oven (2 °C·min⁻¹ ramp) for 4h. Following the electrode preparation steps, we obtained cells with controllable carbon thickness and mass loading properties. It should be noted here the difficulties related with preparing reproducible thin film carbon electrodes. Excessive thickness leads to cracks in electrodes and too thin carbon films caused non-homogeneous active material, making the results not reproducible. Thus, only electrode samples that had an appropriate ratio of active mass to thickness were selected for the purpose of this study. The electrode thickness was measured using a micrometer (Mitutoyo Co.). Samples had mass loadings of 1 mg·cm⁻² and 8 mg·cm⁻², respectively. The electrode density was determined from the area of the electrode multiplied by the thickness of the electrode material, where the thin electrodes showed 0.24 g·cm⁻³ and the thicker ones 0.45 g·cm⁻³ on average.

CDI system.—Studies were conducted in a single-pass reactor under a flow-by hydraulic configuration (Proingesa Co., Spain). The cell design is shown in Fig. 1B. It consists of two sided electrodes that separated by an insulated spacer of 4 mm in thickness. The cell was held together using two steel plates and six bolts that allowed for the dismantling and reconstruction of the cell. The flow circuit consisted of a Masterflex Model 77521–47 pump fitted with a Masterflex pump head, Type 7518-00, interconnected with Viton tubing. The tubing was connected to the cell entry and exit with PTFE connectors. NaCl reagent (98% purity, Sigma-Aldrich) was used as received. Aqueous solutions of 50 mM and 3.5 M salt concentrations were freshly prepared using ultra-pure water (18MO·cm resistivity) from a Milli-Q Integral water purification system. Typically, experiments were performed at a temperature of 298 K and employed 40 cm³ of electrolyte. The pump was calibrated to provide a flow rate of 11 mL·s⁻¹ through the interelectrodic gap. In addition, unless otherwise stated, each experiment was started using a new pair of electrodes. This system allows for ensuring an adequate electrochemical analysis (i.e. capacitances, charge efficiencies). In this fashion for a given concentration of ions, we could quantitatively determine the effect of the electrode thickness on the process. It is important to stress a distinction between the electrochemical measurements performed here and those typically used in other studies based on the salt adsorption. The reactor used here is designed for evaluating charge storage capacitance rather than parameters such as the SAC (mg·g⁻¹) or ASAR (mg·g⁻¹·min⁻¹).

Electrochemical measurements.—The electrochemical performance of the electrodes was tested by chronopotentiometry and chronocoulometry, using a Biologic VMP3 multichannel potentiostat–galvanostat (Biologic, France) coupled with EC-Lab v10.18 software. Complementary, cyclic voltammetry tests were performed for each electrode thickness in K₂SO₄ 0.5 M solution by applying a window voltage from −0.4 to 0.8 V under a scan rate range from 5 to 200 mV·s⁻¹. Electrochemical impedance spectroscopy was also performed using a frequency range from 200 kHz to 10 MHz with a potential amplitude of 10 mV.

The CDI performance of the activated carbon electrodes was evaluated by batch mode experiments conducted using the same experimental procedure as the one reported in a previous publication. From the charge–discharge test profiles, adsorption capacities were determined on the ninth out of 10 cycles, to assure dynamic equilibrium conditions. Capacitance has been calculated integrating the current signal with time, and after dividing by the voltage, we obtained the potential amplitude of 10 mV. The CDI performance of the activated carbon electrodes was evaluated by batch mode experiments conducted using the same experimental procedure as the one reported in a previous publication. From the charge–discharge test profiles, adsorption capacities were determined on the ninth out of 10 cycles, to assure dynamic equilibrium conditions. Capacitance has been calculated integrating the current signal with time, and after dividing by the voltage, we obtained the potential amplitude of 10 mV. The CDI performance of the activated carbon electrodes was evaluated by batch mode experiments conducted using the same experimental procedure as the one reported in a previous publication. From the charge–discharge test profiles, adsorption capacities were determined on the ninth out of 10 cycles, to assure dynamic equilibrium conditions. Capacitance has been calculated integrating the current signal with time, and after dividing by the voltage, we obtained the potential amplitude of 10 mV.

Figure 1. (A) Schematic figures of CDI electrodes with different AC thickness, 50 μm and 180 μm, employed in this work. (B) Basic scheme of the CDI cell.

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Figure 2. Current Density-Time profiles of the CDI-system tested using a CV-CDI Mode and Nyquist diagram for electrodes having 50 \( \mu \text{m} \) and 180 \( \mu \text{m} \) in thickness under different salt conditions: (A) and (B) under \( c_{\text{salt}} = 50 \text{ mM} \), (C) and (D) at \( c_{\text{salt}} = 3.5 \text{ M} \) salt concentration.

drop and the increase of the energy consumption per amount of salt removed. As an indication of these reactions, pH fluctuations or bubbling phenomena might occur. Since none of these indications were observed during our experiments, it is considered that the extension of the faradaic reactions during the CDI operation was limited. Therefore, the electrochemical behavior of this CDI system can be represented primarily by the electrical double-layer capacitance caused by the electrostatic attractive force of the activated carbon electrodes. During testing, conductivity, pH and temperatures were measured periodically (HANNA Instruments HI 2550 pH/ORP & EC/TDS/NaCl Meter).

Results and Discussion

**Effect of electrode thickness on CDI operation using a constant voltage mode.**—To understand the charging/discharging behavior of the system as well as the re-arrangement of ions within the carbon porous network under electrochemical reaction, experiments using the potential step method (chronoamperometry) were initially performed on the prepared carbon electrodes. A charging potential of 1.2 V was applied followed by a discharging step in which a cell potential of 0.0 V was established. As result, the obtained current transients were analyzed (Fig. 2). Electrodes of 50 and 180 \( \mu \text{m} \) thickness were employed in these experiments. This implies that different mass loadings, 1 and 8 mg · cm\(^{-2}\), respectively, were used in the CDI-cell. Note that our standard way of defining specific capacitance (C) in this work is per mass of one electrode (F · g\(^{-1}\)) or per volume occupied by the active material of one electrode (F · cm\(^{-3}\)), see Equation 1:

\[
C = \frac{2 \int_{t_1}^{t_2} i(t) \cdot dt}{\Delta V \cdot Y_{\text{electrode}}}
\]

where \( i \) is the current (A), \( t_1 \) and \( t_2 \) are the time window limits (s), \( \Delta V \) the potential applied (V), and \( Y \) the mass (g) or the volume (cm\(^{-3}\)) of one electrode.

Results of the determination of specific capacitance for brackish water (\( c_{\text{salt}} = 50 \text{ mM} \)) are displayed in Fig. 2A showed that when a potential was applied to the electrodes, the current increases sharply and later decreases exponentially approaching zero following the typical profile previously reported for CV-CDI experiments.\(^9,43\) The initial current density peaks for the electro-adsorption process were observed to be similar to those for the desorption process. This provides some indication of the reversibility of the electro-adsorption process and the lack of faradaic processes. Coherently, the calculated coulombic efficiency reached values over 90% in both cases and only slight pH changes were detected.

As Fig. 2A shows, the highest values of specific capacitance in F and F · m\(^{-2}\) were found when thick electrodes were employed (180 \( \mu \text{m} \)). An important increment of the specific capacitance values with the increase of the electrode thickness was also observed by Andres et al.\(^{39}\) when cyclic voltammetry experiments were performed using carbon electrodes of five different thicknesses. In
addition, this result is also in accordance with previous CDI and MCDI reports\textsuperscript{36-38,40,45} in which the increase of the mass loading led to a higher removal of ions and consequently to a larger capacity of storing ions in the electrical double layer. However, results of Fig. 2A also revealed that the mass loading increase results in a specific capacitance drop in terms of $F \cdot g^{-1}$. In a similar way, Kim et al.\textsuperscript{36} reported a decay in the specific capacitance (measured by electrochemical impedance spectroscopy) and the salt electrosorption capacity for the thicker electrodes (experiments were performed with 200, 300 and 400 $\mu m$ electrodes) when the amount of salt removed was normalized by electrode mass. On the other hand, we noted that the degree of utilizing the electrodes in volumetric terms (F$ \cdot$ cm$^{-1}$) does not seem to depend significantly on electrode thickness at this concentration (17 vs. 20 $F \cdot$ cm$^{-1}$). To explain this seeming anomaly, one must consider that, the active material is distributed over the current collector in such a way that the thick electrode has a much higher activated carbon density (i.e., per occupied volume of electrode) than the thin electrode (451 vs. 212 mg cm$^{-3}$). This behavior indicates that an increase in the thickness may not be equivalent to a proportional increase in the usable mass of the electrodes.\textsuperscript{37} Different hypotheses have been provided in the literature attempting to explain this fact. Apparently, thick electrodes allow for having an active material in a more compact form than when thinner carbon films (50 $\mu m$) are prepared. This packing effect of activated carbon has been reported by other authors\textsuperscript{35,46} and could impact the CDI performance reducing the sites available for ions to be adsorbed inside these porous electrodes. Additionally, Kim et al.\textsuperscript{36} noted that the ion penetrability (defined as the penetration depth of an AC signal with respect to the average pore length) was reduced when the thickness of the electrodes increased noting that thick electrodes are less favorable for the ion diffusion inside the electrode. Nyquist plot response of 50 $\mu m$ and 180 $\mu m$ in a 50 mM electrolyte solution shown in Fig. 2B allowed us to determine the charge-transfer resistance (RCT) from the second intersection of the Nyquist plot response of 50 $\mu m$ and 180 $\mu m$ was confirmed the hypothesis based on the increase of the contact resistance between current collector and porous electrode when thicker electrodes are employed. In this sense, previous studies conducted by Qu et al. determined that the RCT poses the main contributor to the equivalent series resistance\textsuperscript{37} impacting directly on the EDLC time constant. Experiments conducted in brine water (c$_{salt}$ = 3.5 M), shown on Fig. 2C and Fig. 2D, are intended to obtain a better understanding of the electro adsorption rate of the EDLC electrodes is correlated with the time constants of these materials. The time constant is directly tied to ion transport inside the porous structure of the electrodes and is thickness-dependent. This parameter is considered to be highly important in the design of CDI systems.\textsuperscript{33,35,52,53} When a potential difference is applied to a discharged capacitor, charging does not occur instantly. The capacitor acquires a certain charge per unit of time depending on its capacity and circuit resistance. The equations defining this process are the following:

$$q_t = Q_f (1 - e^{-t/RC})$$

$$i_t = I_0 e^{-t/RC}$$

Where $q_t$ and $i_t$ are the charge on capacitor (C) and the current density ($A \cdot g^{-1}$) in the circuit at certain time, $Q_f$ is the final value of charge (C), which increases asymptotically until the maximum charge of the capacitor is reached. $I_0$ is the initial peak current (A). After a time ($t$, units) equal to RC (that is a combination of equivalent series resistance, $R$, and capacitance, $C$), the current in the circuit falls to $1/e$ ($\leq 0.368$) of its initial value. At this time, the charge on the capacitor has reached a fraction ($1 - 1/e$) ($\leq 0.632$) of its final value. The $RC$ product of EDLC electrodes is therefore a measure of the capacitor charging rate and so called time constant.\textsuperscript{35,54} When $RC$ is small, the capacitor charges quickly; when it is larger, the charging process takes longer.

Figs. 3A and 3B show the capacitor charge of the CDI-systems versus time plots recorded in CV-CDI experiments for electrodes with different thicknesses in $c_{salt}$ = 50 mM and $c_{salt}$ = 3.5 M. The initial charge on these capacitors is considered zero. The charge then rises for all of the capacitors to 0.632, the equivalent to 63% of the maximum theoretical capacitance of the capacitor (63% $\cdot$ Q) according to Eq. 1. After some time, the curve approaches asymptotically to 95% of the maximum theoretical capacitance (95% $\cdot$ Q), a point at which one can estimate the maximum capacitance of the system.
As expected for a double layer capacitor system, time constants depend mainly on the thickness of the carbon film at constant salt concentration showing a higher rate capability in the thin electrode: $c_{\text{salt}} = 50 \text{ mM}; \tau = 9 \text{ s (50 } \mu \text{m)}$ and $\tau = 35 \text{ s (180 } \mu \text{m)}$; $c_{\text{salt}} = 3.5 \text{ M: } \tau = 3 \text{ s (50 } \mu \text{m)}$ and $\tau = 12 \text{ s (180 } \mu \text{m)}$. This outcome agrees with the studies of Qu et al.\textsuperscript{55} concerning the characterization of the resistances in CDI systems when different operational modes are employed. The authors noted that the addition in resistance in the CV-CDI mode (as a result of the electrode thickness increase) leads to an extension of energy consumption as well as charging time, and consequently, to the reduction of salt removal rate in the ion adsorption cycle.

From an analysis of the estimated maximum capacitance, one can see that the resistivity of the electrolyte is not trivial because differences for the same electrode thickness are observed. For instance, when the electrolyte concentration is increased, the volumetric capacitance slightly increases in the case of the CDI system assembled with thin electrodes (from 17 to 19 F cm$^{-1}$), while the specific capacitance in the system equipped with thick electrodes is reduced from 21 to 15 F cm$^{-1}$. This is in contrast to the thought that it is reasonable to expect that adsorption capability should have increased with the conductivity of the solution. It is important to note that, under the conditions studied, a range of 15–21 F cm$^{-1}$ of volumetric capacitance can be established as the adsorption capability of CDI-system assembled with these carbon film electrodes (50 $\mu$m–180 $\mu$m) when a CV-CDI mode is used. To explain this, one must consider that at CV-CDI mode in such thick-film carbon design, ion transport can find limitations with respect to accessing the inner pore sites of the electrodes provoking ions to be adsorbed first in the external part of the electrode making it even more difficult access the inner part. Because of this, the overall salt adsorption of the system (per total volume) decreases when we add extra thickness, despite the fact of increasing the active material. Cyclic Voltammetry experiments performed by Kim et al.\textsuperscript{36} with electrodes of different thicknesses in 1 M NaCl solution showed how the increase of the scan rate (from 2 to 50 mV s$^{-1}$) led to the distortion of the quasi-rectangular shape of the cyclic voltammogram. In the case of the thicker electrode, this distortion was more relevant. This revealed the retarded current response of the thicker electrode when high voltage pulses (scan rate) were applied as a result of the higher resistance to the ion transportation through the porous carbon electrode. Because of this behavior, the thicker electrodes presented the worst rate capability. In Fig. 4 cyclic voltammograms of different thickness under 100 mV s$^{-1}$, 20 mV s$^{-1}$ and 5 mV s$^{-1}$ confirmed previous statements. Under low scan rates conditions, thicker electrodes showed rectangular shape as well as an increase in the area of the voltammogram, directly related to energy storage, in comparison to thinner electrodes that showed a more stable performance in terms of specific capacitance regardless of scan rate. Thus, under such conditions in which time of charging is consequently longer (5 mV s$^{-1}$, Fig. 4A), ions could diffuse through the porous internal structure leading to a better electrical response even in thicker electrodes. Therefore, at such a low energy demanding condition there is no significant effect on the specific capacitance related to electrode’s thickness but to the mass loading of the electrodes. However, when the scan rate was increased at 20 mV s$^{-1}$ (Fig. 4B), the distortion of the voltammogram was observed for 180 $\mu$m electrodes (Fig. 5B) while the quasi-rectangular shape was still being maintained in the case of the 50 $\mu$m electrodes. This behavior was even more evident when the scan rate was increased to 100 mV s$^{-1}$ (Fig. 4C) revealing the significant influence of the electrode thickness when fast charging rates were employed. Finally, in Fig. 4D these statements were clearly supported: the larger the electrode thickness, the lower rate capability when scan rate increases. For 50 $\mu$m electrodes, the specific capacitance was maintained even under high scan rates.

**Effect of electrode thickness when operating the CDI system in a constant current mode.**—Despite the fact that the CV-CDI mode has been widely applied in a vast majority of the CDI laboratory test,\textsuperscript{56,57} CC-CDI mode studies are becoming more relevant during more recent years.\textsuperscript{42,48,58–61} Reasons supporting the use of CC-CDI mode include: i) a higher control of the charging rate than in the CV-CDI mode, in which concentration polarization might occur at the electrodes surface so that secondary reactions can also take place giving rise to a loss in coulombic efficiency. This leads to the limitation of the initial current peak observed in the CV experiments that significantly impacts increasing charge efficiency and decreasing energy consumption up to 30%.\textsuperscript{56,58} ii) Moreover, the CC mode allows one to control the time that the electrode potentials are close to the values where faradaic reactions occur.\textsuperscript{61} In this way, longer times of CDI cycling can be reached without experiencing the effects of the electrode oxidation such as the decay of the electrosorption capacity or an increment in energy consumption.\textsuperscript{98,92–94} iii) Regarding energy recovery, both aforementioned aspects would have a positive impact on the amount of energy that might be recovered in the electrode regeneration step in which salt desorption is performed. Thus, the higher control of the charging process along with the lack of faradaic reactions would lead to a higher amount of energy stored during the charging step of the CDI. Moreover, Kang et al.\textsuperscript{21} determined that the amount of energy recovered using the CC-CDI mode was higher than in the case of the CV-CDI mode when a buck-boost converter employed to investigate energy recovery. By applying a constant current pulse (CC-CDI mode), one might expect ion adsorption to occur in a more orderly fashion and occupy most of the volume within the

Figure 3. Capacitor charge of the CDI-system for different salt concentration and electrode’s thickness (A) $c_{\text{salt}} = 50 \text{ mM}$ with 50 $\mu$m and 180 $\mu$m electrodes. (B) $c_{\text{salt}} = 3.5 \text{ M}$ with 50 $\mu$m and 180 $\mu$m electrodes.
electrode structure. However, in order to accomplish this, one should use an adequate current density which will depend on the amount of active material present and the geometric area of the electrode. iv) Additionally, more constant effluent concentrations have been reported using CC than CV.58,60,65 On the other hand, studies comparing both modes of operation observed faster and higher salt removal using the CV-CDI mode.56 However, one must caution that in the CV-CDI, results suggest that fast charging appear to lead to a rapid ion adsorption process on the electrode surface producing a dramatic reduction of the salt concentration. Kim et al., showed by potential sweep experiments performed in a single pass mode that an increase in scan rate resulted in a sharp and quick drop in the salt concentration of the effluent.36 Despite the important drop in the electrolyte conductivity, the overall salt adsorption capacity (mg g\(^{-1}\)) and charge (C g\(^{-1}\)) of the CDI process dropped when faster charging scan rates (mV s\(^{-1}\)) were selected. These results are in accordance with the behavior of the electrodes having different thicknesses observed in Fig. 4.

In order to optimize the use of the active material in the electrode structure, we compare specific constant current pulses starting with values equivalent to the time constant (\(RC\)) obtained in previous CV-CDI mode testing. Subsequently, current densities were reduced based on our hypothesis that this would allow ions to be stored in a more appropriate manner within the porous structure of the electrode (Fig. 5). Cell potential versus time plots recorded (shown in Figs. 5A and 5C) showed a linear response with a positive slope during charging and a linear but negative slope during discharge, as expected for a double layer capacitor system. A CV step was established between charge and discharge with the aim of reducing the influence of the previous charge to the performance of the discharge and vice versa, as has been explained in our previous studies.32,41 In this way, only the effect of the electrode thickness and salt concentration was evaluated. The specific capacitance values obtained for \(c_{\text{salt}} = 50\) mM (Fig. 5A) when 50 \(\mu\)m electrodes thickness were used, showed a stable electrosorption capacity at \(\approx 20\) F cm\(^{-3}\) over the entire range of current rates that were applied. Interestingly, the specific capacitance increased to 27 F cm\(^{-3}\) (beyond the maximum capacitance obtained for the CV-CDI mode) when the CDI cell assembled with 180 \(\mu\)m was tested using the CC-CDI mode of operation at the lowest current density. This supports the concept that, under these conditions (\(<250\) mA g\(^{-1}\)), a slow diffusion of ions into the electrode material occurred. In this way, the ions had access to the inner part of the electrode increasing the usable volume of active material in the electrodes and consequently boosting the volumetric specific capacitance. As has been reported in the supercapacitor field,66 higher ion diffusion barriers in the inner region of the electrode were observed in the case of thicker electrodes resulting in higher internal resistance. Depending on the charging current employed, this would lead to a different performance in terms of ion storage in the EDL. In addition, the stable electrosorption capacity obtained for thin electrodes seems to be mainly due to the fact that the electrode is thin enough to reduce the internal resistance providing an easier access for the ions to penetrate into the pores within the 3D electrode structure. Therefore, the variation of the charging current in the case of the thinner electrode did not affect volumetric specific capacitance as in the thicker electrodes.

![Figure 4](link-to-image-url) Cyclic voltammogram of 50 \(\mu\)m and 180 \(\mu\)m electrodes in 0.5 M K\(_2\)SO\(_4\) at different scan rates (A) 5 mV s\(^{-1}\) (B) 20 mV s\(^{-1}\), (C) 100 mV s\(^{-1}\), (D) Specific capacitance of 50 \(\mu\)m and 180 \(\mu\)m electrodes in 0.5 M K\(_2\)SO\(_4\) vs. Scan rates.
Figure 5. (A) Specific capacitance versus current density (mA g\(^{-1}\)) results of the CDI unit assembled with 50 \(\mu\)m and 180 \(\mu\)m electrodes under \(c_{\text{salt}} = 50\) mM salt conditions. Inset: Charge-discharge profiles corresponding with the same experimental conditions. (B) Charge efficiency versus current density (mA g\(^{-1}\)) of the CDI units tested using 50 \(\mu\)m and 180 \(\mu\)m electrodes under \(c_{\text{salt}} = 50\) mM salt conditions. (C) Specific capacitance versus current density (mA g\(^{-1}\)) results of the CDI unit assembled with 50 \(\mu\)m and 180 \(\mu\)m electrodes under \(c_{\text{salt}} = 3.5\) M salt conditions. Inset: Charge-discharge profiles corresponding with the same experimental conditions. (D) Charge efficiency of the CDI units tested using 50 \(\mu\)m and 180 \(\mu\)m electrodes versus current density (mA g\(^{-1}\)) under \(c_{\text{salt}} = 3.5\) M salt conditions.

The charge efficiency, which is the ratio between the electrical charge stored and the energy used for charging, quantifies how much of the energy employed in the charging process has been consumed in the adsorption of ions during the deionization step\(^{67}\). Results displayed in Fig. 5B and Fig. 5D are in accordance with the literature showing a reduction of charge efficiency when higher charging currents were employed\(^{48,56}\). It is interesting to note that the charge efficiency of the CDI-system assembled with 180 \(\mu\)m electrodes is more strongly affected by changing current densities than when using 50 \(\mu\)m electrodes, as the thicker materials hinder fast diffusion of ions into the porous electrode. Thicker electrodes showed larger average pore length. Thus, when higher current densities are established, the charging time is reduced and the voltage drop in the diffuse layer is increased, thereby reducing the charge efficiency. On the other hand, this adsorption rate-controlling method does not significantly affect the charge efficiency of the CDI-system assembled with thin electrodes. Therefore, it can be concluded that thin electrodes show a higher stability in performance when the CC-CDI mode was employed using different charging currents.

At a higher solution concentration (\(c_{\text{salt}} = 3.5\) M, Fig. 5C), due to the abundant amount of ions in the electrolyte, the effect of higher ion diffusion barriers in the inner region is even more remarkable being detected also in the CDI-system assembled with 50 \(\mu\)m electrodes thickness. When the process is adjusted to a lower rate of applied current, the CDI-system shows a considerable increase in ion adsorption capacity, up to 25 F\(\cdot\)cm\(^{-3}\) for the thin electrodes and 30 F\(\cdot\)cm\(^{-3}\) for the thick electrodes. This is once again beyond the range defined as the adsorption capability when a CV-CDI mode was used (indicated by the shaded rectangle). This means that by controlling current it is effectively possible to adjust the adsorption rate to distribute the ions into the inner pore sites of the electrodes. In addition, it should be stressed that this result agreed with the ones obtained from the CV experiments, in which low scan rates (slow capacitor charging mode) led to the highest values of capacitance for both pair of electrodes.

The increase of the specific capacitance (higher levels of charge stored) during the charging step would also impact energy recovery leading presumably to a higher energy retrieved during the ion desorption step. The percentage of energy recovered in the case of 50 \(\mu\)m electrodes varies between 50–66% whereas lower ratios were achieved by using 180 \(\mu\)m electrodes, 40–55%. This inference was also extracted by Kang et al. who achieved higher energy recovery...
ratio using lower charging currents and higher salt concentration in their feed solutions.\textsuperscript{21}

In Fig. 5D, the charge efficiency suggests the strong dependence of current rate on the distribution of ions across the entire structure of the electrodes. Both systems, assembled with thin and thick electrodes, experience diffusive problems that decrease performance when high current rates are applied. This reduction in charge efficiency is particularly severe at current densities associated with the time constant (RC) obtained using the CV-CDI mode (625 and 5400 mA \cdot g\textsuperscript{-1} for thin and thick carbon films, respectively).

These results correlate well with the deionization step when a constant voltage pulse is applied to a process in which ions are adsorbed very rapidly mainly on the more external part of the electrodes. This is explained by the inaccessibility of the small micropores in the carbon that cannot refill the major volume fraction of porous matrix but are not easily available when fast kinetics occur.\textsuperscript{18}

In contrast, if the adsorption rate is adjusted to a given current density, ions are adsorbed homogeneously both on the superficial as well as within the inner part of the electrode. Therefore, the usable three-dimensional structure of electrode will be enlarged, increasing the net capacity of ion removal and achieving a higher deionization efficiency. Furthermore, time constant (RC) analysis may be used as a tool to determine the most optimum operating current using the equivalence with the time constant (RC) obtained in CV-CDI mode testing. The time constants in the case of the CC-CDI mode tests were calculated by multiplying the ohmic drop measured at the beginning of deionization step and the capacitance.

Based on the above analysis, we may associate the optimum current density of the CDI system assembled with electrodes having a 50 \(\mu\text{m}\) thickness to 1.9t time constant for brackish water treatment, and 2.2t for brine waters. The time constants obtained for the CDI-system assembled with electrodes of 180 \(\mu\text{m}\) in thickness are 1.4t for brackish water treatment and 1.8t for brine waters. Our analysis of the time constants, allow one to select the adequate current density for each electrode thickness and for each salt concentration in order to achieve a larger usable three-dimensional portion of the porous electrode. Indeed, this particular manner to extract the time constant can be used in the design of CDI systems for example by characterizing the performance of the reactor to determine the appropriate power density aiming to maximize the use of 3D structure of the electrodes. Furthermore, the characterization proposed here allows one to evaluate the CDI performance for water treatment application in unusual situations; for example when changes in the surface chemistry of the carbon electrodes arises over time, as has been reported by many groups in recent years.\textsuperscript{9-13} This optimization would also apply in the case of the unexpected accumulation of contaminants or unforeseen increases in the water flow rate happens. By doing this, one can evaluate the CDI operating mode in advance, extracting the time constant for different situations in which flexible operational patterns need to be implemented for effective ion adsorption.

In this sense, other potential applications of this time constant analysis might include being a unique and novel technique for monitoring the state of health of CDI systems. Deionization is ever increasingly used in difficult configurations with very demanding duty schedules and feed water compositions. Thus, effective management and control of CDI systems to detect or prevent electrode degradation as well as to guarantee a safe operation is extremely important, and developing these news tools for practical applications may be essential. We therefore believe that these operational aspects are relevant to the lifetime of a CDI system operating in real world scenarios.

In terms of comparing salt adsorption capacity between CC-CDI and CV-CDI modes of operation, specific capacitances for the charging process for both methods are compiled in Table I. The use of a CV-CDI mode resulted in faster salt adsorption due to stronger electrostatic attraction than that of a constant current mode. However, despite faster salt adsorption obtained using the CV-CDI mode, the CC-CDI mode showed a 25%–35% increase in capacitance when these CDI units were tested with 50 \(\mu\text{m}\) electrodes and a 35%–85% increase the thicker electrodes were employed.

| Table I. Specific volumetric Capacitance (F \cdot cm\textsuperscript{-3}) under different operational modes, electrode’s thickness and salt concentrations. |
|---------------------------------------------------------------|
| Constant Voltage Mode | Constant Current Mode | Improvement% |
|------------------------|------------------------|--------------|
| 50 mM NaCl | 3.5 M NaCl |
| 50 \(\mu\text{m}\) | 180 \(\mu\text{m}\) | 50 \(\mu\text{m}\) | 180 \(\mu\text{m}\) |
| 17 | 20 | 24 | 14 |
| 23 | 27 | 30 | 26 |
| 35 | 35 | 25 | 86 |

These results are consistent with our earlier work in the CDI field,\textsuperscript{42} and suggests that active material selection for providing competitive electro-adsorption systems might not only be related to the surface area of porous carbon electrodes commonly used in CDI systems. In addition, one should choose materials with a given thickness with the proper activated carbon density (i.e., active material per occupied volume of electrode), and control the rate of adsorption for a given concentration of the electrolytes in solution.

Conclusions

This study has shown that the selection of the operational mode is highly relevant because it is directly related to the form in which ions are stored in the electrodes, affecting also electrical energy consumption (i.e. energy recovery) or the charge efficiency of the CDI process. Moreover, this work shows the utility of Time Constant analysis for determining the optimum current density range in which CDI systems operating at CC-CDI mode could achieve the best performance in terms of salt adsorption and charge efficiency. The study of time constants has successfully demonstrated the importance of controlling the rate of ion adsorption in order to assure a correct distribution of ions within the 3D structure of the electrode material. From the results obtained in this work, it is clear that when the CV-CDI mode is used, a distribution of ions through the whole electrode structure is not maximized. This means that ions are adsorbed preferentially only on the most accessible part of the electrode reducing consequently its adsorption capability. However, when the CC-CDI mode experiments were conducted, it was possible by controlling the current intensity to adjust the ion adsorption kinetics achieving higher amounts of charge storage and therefore ions removed from the solution.

Finally, the results reported in this manuscript show that when setting up a CDI system, one should not only consider the selection of the electrode material, but also the manner of placing the material on the current collector (thickness, active material per occupied per unit volume) as well as the most suitable operational mode based on water salinity. An appropriate decision will lead to increase the ion removal capability and improve energy efficiencies in the CDI process.

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