

A Covalently Integrated Reduced Graphene Oxide–Ion-Exchange Resin Electrode for Efficient Capacitive Deionization

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Capacitive deionization (CDI) is an emerging, cost-effective alternative for energy-efficient desalination technology. Efficient electrode materials based on individual reduced graphene oxide (rGO) nanosheets are produced by functionalizing them with polystyrene (rGO–PS) through an in situ polymerization process involving rGO, styrene monomer, and divinylbenzene. The rGO–PS-integrated composite nanostructures are subsequently functionalized with sulfonate and quaternary amine functionalities to achieve positively and negatively charged electro-adsorbent ion-exchange resins (EAIERs), respectively. These EAIERs ‘molecular constructs’ are used to fabricate CDI electrodes, and deionization is performed to remove various ions. These molecular constructs promote faster charge transfer at the electrode–electrolyte interface and maintained the electrical conductivity of the active rGO. This leads to a high electroadsorption capacity of 15.93 mg g^{-1} of Cl^- using NaCl solution with a conductivity of $802 \text{ }\mu\text{S}$ in laboratory batch experiments, which is approximately five times higher than the adsorption capacity of rGO electrodes reported earlier ($\approx 2\text{--}3 \text{ mg g}^{-1}$) in comparable experimental conditions. No significant Faradaic redox reactions or chemical changes are observed on the electrode surface, which make these electrodes exhibit excellent electrochemical stability even after multiple adsorption/desorption cycles.

terms of equipment and energy consumption.^[6,8–11] Capacitive deionization (CDI) is an emerging technology which involves adsorption and desorption of ions on the electrode surface by application of low potential difference ($\approx 1.2\text{--}1.8 \text{ V}$) across a pair of porous carbon electrodes, thereby making it both energy and cost-efficient compared to other existing desalination methods. When a flowing water stream is passed across a CDI system, cations and anions move toward oppositely charged electrodes and get adsorbed on them, thereby generating deionized and ‘drinkable’ water, starting from brackish water. Subsequently, adsorbed ions can be removed from the electrode by reversing the polarity, thereby regenerating the electrode surface, ready for reuse for next adsorption cycle.^[5] Thus, clean water can be produced continuously by repeating the adsorption and desorption cycles. CDI is a cost-effective, point-of-use method with a high theoretical desalination efficiency.^[5] However, its practical applications for desalination are yet to be recognized at a

The availability of clean potable water at an affordable cost is a growing challenge for mankind. Recently, the drinking water crisis has reached alarming levels due to the increasing population, climate change, and contamination of various water sources.^[1–7] To meet the growing demand for affordable drinking water, several technologies (such as reverse osmosis, ultrafiltration, adsorption, photocatalytic degradation, and distillation) are being utilized, some of which are highly expensive in

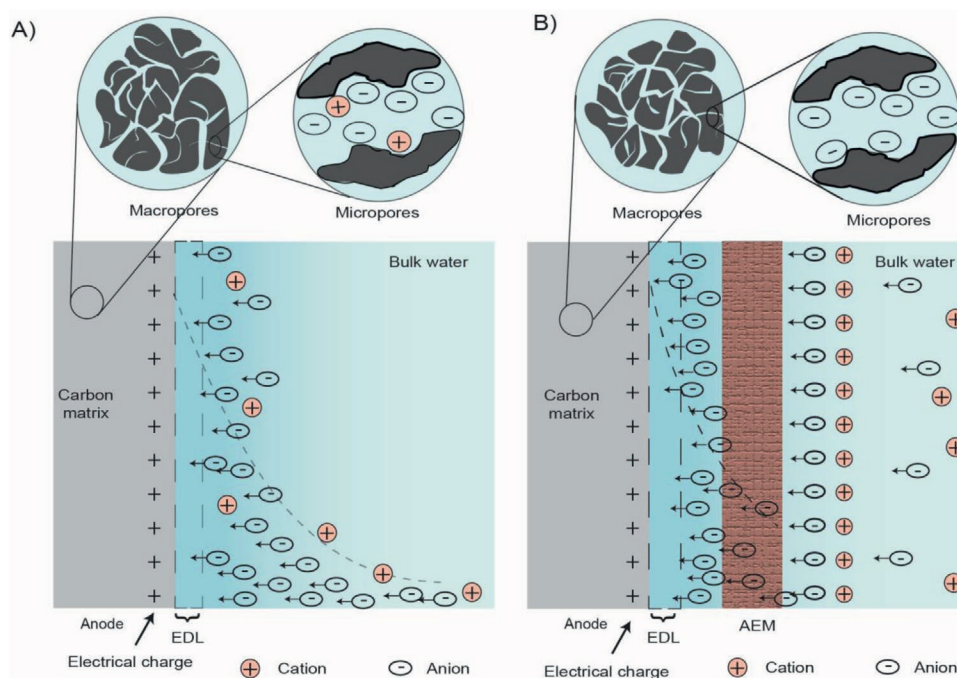
large scale, and research is being carried out to synthesize new materials with improved adsorption capacities.^[5,12–14] Related technologies such as Faradaic deionization and the use of different 2D materials in CDI are also explored intensely.^[15–17]

Various carbonaceous materials and their composites are being used as CDI electrodes because of their high salt adsorption capacities in the range of several mg g^{-1} .^[18–25] Graphene, and graphene-derivatized materials, such as, graphene-like nanoflakes,^[26] activated carbon,^[27] activated carbon nanofiber (ACF),^[28] reduced graphene oxide (rGO),^[27,29] carbon nanotubes (CNT),^[29] graphene–CNT composites,^[29,30] rGO–ACF,^[28] 3D macroporous graphene architectures,^[31] sponge-templated graphene,^[14] graphene– Fe_3O_4 ,^[32] graphene chitosan– Mn_3O_4 ,^[33] rGO–activated carbon composites,^[27] and functionalized graphene nanocomposite,^[34] have been used as CDI electrodes. The adsorption capacities of graphenic composites, such as graphene/carbon nanotube, CO_2 activated rGO, sulfonic functional graphite nanosheets, $\text{SO}_3\text{H}/\text{NH}_2$ graphene/activated carbon, MgAl–Ox/G nanohybrids, 3D-graphene architecture, and graphene sponge measured were 1.4, 6.26, 8.6, 10.3, 13.6,

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Scheme 1. Ions adsorption mechanism for A) CDI and B) MCDI electrodes at the anode, where AEM denotes anion-exchange membrane. The corresponding process occurs at the cathode. (B) shows the enhanced electroadsorption in comparison to (A).

14.7, and 14.9 mg g⁻¹, respectively, for an input of 500 ppm NaCl solution.^[29,35–40]

The main objective of the CDI technology is to make a cost- and energy-efficient desalination process. Thus, synthesizing new materials and improving electrode architecture are the major tasks driving the progress of CDI technology. The electrode's performance largely depends upon the desalination capacity of the electrode materials and initial salt concentration. Mostly, carbon materials are utilized for electrode fabrication, but novel materials can also be integrated with carbon matrix to obtain enhanced electrode performance.^[12] Electrode materials must have a high specific surface area, high electrical conductivity, and high electrochemical stability over different pH and voltage ranges (≈1.2–1.8 V). Additionally, electroadsorption capacity is also affected by total pore volume, pore size, and pore connectivity of the active electrode materials. Furthermore, suitable porosity of the electrode materials, excellent wetting behavior, and high bio-inertness to prevent biofouling are important factors for improving desalination performance. Besides electrode characteristics, input water flow rate, configuration of electrode stacks, lifetime of the electrodes, and the process's cost are other parameters that should be taken into account to design an efficient CDI technology.^[12,41]

Scheme 1 illustrates the adsorption mechanism of regular CDI and membrane CDI (MCDI) electrodes. In a regular CDI, when a voltage is applied across the electrodes, ions with opposite charges also referred to as counter-ions, move toward electrodes of opposite polarity (cations toward cathode and anions toward anode) and are adsorbed within the intraparticle porous network of the carbon electrode, while ions having the same charge (co-ions) are repelled from the electrodes of the same polarity (anions are repelled from cathode and cations are

repelled from anode). The co-ions present in the spacer channel, or separator (a gap between anode and cathode), further prevent the counter-ions from coming in contact with the electrode surface. Moreover, some of the co-ions, which may have accumulated in the micropores/macropores of the electrode, neutralize the adsorbed counter-ions, leading to a decrease in the adsorption capacity of the electrodes. In addition to the aforementioned drawbacks, poor electrochemical stability of regular CDI is another challenge. All of these have resulted in the invention of MCDI. In MCDI, ion-exchange membranes (IEMs, anion-exchange resin on the anode side, and vice versa) are incorporated in front of the carbon electrodes. Membranes containing covalently bound linkers, such as sulfonate or quaternary amine-containing IEMs, are typically used due to their high internal charge, which plays a significant role in selective transport of counter-ions. During MCDI, counter-ions are exchanged through the membrane (cations at cathode and anions at the anode, as the electrodes are coated with cation- and anion-exchange membranes, respectively). They can be adsorbed on the porous carbon surface, resulting in the formation of an electrical double layer (EDL) within the intraparticle nanostructures (micropores) of the porous carbon electrodes.^[42] However, due to presence of a membrane on top of the electrodes, many counterions from the solution pass through the membrane to reach the active electrode surfaces. This movement of counter-ions results in the formation of an enhanced EDL at the electrodes. Moreover, counter-ions are also adsorbed on the respective membrane surfaces. Thus, the co-ions are blocked, and they reside in the vicinity of the membrane in the solution. Net effect is that IERs enhance the adsorption capacity of MCDI electrodes.^[12,42–44] As the membrane is placed right over the carbon surface, the membrane layer extends well into the diffuse layer.

Thus, an MCDI system shows a higher salt removal rate or desalination performance. However, ion removal per unit energy consumption in MCDI is lower compared to regular CDI.^[12,44] Although MCDI exhibits several advantages compared to conventional CDI, its major drawback is the weak adhesion between the electrode material and the IEM, leading to high charge transfer resistance at the electrode–electrolyte interface. Moreover, all the IEMs are hydrophobic and have poor wetting characteristics, which lead to low removal efficiency of the ions, even at low salt concentrations.^[12]

In general, electroactive materials are printed on a stable conducting surface during CDI electrode fabrication. This usually requires the use of a non-conducting binder, such as polyvinylidene fluoride (PVDF) and polyvinyl alcohol, which reduces the available electrochemical surface area and conductivity of the electrode materials. This can be resolved by integrating electro-adsorbent materials with the ion-exchange resin via covalent linkages. Graphene and its derivatives have proved extremely advantageous in this context. Due to its large surface area, high electrical conductivity, and tunable functionality, it is possible to retain the electrodes' adsorption capacity even while maintaining proper covalent linkages. Selective functionalization of rGO with ion-permeable membranes by forming a single molecular construct enables the possibility of enhanced adsorption and ion permeation characteristics.^[45]

In this work, CDI electrodes were prepared by forming covalent linkages between rGO and IERs, which were used for selective anion and cation permeation during the desalination process. This methodology also improves the adsorption capacity of the target ions (counter-ions) and the blocking of the co-ions, allowing rapid desalination of brackish water. By this process, the material retains its conductivity and wetting characteristics, unlike conventional MCDI. It is essential to point out that mixing graphene and ion-exchange resin without any covalent linkage does not produce the desired result.^[46] In MCDI, IER is coated on electrode material through covalent linkages that decrease electrical conductivity of the electrode and simultaneously increase the charge transfer resistance at the electrode/electrolyte interface. However, this can be overcome by molecular constructs. Hence, our materials are expected to exhibit higher adsorption capacity and energy efficiency. Our technology has proved to be suitable for commercial implementation after the evaluation of its performance using various electrochemical and spectroscopic studies.

CDI electrode materials with molecular constructs were synthesized through in situ polymerization of styrene monomer in the presence of rGO. CDI electrodes were fabricated on bare graphite sheets, which were further characterized by different spectroscopic and microscopic techniques. Detailed synthesis and fabrication processes have been discussed in the Experimental Section. **Figure 1A** presents a schematic of the CDI cell integrated with electro-adsorbent ion-exchange resins (EAIERs) electrodes. The EAIERs were coated on graphite sheets, which act as current collectors, and a DC potential (± 1.5 V) was applied to the electrodes to drive the counter-ions to the electrode surface from the input feed water. A spacer was placed between the two electrodes. An expanded view depicts the structure of the molecular construct of both +ve EAIERs and –ve EAIERs, namely cathode and anode, respectively. High-resolution scanning

electron microscopy (HRSEM) images (**Figure 1B,C**) of both the electrode materials are shown in an expanded view in **Figure 1A**. Electron microscopy images using HRSEM (magnified view in **Figure 1A**/**Figure 1B,C**) and TEM (**Figure 1D,E**) confirmed that both the electrode materials had hierarchical structures with multiple rGO sheets arranged in a stacked manner. This structure shows a higher accessible surface area for a large number of ion adsorption/desorption cycles. Characterization of the starting materials is presented in the Supporting Information.

Fourier transform infrared (FT-IR) spectra, shown in **Figure 2** present the vibrational modes of different functional groups of electrode materials. The spectral features are assigned in **Table 1**. A discussion of these features is presented as part of Supporting Information. The aforementioned spectral features validate the covalent linkage between rGO and polystyrene (PS), in addition to the formation of anionic and cationic EAIERs.

Electrochemical adsorption and desorption behavior of both the electrodes was studied using cyclic voltammetry (CV) measurements in a conventional three-electrode configuration. A DC potential was applied at the working electrode (EAIERs coated graphite electrode) with respect to Ag/AgCl electrode, using 1 M NaCl solution, and the resulting capacitive current was measured between the working and platinum mesh counter electrodes. **Figure 3A,B** depicts the cyclic voltammograms obtained at different scan rates from 1 to 1000 mV s^{–1} for cathode and anode, respectively. A noticeable change in the shape of the CV curve at higher scan rates was observed. At lower scan rates, the electrolyte penetrates within the pores of EAIERs unrestricted, which results in the formation of both an electrical double layer capacitance (EDLC) and diffusion capacitance at the interface of the hierarchical surfaces. However, at higher scan rates, ions do not have sufficient time to penetrate within the porous structures due to the ionic transport resistance, which affects the formation of diffusion capacitance at the electrode surface. Scan rate-dependent specific capacitance profiles of both +ve and –ve EAIERs are plotted in **Figure S5**, Supporting Information, demonstrating that electrodes exhibit higher specific capacitance at a lower scan rate and vice versa. This specific capacitance is the contribution of both EDLC and diffusion capacitance. EDLCs are formed at the interfaces due to the high surface charge density of the EAIERs electrodes. The formation of diffusion capacitance largely depends on the electrodes' porosity and the electrical potential applied to the electrodes.

Electrochemical impedance spectroscopy (EIS) was performed to understand the effect of the electrode materials' electronic conductivity on the interfacial (electrode/electrolyte) charge transport property and resulting electroadsorption behavior. EIS was carried out by applying a fixed AC signal of 10 mV at the CDI electrode, and the frequency of the motion was varied from 3 MHz to 5 mHz, simultaneously. The total impedance of the electrochemical cell (adopted with three-electrode configuration) was measured as a function of the applied frequency at the electrode. **Figure 3C,D** shows the Nyquist Plots of +ve and –ve EAIER electrodes (the expanded views are shown in inset), which depicts the variation of the imaginary part of the total impedance with the real part. Each plot is majorly constituted of two impedance regions, a small semicircle at the high-frequency region (3 MHz–1.5 KHz), followed by a straight line

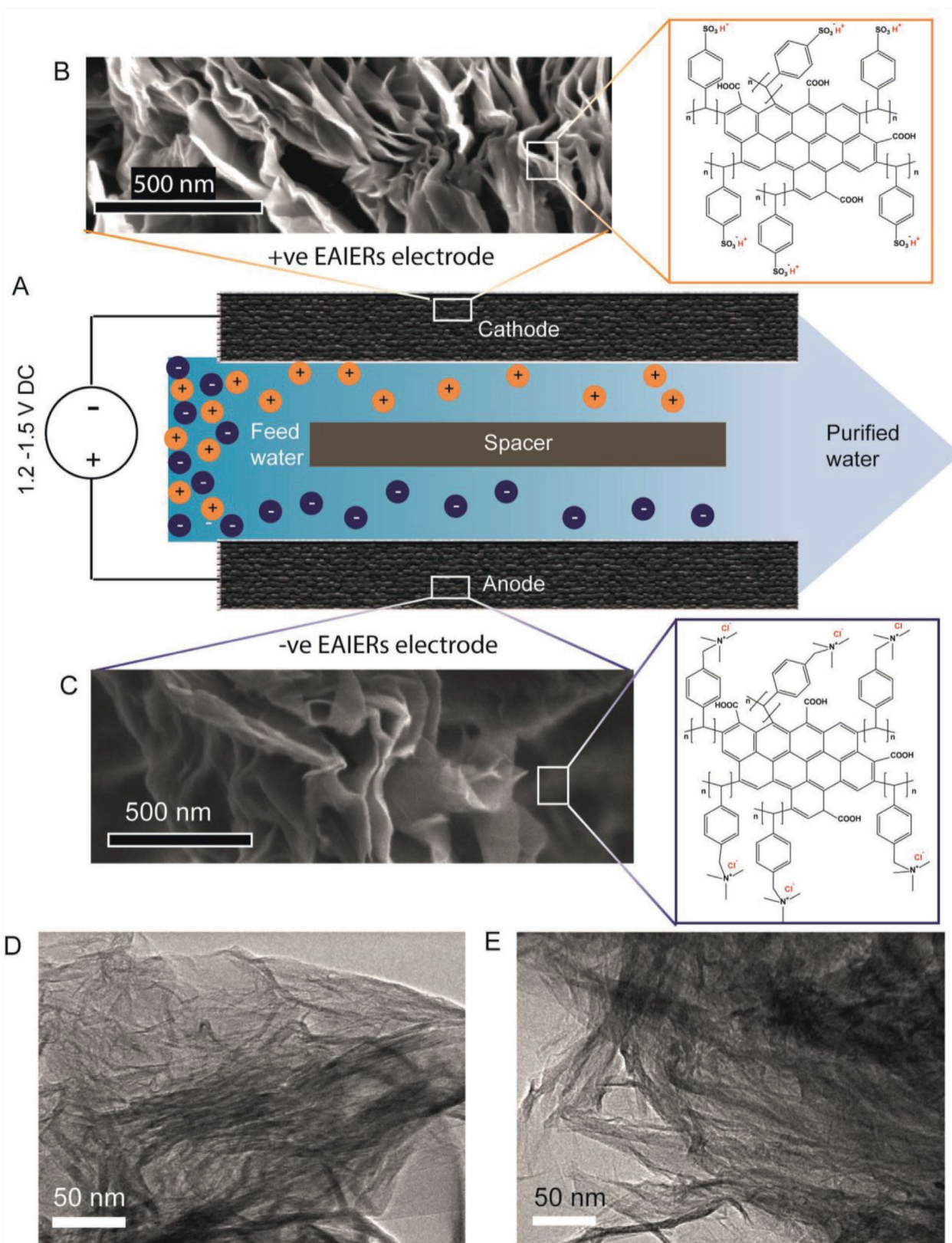


Figure 1. A) Schematic design of a cell with integrated EAIERs (molecular construct) for capacitive deionization (CDI). The rGO sheets have $-\text{COOH}$ functionalization. Expanded views show the HRSEM images (B and C) of +ve and -ve EAIERs, respectively. Corresponding molecular structures are also shown. TEM image of D) +ve EAIERs and E) -ve EAIERs materials. The scale bars are 500 and 50 nm for HRSEM and TEM, respectively.

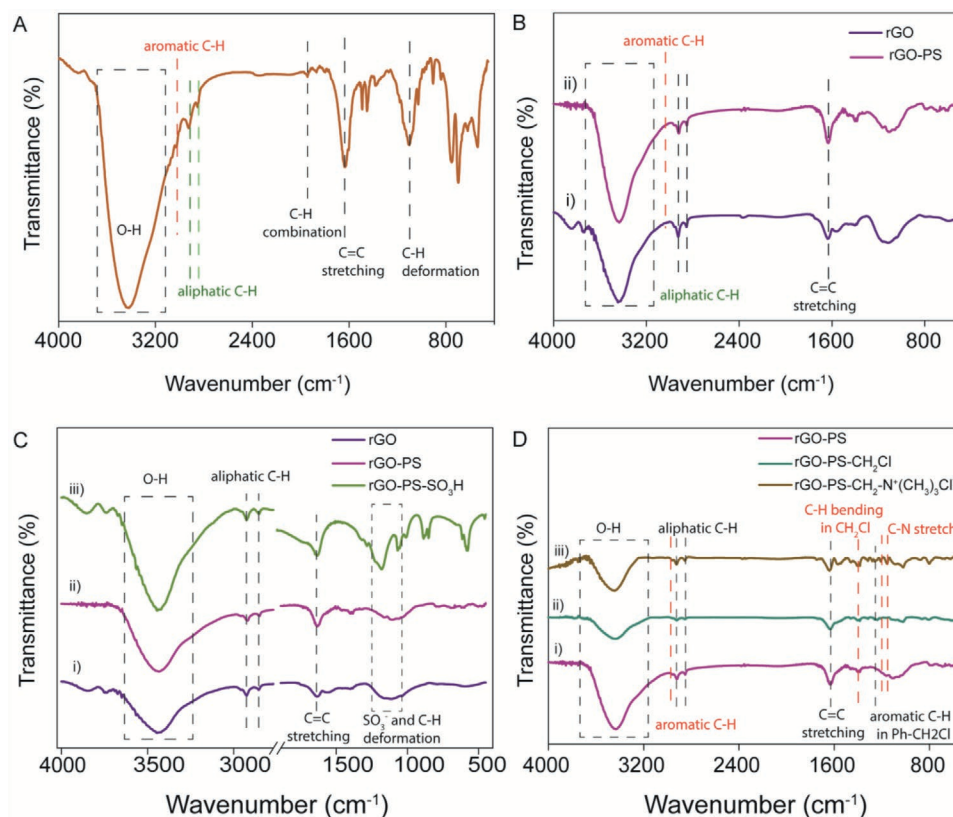


Figure 2. Fourier transform infrared (FT-IR) spectra of A) PS, B) rGO and rGO-PS, C) rGO, rGO-PS, and rGO-PS-SO₃H (+ve EAIERs), and D) rGO-PS, rGO-PS-CH₂Cl, and rGO-PS-CH₂-N⁺(CH₃)₃Cl⁻ (-ve EAIERs). Essential features are labeled. Chemical functionalization is evident.

in the low-frequency area (1.5 KHz–5 mHz). The first intercept of the semicircle (leftmost) is known as the equivalent series resistance (ESR), which is related to the combined effect of the material resistance of rGO-PS, the contact resistance between graphite sheet and the EAIERs coating, and the ionic resistance of the electrolyte (R_s). Thus, the ESR value (1.56 ohm) confirms that the working electrode (EAIERs) retains the conductivity of bare rGO, even after covalent functionalization of rGO with PS. The quasi-semicircle with a small arc radius suggested a low charge transfer resistance at the electrode–electrolyte interface (R_{ct}) for both the electrodes. High conductivity and enhanced surface charge density of EAIERs result in fast electroadsorption of ions. In the low-frequency region, the straight line implies the formation of an EDLC at the electrode–electrolyte interface. Moreover, the straight line parallel to the y-axis

(inset figure) also suggests fast ion diffusion to the electrodes, leading to a low Warburg diffusion resistance (W). Thus, both +ve and -ve EAIERs electrodes have good accessibility for ions to/from an EDL at their surfaces. To sum up, the EAIERs electrodes possess low internal resistance because of the covalent interaction between rGO and PS. Therefore, low R_{ct} is retained in the composite material (rGO-PS), compared to bare rGO.^[47] Figure S6A,B, Supporting Information, represents Bode plots for cathode and anode, respectively, which further confirm the capacitive nature of the electrode. Furthermore, the frequency-dependent phase angle of both the electrodes was determined from the EIS measurement, and these were maximum ($\approx 75^\circ$) for both the electrodes in the low-frequency region. This confirmed the formation of EDL on the electrodes during the adsorption cycle.

Table 1. IR features of PS, rGO, rGO-PS, and -ve and +ve EAIERs, with assignments.

Wavenumber (cm ⁻¹)	Assigned vibrations	Wavenumber (cm ⁻¹)	Assigned vibrations
3450–3520	O–H stretching	1411	aliphatic C–H in chloromethyl –CH ₂ Cl
2850–3035	aliphatic and aromatic C–H stretching	1261	aromatic C–H of Ph–CH ₂ Cl groups
1740–1745	C=O stretching of a carboxylic acid group	1224 and 1180	S=O bond of SO ₃ H
1631–1638	C=C stretching	1208 and 1154	C–N stretching frequencies of the tertiary amine group
1450	C–H deformation		

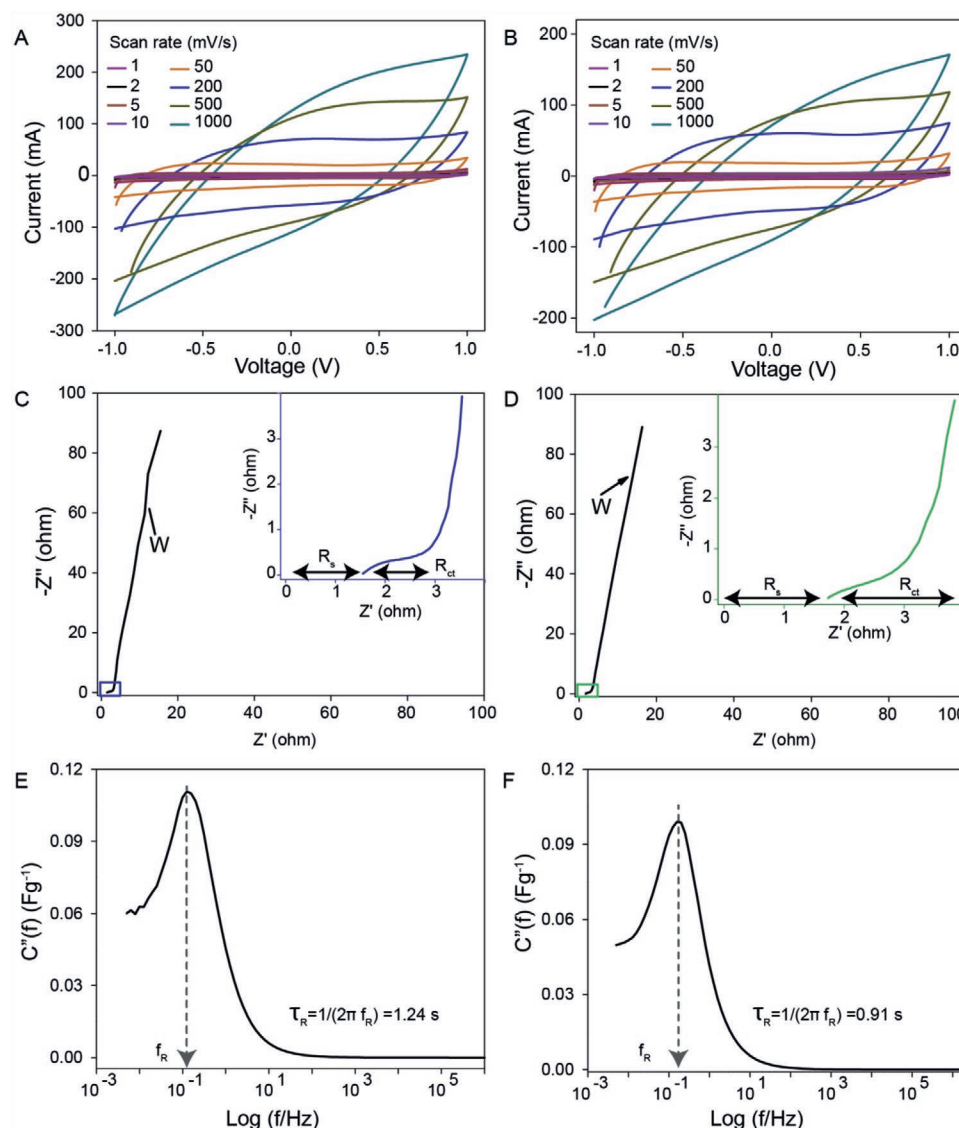


Figure 3. Cyclic voltammetry (CV) of A) +ve EAIERs electrode (cathode) and B) -ve EAIERs electrode (anode) at different scan rates; Nyquist Plots of C) +ve EAIERs electrode (the inset chart shows the magnified high-frequency region) and D) -ve EAIERs electrode (the inset chart shows the magnified high-frequency region); E,F) imaginary part of complex capacitance (C'') versus frequency for cathode and anode, respectively, in 1 M NaCl electrolyte.

Electrochemical adsorption and desorption rates of the electrodes and the contribution of EDLC for desalination can be determined qualitatively through frequency-dependent interfacial capacitance analysis. In this context, frequency-dependent variations of both real ($C'(f)$) and imaginary ($C''(f)$) capacitances were calculated through EIS measurements for both the electrodes, and the resulting profiles are shown in Figure S6C,D, Supporting Information, and Figure 3E,F, respectively. Frequency-dependent imaginary capacitance profiles of both electrodes were calculated from Nyquist impedance plots. Figure S6C,D, Supporting Information, show $C'(f)$ profiles were having three distinct regions. In the high-frequency region (1 to 2×10^6 Hz), the capacitance $C'(f)$ becomes almost zero, which indicates that the electrode behaves like a resistor (R). However, in the low-frequency region, the capacitance is almost constant (within $\pm 10\%$) up to a specific frequency (5 – 100 mHz),

indicating adsorption/desorption of ions occurred through physisorption, indicating pure capacitive behavior of the electrodes in this regime. In between high-frequency and low-frequency regions, that is, 100 mHz– 1 Hz, the $C'(f)$ decreases linearly with frequency, which indicates the loss of charge during the adsorption/desorption process. Furthermore, $C''(f)$ profiles for both the electrodes shown in Figure 3E,F represent irreversible energy dissipation and ion relaxation process during adsorption/desorption.^[48] Irreversible energy dissipation is related to loss of charges in the form of heat. It is well known that the adsorption/desorption kinetics of ions depends not only on the electrode's electronic conductivity but also on the electrode surface's structure and porosity.^[25] Since HRSEM and TEM images (Figure 1) of our composite electrodes show a larger number of nanosheets assembled into a wrinkled microporous morphology, the ions which were adsorbed at the outward surface

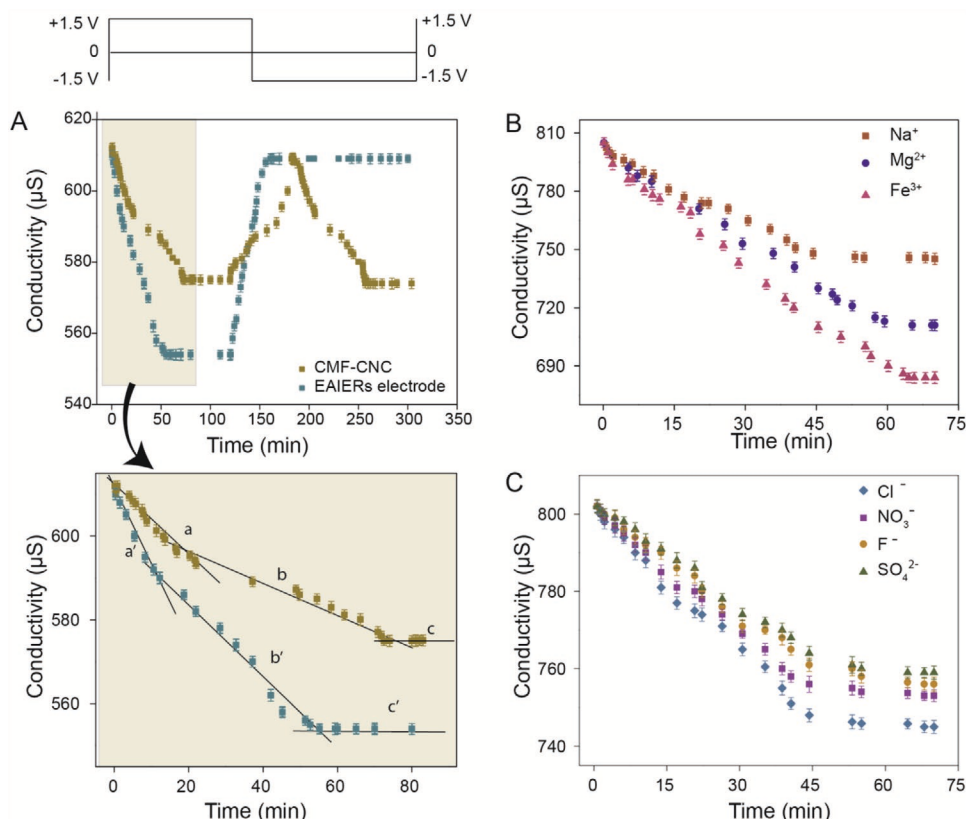


Figure 4. A) Comparison of CDI performance between covalently integrated EAIERs (rGO–PS functionalized) electrode and melamine-functionalized carbon nanocellulose (CMF-CNC) derived electrode in 610 μS NaCl solutions. Electrodesorption kinetics for both the integrated EAIERs and CMF-CNC electrodes are shown in the expanded views below. Three distinct regimes of adsorption are shown, marked with a, b, and c, and a', b', and c' for CMF-CNC and EAIERs electrode, respectively. Variation in the potential of the electrodes with time is shown on top of the (A). CDI performances of EAIERs electrodes using different B) cations (Na^+ , Mg^{2+} , and Fe^{3+}) and C) anions (Cl^- , NO_3^- , F^- , and SO_4^{2-}) with solution conductivity of 802 μS . The operating potential was maintained at 1.5 V during the measurements.

(wrinkled sheets) of hierarchical structures come out with faster desorption kinetics. However, the ions that were adsorbed at the interlayer of the porous structure's nanosheets might not have had sufficient time to desorb entirely before the beginning of the next adsorption cycle.^[49] In Figure 3E,F, the peak maximum represents the frequency at which ions were relaxed or released without facing any resistive barrier due to the contribution of both electronic and ionic conductivities. The relaxation time constant (τ_R) can be calculated from the peak frequency (f_R), and this can be calculated using the equation, $\tau_R = 1/(2\pi f_R)$.^[50] This time constant represents the minimum time required to discharge all the ions from the electrode surface. The value of τ_R was found to be nearly the same for both the electrodes. These values were (1.24 and 0.91 s) comparable to the τ_R value for other rGO based electrodes reported earlier.^[48,50]

Figure S7, Supporting Information, shows a schematic representation of the experimental set-up for analyzing ions undergoing adsorption–desorption during CDI. A DC power source (± 1.5 V) was connected to the electrodes that drive the ions present in the solution toward the electrodes (anions to anode and cations to cathode). A total-dissolved-solids meter was immersed in the solution to measure the time-dependent changes in the solution's conductivity during the adsorption/desorption processes. The adsorption/desorption performance

of EAIERs electrodes was compared with our previously reported work with conventional carbon-based CDI electrodes.^[24] For that, carbon powder prepared from melamine functionalized nanocellulose (MF-CNC) was used for traditional CDI (CMF-CNC). The synthesis protocol of CMF-CNC was reported elsewhere.^[51] A comparative adsorption/desorption study of EAIERs and CMF-CNC electrodes was carried out using an NaCl solution with ionic conductivity of 610 μS . It is evident from Figure 4A that the EAIERs electrodes have higher adsorption capacity (≈ 15.86 mg g^{-1}) than CMF-CNC electrodes (≈ 7.45 mg g^{-1}) for Cl^- ions. In the EAIERs electrodes, the adsorption occurred for the first 58 min, leading to equilibrium. This adsorption equilibrium was allowed to continue up to 120 min. After 120 min, by reversing the applied potential's polarity to the electrodes, the desorption process was initiated. In this time interval, the conductivity of the solution approached an initial value of 610 μS , as all the adsorbed ions were desorbed, and thus, adsorption sites were regenerated. The electroadsorption/desorption remained at equilibrium until the potential was reversed. Similarly, CMF-CNC electrodes were also tested for a comparative study of adsorption and desorption capacities with EAIERs electrodes.

CMF-CNC electrodes required ≈ 73 min to attain the adsorption equilibrium (Figure 4A). By reversing the polarity,

desorption started, and adsorption sites were regenerated at the electrode after 120 min. However, unlike EAIERs, the CMF-CNC electrodes started to adsorb ions before desorption of all the ions from the electrodes, which reflected in the desalination performance of CMC-CNC electrodes. This is the crucial difference between EAIERs and CMF-CNC electrodes in terms of desalination efficiency. Electroadsorption kinetics for the integrated EAIERs and CMF-CNC electrodes are shown as a zoomed-in view of Figure 4A, and the EAIERs electrodes show three distinct adsorption kinetics before reaching the equilibrium. Initially, the adsorption was fast in the first ≈ 11 min, and it was moderate within ≈ 11 –53 min; but in the final ≈ 53 –64 min, adsorption was very slow.

Similarly, CMF-CNC electrodes also showed three distinct kinetics; initially, faster adsorption in the first ≈ 20 min, followed by moderate adsorption during ≈ 20 –71 min, and finally, slower adsorption during ≈ 71 –80 min. These results revealed that EAIERs electrodes have more active adsorption sites than conventional CDI electrodes (CMF-CNC). Furthermore, the covalent linkage between rGO and IER (synthesized material), which maintained the electronic conductivity of the EAIERs electrodes compared to rGO, further reduces the charge transfer resistance at the electrode–electrolyte interface during adsorption/desorption processes. Thus, EAIERs electrodes exhibited faster adsorption/desorption rate at their surfaces, resulting in a higher desalination efficiency than standard MCDI electrodes. In MCDI, the presence of a membrane on top of the electrode surface increases the charge transfer resistance at the electrolyte interface, effectively reducing the overall adsorption capacity of active electrodes. However, high adsorption capacity with faster desorption kinetics was observed for EAIERs electrodes (Figure 4A). Therefore, synthesized materials, which would be more energy efficient (desalination per unit energy consumption, $\text{mg g}^{-1} \text{ watt}^{-1}$) with higher adsorption capacity, could be utilized for developing future CDI electrodes. The comparison of desalination efficiency of different electrode materials in terms of their salt adsorption capacities, reported in the recent past, is shown in Table 2. It is clear that the synthesized EAIERs electrode materials are superior to the reported ones.

Other than surface porosity and electronic conductivity, the electrochemical adsorption capacity of the electrode materials also depends on i) hydrated ionic radii, ii) ionic charge, and iii) initial concentration of the solution. To determine the adsorption capacity, considering the above factors, a set of different cations (Na^+ , Mg^{2+} , and Fe^{3+}) and anions (NO_3^- , F^- , Cl^- , and SO_4^{2-}) were taken. Here, Cl^- ions were chosen as the common anion for all cations, and Na^+ was the common cation for all anions. The electrochemical adsorption–desorption capacity of EAIERs electrodes and corresponding changes in the conductivity of the solution was monitored. Conductivity profiles of the electrolyte containing each of the aforementioned ions during the adsorption–desorption process are shown in Figures 4B,C, and Figures S8, S9, and S11, Supporting Information. A comparative study of the adsorption capacity of EAIERs electrodes was performed in the presence of different cations (Fe^{3+} , Mg^{2+} , and Na^+). Initial ionic conductivity of the solution with each of these ions was maintained as $802 \mu\text{S}$, as shown in Figure 4B. It is evident that the adsorption capacity of the

electrode corresponding to individual cations follows the trend, $\text{Fe}^{3+} > \text{Mg}^{2+} > \text{Na}^+$. It was noticed that the adsorption capacity of the EAIERs electrode increased with an increase in charge of the individual cation. Therefore, properties such as the ionic charge, ionic radii, and hydrated radii of different cations (Na^+ , Mg^{2+} , and Fe^{3+}) and anions (NO_3^- , F^- , Cl^- , and SO_4^{2-}) affect the adsorption capacity. In the case of cations, adsorption capacity increased with an increase in valency; however, the reverse trend was observed in the case of anions (with the same cation, Na^+). The hydrated radius of Fe^{3+} is the largest, and Na^+ is the smallest among these cations. Therefore, adsorption of cations should follow the order, $\text{Na}^+ > \text{Mg}^{2+} > \text{Fe}^{3+}$; however, the reverse trend was observed experimentally. In the case of cations, the charge of the ion is the predominant factor than the hydrated radius. When a potential was applied at the electrodes, the cation with a higher charge should undergo higher adsorption than a lower charged cation. Therefore, trivalent Fe^{3+} was adsorbed at a faster rate than divalent Mg^{2+} , followed by monovalent Na^+ .^[52] However, in the case of anions, adsorption capacity decreases with an increase in the charge of anions. Adsorption capacities for all the anions are shown in Figure 4C. In the case of anions, hydrated radii are more important than their charges. The size of the hydrated radii of anions decreases as $\text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^- > \text{Cl}^-$. Anions with the smallest hydrated radii would pass through the pores efficiently and reach the electrode surface at faster kinetics, and adsorption capacity follows the trend, $\text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{SO}_4^{2-}$.^[3] Conductivity profiles of the solution after electroadsorption in the presence of cations and anions with initial ionic conductivity of 450 and $610 \mu\text{S}$ are shown in Figure S8, Supporting Information.

Adsorption capacities of covalently integrated EAIERs electrodes using various solutions, each with different conductivity, are depicted in Figure S9A–C, Supporting Information. The adsorption capacity of EAIERs electrodes increased with an increase in the concentration of NaCl. The observed values of adsorption capacity were 14.45, 15.86, and 15.93 mg g^{-1} for Cl^- ions of NaCl, with ionic conductivities of 450, 610, and $802 \mu\text{S}$, respectively. The obtained adsorption capacities were much higher in comparison to pristine rGO or graphene-based CDI electrodes (Table 2).

To investigate the reproducibility of the electrode's adsorption/desorption performance, it was carried out with the same measurement for 20 cycles. Four adsorption/desorption cycles were presented in Figure S9, Supporting Information. It was observed that adsorption–desorption efficiency (ratio between adsorption and desorption rate) was the same and remained constant even after 20 cycles (Figure S10, Supporting Information). There was no significant change observed in the desalination efficiency even if the electrode was run for a longer time more than 400 adsorption–desorption cycles. Stability of the electrode was assessed by performing the experiment repeatedly over a period of nearly a year. No noticeable effect in performance was observed. Due to high electrochemical stability of our electrodes during electrochemical cycles, they can be implemented in practical CDI technology.

Figure S11A–C, Supporting Information, shows the conductivity versus time plots upon varying the concentration of MgCl_2 in solution. The adsorption capacities of Mg^{2+} ions were found to be 20.40, 23.51, and 26.63 mg g^{-1} for the input

Table 2. Comparison of electrode materials efficiency in terms of salt adsorption capacity in mg g^{-1} reported in the recent past.

Materials	Initial concentration (mg L^{-1})	Adsorption capacity (mg g^{-1})	Year of publication/Reference
Graphene	86.9	0.88	2012 ^[26]
Graphene	25	1.85	2009 ^[57]
rGO–CA composite	65	3.23	2012 ^[27]
rGO	65	1.8	
Activated carbon	65	1.51	
3D Macroporous graphene architectures	≈ 52	3.9	2013 ^[31]
Sulfonated graphite nanosheet	250	8.6	2012 ^[35]
Sponge-templated graphene	106	4.95	2014 ^[14]
rGO–activated carbon nanofiber (rGO–ACF)	400	7.2	2014 ^[28]
Graphene sponge	500	14.9	2015 ^[40]
Microporous graphene	≈ 74	11.86	2015 ^[58]
3D Porous graphene	300	18.43	2016 ^[59]
Graphene/carbon nanotube	500	1.4	2013 ^[29]
rGO–activated carbon composites	≈ 25	2.94	2012 ^[60]
rGO–resol (rGO–RF)/rGO–CA	40	3.47	2012 ^[61]
Graphene oxide/ZrO ₂	50	6.3	2016 ^[62]
MnO ₂ -Nanorods@graphene	≈ 50	5.01	2014 ^[63]
Sulfonic functional graphite nanosheet	$500 \mu\text{S cm}^{-1}$	8.6	2012 ^[64]
Graphene–Fe ₃ O ₄ (E-Gr-Fe ₃ O ₄)	$300 \mu\text{S cm}^{-1}$	10.3	2015 ^[65]
rGO	$300 \mu\text{S cm}^{-1}$	6.00	
Graphene–chitosan–Mn ₃ O ₄ composites	$100 \mu\text{S cm}^{-1}$	9.32	2015 ^[33]
	$300 \mu\text{S cm}^{-1}$	12.76	
	$500 \mu\text{S cm}^{-1}$	14.83	
3D Graphene architectures	500	14.7	2016 ^[38]
Anion-exchange polymer layered graphene composites (A-NRGS)	$300 \mu\text{S cm}^{-1}$	11.3	2017 ^[66]
	$300 \mu\text{S cm}^{-1}$	8.6	
N-doped rGO sponge composite (NRGS)	$300 \mu\text{S cm}^{-1}$	6.2	
rGO			
Few-layered graphene (HCG)	$50 \mu\text{S cm}^{-1}$	1.72	2015 ^[67]
Highly-crumpled N-doped graphene	$50 \mu\text{S cm}^{-1}$	1.96	
N-doped electrospun rGO–carbon nanofiber composite (NG–CNF)	$\approx 100 \mu\text{S cm}^{-1}$	3.91	2015 ^[68]
SO ₃ H–graphene–carbon nanofibers	400	9.54	2015 ^[69]
SO ₃ H/NH ₂ graphene/activated carbon	500	10.3	2014 ^[36]
Hierarchical hole-enhanced 3D graphene	80	8.0	2018 ^[70]
Spherical macroporous	$0.5 \times 10^{-3} \text{ M}$	5.7	2018 ^[71]
3D intercalated graphene nanocomposite	500	22.09	2018 ^[72]
MgAl–Ox/G nanohybrids	500	13.6	2018 ^[37]
3D channel-structured graphene (CSG)	295	9.6	2019 ^[73]
CO ₂ activated rGO(AGE)	500	6.26	2019 ^[39]
GO/hierarchical porous carbon	55.72	7.74	2018 ^[74]
SiO ₂ activated GO (GR/NMC)	500	18.4	2018 ^[75]
p-phenylenediamine functionalized GO	$\approx 100 \mu\text{S cm}^{-1}$	7.88	2018 ^[76]
Mesoporous G@MC heterostructured	500	24.3	2018 ^[77]
Graphene/Co ₃ O ₄ composite	250	18.63	2018 ^[78]
N-doped graphitic carbon polyhedrons	500	17.77	2019 ^[79]
EAIERS	$802 \mu\text{S cm}^{-1}$	15.93	2020 (This work)

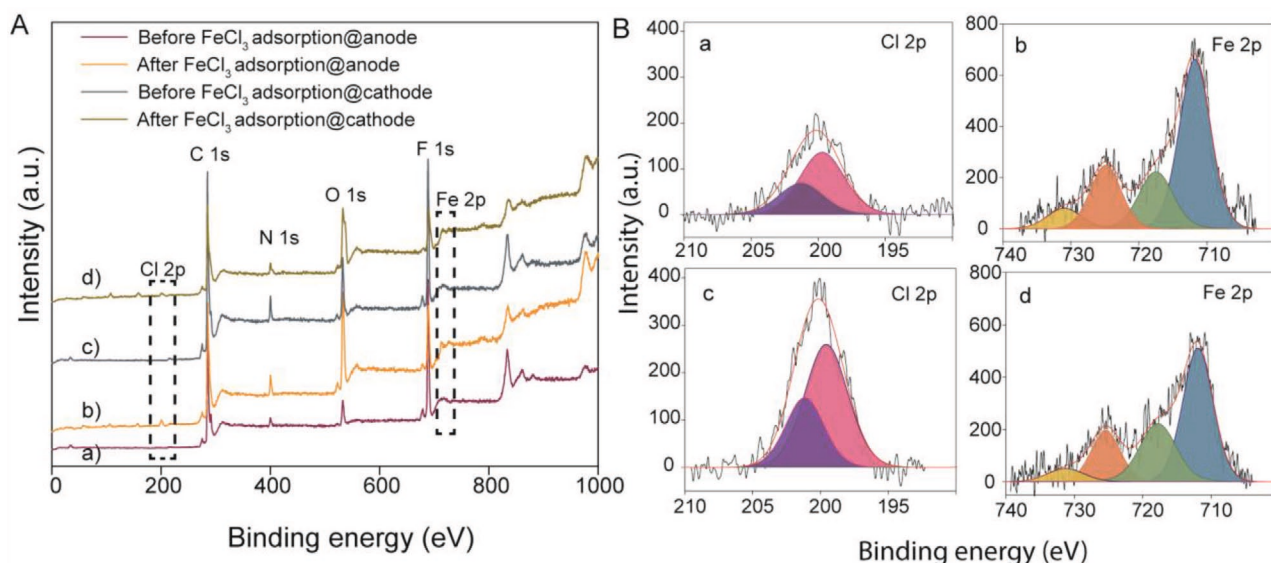


Figure 5. A) XPS survey spectra of the material after single adsorption, a) anode and c) cathode (before adsorption); b) anode and d) cathode (after FeCl₃ adsorption), and B) deconvoluted XPS spectra of a) Cl 2p, b) Fe 2p of the cathode and c) Cl 2p, d) Fe 2p of anode after adsorption of FeCl₃. Peaks appearing at 717.35 eV (green) and 731.34 eV (yellow) are the satellite peaks of Fe 2p_{3/2} (blue) and 2p_{1/2} (brown), respectively.

conductivities of 450, 610, and 802 μS , respectively. Figure S11 D–F, Supporting Information, shows that for Fe³⁺, the values were 28.9, 32.58, and 34.28 mg g^{−1} for initial conductivities of 450, 610, and 802 μS , respectively. It was observed that the adsorption capacities of EAIERs electrodes increased with an increase in the concentration of ions (Figure 4B,C, and Figures S8, S9, and S11, Supporting Information). The observed results, comparable with other reported graphenic composites, revealed that our material exhibited improved adsorption capacity than bare rGO (approximately five times higher than reported) (Table 2).

Further, change in morphology, and chemical composition of the electrode surface, after one electrochemical adsorption cycle was investigated by SEM energy dispersive spectroscopy (EDS) (Figure S12, Supporting Information) and X-ray photoelectron spectroscopy (XPS) analysis (Figure 5), respectively. Before performing these experiments, electrodes were kept in a solution containing MgCl₂ and FeCl₃ for a long time until adsorption equilibrium was achieved. Subsequently, they were washed with deionized water to remove the physisorbed ions. Elemental composition, after electroadsorption of MgCl₂ on the electrode surface, was determined by EDS measurements, and the results are shown in Figure S12A,B, Supporting Information. Mg²⁺ and Cl[−] were adsorbed on cathode and anode, respectively. The inset of Figure S12, Supporting Information, shows the EDS elemental mapping of the ions after physisorption.

Figure 5 shows the XPS survey spectra of both anodic and cathodic EAIERs electrodes before and after the adsorption of FeCl₃. In the XPS survey spectra, no significant changes were observed in the binding energies of carbon, nitrogen, oxygen, and fluorine of both cathode and anode, even after electrochemical adsorption. The XPS survey spectra (Figure 5A) and deconvoluted XPS spectra (Figure 5B) revealed the enhanced intensity of Fe³⁺ and Cl[−] ions at cathode and anode, respectively.

However, small amounts of Cl[−] on cathode and Fe³⁺ on anode were detected at the electrodes, which might be attributed to physisorption.

The electrode's stability during electrochemical measurements is crucial in CDI technology, as adsorption/desorption occurs continuously. Thus, a cyclability test was performed by measuring continuous CV in a 1 M NaCl solution at a scan rate of 50 mV s^{−1}. Figure S13, Supporting Information, depicts CV cycles of +ve and −ve EAIERs electrodes, which revealed that the electrode's adsorption/desorption occurred at the same rate for 400 cycles. CV cycles of both the electrodes exhibited nearly the same current in the anodic and cathodic sweep, demonstrating the electrode's electrochemical stability. Therefore, it can be concluded that no leaching or corrosion occurred on the electrode surface during the desalination process.

The present work describes the preparation of CDI electrodes via in situ polymerization of styrene on rGO to create a single molecular construct for excellent electroadsorption and selective ion permeation. The functionalization of nanostructured rGO–PS composite resulted in positively and negatively charged EAIERs. These molecular constructs preserved the active composite material's electronic conductivity, comparable to bare rGO, thereby promoting faster non-Faradaic charge transfer at the electrode–electrolyte interface. The synthesized EAIERs molecular constructs were used as CDI electrodes for removal of different cations (Fe³⁺, Mg²⁺, and Na⁺) and anions (Cl[−], NO₃[−], F[−], and SO₄^{2−}). The electroadsorption capacity of EAIERs electrode was ≈ 15.93 mg g^{−1} for Cl[−] using 802 μS NaCl solution in lab-scale experiments, the highest observed so far in comparable situations. This occurs as the electrode material has a large electrochemical surface area with a hierarchically porous structure and low interfacial charge transfer resistance. These EAIERs electrodes also exhibited high electroadsorption performance, fast deionization rate, and good regeneration

capability. Thus, we believe that this electrode fabrication methodology could lead to improving the existing membrane-based CDI technology. Molecular construction gives new generation CDI electrodes with enhanced capacity for cost-effective brackish water desalination.

Experimental Section

Materials and Chemicals Used: Natural graphite flakes (95% of carbon) were obtained from Active Carbon India Pvt. Ltd. Ammonia (NH_3 , 30%), hydrazine hydrate (N_2H_4), sulfuric acid (H_2SO_4 , 95–98%), and hydrochloric acid (HCl, 36%) were procured from Rankem Chemicals Pvt. Ltd., India. Phosphorus pentoxide (P_2O_5 , 95%), and hydrogen peroxide (H_2O_2 , 98%), were purchased from SD Fine Chemicals Pvt. Ltd., India. Merck, India. Potassium permanganate (KMnO_4 , 98.5%), and potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$, 98%), were procured from Sisco Research Laboratories Pvt. Ltd., India. Styrene monomer (C_8H_8) was purchased from Avra Synthesis Pvt. Ltd., India. Nitric acid (HNO_3 , 65–68%) and sodium hydroxide (NaOH) were purchased from Merck, India. Acetone, sodium chloride (NaCl), magnesium chloride (MgCl_2), ferric chloride (FeCl_3), sodium nitrate (NaNO_3), sodium fluoride, and sodium sulfate were purchased from Loba Chemie, India.

All chemicals were of analytical grade and were used as received without further purification. Glassware was cleaned thoroughly with aqua regia ($\text{HCl}:\text{HNO}_3$, 3:1 vol%), rinsed with deionized water, and dried in an oven before use. Deionized water was used for the swelling. All solutions and suspensions were prepared in deionized water unless otherwise mentioned.

Preparation of Graphene Oxide: GO was synthesized from graphite powder using modified Hummer's method.^[53] Graphite powder (2 g) was oxidized in a hot solution (100 °C) of concentrated H_2SO_4 (25 mL) containing $\text{K}_2\text{S}_2\text{O}_8$ (4 g) and P_2O_5 (4 g). The resulting dark blue mixture was thermally isolated and slowly cooled to room temperature for 6 h. The mixture was diluted to 200 mL and filtrated subsequently with a Whatman filter paper, and finally, the filtrated product was dried overnight at 60 °C in an oven. The preoxidized graphite powder (2 g) was added to 92 mL of cold H_2SO_4 (0 °C), to which KMnO_4 (12 g) was added gradually under continuous stirring in an ice-bath. After 15 min, NaNO_3 (2 g) was added to the mixture. The solution was further stirred for 2 h at 35 °C, and distilled water (200 mL) was added to it. The reaction was stopped after adding a solvent mixture containing 300 mL distilled water and 10 mL H_2O_2 (30%). The product was washed with HCl (1:10) and further with water, and finally, suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids. Subsequently, the dispersion was sonicated (300 W) for 2 h, aiming for better exfoliation of GO sheets. However, unexfoliated graphite oxide was removed by centrifugation. UV–vis and Raman spectroscopy techniques were performed as spectroscopic characterization of GO, and it was studied further by high-resolution transmission electron microscopy (HRTEM).

Preparation of Reduced Graphene Oxide: At first, as-synthesized freeze-dried GO of 1 g was taken and dispersed in 1000 mL of deionized water. The GO solution was further mixed with a solvent mixture of ammonia and aqueous potassium hydroxide to adjust the alkalinity (pH $\approx$ 10) of the GO dispersion, and the resulting solution was kept under continuous ultrasonication for 1 h. Ultrasound created an exfoliation of the lamellar GO structure, and this further leads to electrostatic repulsion between the interlayers of the lamellar structure. By this process, stacked layers were peeled off, and the authors obtained a uniform or homogeneous dispersion of GO. Subsequently, 1 mL N_2H_4 solution was added to the above dispersion under stirring conditions. Further, the solution was stirred in an oil-bath, where the temperature was set to 95 °C. The solution was refluxed overnight under this condition.^[54] After completion of the reaction, the color of GO suspension was converted from brown to black, which suggested the formation of rGO. The resulting suspension was filtered and washed several times with deionized water. The washed

solid rGO was dried under a vacuum. A small amount of solid rGO was dispersed in deionized water by ultrasonication. Finally, this dispersion was used for the synthesis of the rGO–PS composite.

Activation of Styrene: Styrene (C_8H_8 , chemically pure) was alternately washed thrice with 0.5 M NaOH and deionized water to remove the polymerization inhibitor. Activated styrene was further used for the polymerization process.

Synthesis Protocol of an Integrated Electro-Adsorbent Ion-Exchange Resin Composite: Detailed synthesis protocol of both GO and rGO is described in the Experimental Section. The characterization data of GO are shown in Figure S1, Supporting Information. Before starting the polymerization process, as-prepared rGO (1 g), activated styrene monomer, and divinylbenzene were taken in the ratio of 10:1:0.1 (in wt%) in 25 mL of deionized water, and the mixture was ultrasonicated for 10 min to obtain a uniform dispersion. The polymerization process was further carried out in an inert atmosphere (using N_2 gas). Under this condition, the solution was stirred for 15 min, and 320 mg of $\text{K}_2\text{S}_2\text{O}_8$ was added successively to the reaction mixture. Initially, the reaction mixture was stirred at room temperature for 30 min; after that, the temperature of the solution mixture was increased gradually to 70 °C and maintained at the same temperature for 1 h. The temperature was further increased to 80–85 °C and kept the solution for 12 h under the same condition. Finally, the temperature was raised again to 90–95 °C and kept there for another 2 h. After completion of the reaction, rGO–PS composite was washed with hot deionized water and dried overnight at 90 °C in a hot air oven.

For synthesizing anionic EAIERs (–ve EAIERs), anchoring of chloromethyl groups to the network of the polymer composite (rGO–PS) was essential. For this, the Friedel–Craft alkylation reaction was performed. Subsequently, the polymer composite (1 g) and chloromethylmethylether (3 mL) were mixed in 10 mL deionized water, and the mixture was allowed to stir for 2 h at room temperature. Afterward, ZnCl_2 ($\approx$ 380 mg) was added to the reaction mixture, and the mixture was stirred for 12 h at 35–38 °C. The chloromethylated product was washed with acetone several times and dried at 60 °C overnight. The obtained product was allowed to swell by immersing in 1,2-dichloromethane for 2 h. Subsequently, trimethylamine hydrochloride (1 g) was added to the resultant mixture, and the reaction was continued for the next 6 h at room temperature. The final chloro-aminated product (rGO–PS– $\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ or –ve EAIERs) was dried overnight at 60 °C.^[55]

To synthesize cationic EAIERs (+ve EAIERs), rGO–PS composite (1 g) was dispersed in 20 mL of 4 M H_2SO_4 , and the dispersion was stirred for 24 h at 100 °C. After completion of this reaction, the rGO–PS– SO_3^-H^+ (+ve EAIERs) was formed, and the final product was dried in a hot air oven at 60 °C.^[56]

Preparation of Electrodes: To fabricate the electrodes using as-prepared materials, EAIERs (300.3 mg) and 15 wt% of PVDF were dispersed in DMF, and the resulting solution was stirred to prepare a homogeneous viscous slurry. It was coated on a graphite sheet ($\approx$ 250 μm thickness), and the electrode was kept in an electrode coater for curing. Finally, the coated sheet was immersed in DI water overnight. A lab-scale CDI batch experiment was performed using a single pair of oppositely charged EAIERs electrodes (size $5 \times 3 \text{ cm}^2$). Furthermore, the conventional CDI electrodes prepared using CMF-CNC (422.4 mg) as the carbon source were fabricated using the above procedure.

Capacitive Deionization Set-Up: A CDI set-up was prepared with a two-electrode configuration using –ve EAIER (anode) and +ve EAIER (cathode), and an interelectrode spacing of $\approx$ 0.2 mm was maintained with a nylon membrane. This two-electrode configuration was immersed in a 100 mL beaker containing 85 mL of saline water with different ions. The initial conductivity of the solution was maintained as 450, 610, and 802 μS , in separate experiments. By applying a potential ($\approx$ 1.2–1.8 V DC) to the electrodes, the cations and anions of the input feed water got adsorbed electrostatically on the cathode and anode, respectively. This process was continued until the electrodes become saturated, and the system attained equilibrium. The regeneration (desorption) was conducted by reversing the polarity of electrodes, where all the adsorbed

ions were desorbed. The same surface was used further for the next set of adsorption–desorption cycles. The maximum adsorption capacity of the material was calculated from the equilibrium adsorption curve. The temperature of the solution was maintained at $\approx 23\text{--}25^\circ\text{C}$ during the adsorption and desorption process.

The electroadsorption capacity (Q , mg g^{-1}) of electrodes was calculated by using the formula:

$$Q = (C_i - C_f) \times V / m \quad (1)$$

where C_i and C_f were initial and final concentrations of the solution (mg L^{-1}), V was the volume of the solution (mL), and m was the total mass of the electrodes (in g).

Instrumentation: Morphological studies of the electrode surface, elemental analysis, and elemental mapping were carried out using a scanning electron microscope equipped with energy dispersive analysis of X-rays (EDAX or EDS) (FEI Quanta 200). Also, HRSEM images of the electrode materials were obtained through Thermo Scientific Verios G4 UC SEM. The HRTEM images of the electrodes were obtained with JEOL 3010 (JEOL, Japan), which was operated at 200 keV and before HRTEM measurements, the samples were drop-casted on carbon-coated copper grids and allowed to dry under ambient conditions. XPS measurements were performed using ESCA Probe TPD of Omicron Nanotechnology with polychromatic Mg K α as the X-ray source ($h\nu = 1253.6\text{ eV}$), and the binding energy was calibrated with respect to C 1s at 284.5 eV. Raman spectra were obtained with a WITec GmbH, Alpha-SNOM alpha 300 S confocal Raman microscope having a 532-nm laser as the excitation source. A PerkinElmer Lambda 25 spectrophotometer was used to measure the UV–vis spectral feature of the sample. Raman spectra of GO were collected by a confocal Raman spectroscope (WITec GmbH CRM200). IR spectra of electrode materials were taken by PerkinElmer FT-IR spectrometer. The Eyela Freeze Dryer (Model No: FDU–1200) was used for drying the sample.

The Eutech Cyber scan PC650 multiparameter monitor (Thermo Scientific, India) was used for ionic conductivity measurement. The electrochemical capacitive behavior of EAIRs was determined by CV using CH Electrochemical Analyzer (CH 600A). The CV was performed at various scan rates ($1\text{--}1000\text{ mV s}^{-1}$) in a potential range of -1.0 to $+1.0\text{ V}$. The specific capacitance was calculated from the CV curve based on the following equation:

$$C_s = \left(\frac{1}{mR\Delta V} \right) \times \int I(V) dV \quad (2)$$

where C_s was the specific capacitance, m was the mass of the active material, R was the scan rate, dV was the potential window of scanning, and $\int I(V) dV$ was the integral area under the CV curve. The electrochemical capacitive behavior of EAIRs was determined by CV. All electrochemical measurements were carried out at room temperature in a three-electrode cell with 1 M aqueous NaCl solution. An electrochemical cell with three-electrode configuration was adopted with an rGO–PS-coated graphite sheet, Ag/AgCl, and Pt mesh used as working, reference, and counter electrode, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

capacitive deionization, desalination, ion-exchange resins, reduced graphene oxides, water purification

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