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Title: Morphology-dependent electrochemical performance of MnO₂ nanostructures on graphene towards efficient capacitive deionization

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Abstract: Capacitive deionization (CDI) is an emerging desalination technology that still needs further development to enhance its performance for practical implementation. Herein, we present a hybrid CDI approach, which integrates the electrical double-layer (EDL) with the sodium-ion battery concept to improve the separation of sodium and chloride ions from saline water. The hybrid CDI cell is achieved by using hydrothermally-grown prawn-like α -MnO₂/graphene (α -MnO₂/G) nanocomposite as anode material, and graphene at the cathode. In this paper, the effect of MnO₂ morphology on the electrode electrochemical performance and its effect on capacitive deionization performance have been fully investigated. In this configuration, the Na⁺ ions are inserted by the electrochemical reaction at the α -MnO₂/G electrode, whereas Cl⁻ ions are captured by the graphene-based electrode. The morphological dependent electrochemical properties of the obtained nanocomposites were studied deeply through CV and EIS analysis. The established the morphological optimized hybrid CID cell provides an electrical capacitance as high as 375 F g⁻¹ at 10 mV s⁻¹, cation-selectivity, good electrical stability and low internal resistance. The hybrid CDI device also shows a stable and reversible salt insertion/de-insertion capacity up to 29.5 mg g⁻¹ at 1.2 V. These results demonstrate the suitability of prawn-like α -MnO₂/G nanocomposite to produce high-performance hybrid CDI cells.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request

To

27th May 2019

The Editor,

Electrochimica Acta

Subject: to submit the manuscript “**Morphology-dependent electrochemical performance of MnO₂ nanostructures on graphene towards efficient capacitive deionization**”

Dear Editor,

We would like to submit our manuscript to your esteemed journal for publication.

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We are looking forward to your positive response.

Sincerely,

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Morphology-dependent electrochemical performance of MnO₂ nanostructures on graphene towards efficient capacitive deionization

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Abstract

Capacitive deionization (CDI) is an emerging desalination technology that still needs further development to enhance its performance for practical implementation. Herein, we present a hybrid CDI approach, which integrates the electrical double-layer (EDL) with the sodium-ion battery concept to improve the separation of sodium and chloride ions from saline water. The hybrid CDI cell is achieved by using hydrothermally-grown prawn-like α -MnO₂/graphene (α -MnO₂/G) nanocomposite as anode material, and graphene at the cathode. In this paper, the effect of MnO₂ morphology on the electrode electrochemical performance and its effect on capacitive deionization performance have been fully investigated. In this configuration, the Na⁺ ions are inserted by the electrochemical reaction at the α -MnO₂/G electrode, whereas Cl⁻ ions are captured by the graphene-based electrode. The morphological dependent electrochemical properties of the obtained nanocomposites were studied deeply through CV and EIS analysis. The established hybrid CID cell provides an electrical capacitance as high as 375 F g⁻¹ at 10 mV

s⁻¹, cation-selectivity, good electrical stability and low internal resistance. The hybrid CDI device also shows a stable and reversible salt insertion/de-insertion capacity up to 29.5 mg g⁻¹ at 1.2 V. These results demonstrate the suitability of prawn-like α -MnO₂/G nanocomposite to produce high-performance hybrid CDI cells.

Keywords: graphene; prawn-like MnO₂; supercapacitor; battery system; capacitive deionization

1 Introduction

Over the past few decades, the continuous rise in fresh water demands due to industrial and population over-growth has become one of the greatest humanitarian challenge [1, 2]. For many years, the membrane and thermal desalination industries have ubiquitously sustained the large-scale water security. Nonetheless, the high running costs membrane and thermal technologies have prompted the needs for more eco-friendly separation processes just as the capacitive deionization (CDI) [3-5]. In this nascent technology, the continuous removal of soluble salts is achieved by electromigration and subsequent storage of ions at the surface of two porous carbon electrodes subjected to a potential difference of 1.0 to 1.4 V [6, 7]. Carbon-based electrodes are ubiquitous since they offer a number of advantageous features, such as high surface-area material abundance, electrochemical stability, low internal electrical resistivity, high specific capacitance, and environmental compatibility [8-10]. The efficiency of ion removal largely depends on the charge storage capacity of the electrical double layers (EDLs) produced at the surface of the electrodes, as well as the ion intercalation/de-intercalation kinetics [1, 11-13]. At present, classic porous carbon electrodes produce a maximum salt electrosorption capacity as low as 0.1 to 10 mg g⁻¹ [14], which strictly limits the performance of the basic CDI cell to low-salinity and bench-scale applications. The more recent incorporation of nanomaterials such as carbon nanotubes (CNT) and graphene (G), as well as meso-structuring, has led to substantial capacity improvements up to 5-20 mg g⁻¹ [15-19]. The alternative use of three-dimensional macroporous G architectures, such as sulphonated reduced-graphene oxide (rGO) on carbon fiber, hybrid G/CNT, and rGO/activated carbon composites has also found potentials for high-performance CDI applications. Despite a suite of exceptional mechanical flexibility, electrical conductivity, wide potential windows, and high thermal and chemical stability [20-23], G-based materials do not offer enough high-throughput capabilities and ion-selectivity which are highly desired for industrial application [23-25]. Therefore, the alternative use of redox promoters, such as

transition-metal oxide nanoparticles (NPs) which are extensively studied in electrochemical batteries, e.g. TiO_2 , SnO_2 , MXene, CoFe_2O_4 , $\text{Na}_{0.44}\text{MnO}_2$, and MnO_2 , is also documented in the CDI literature [26-31]. Despite their low electrical conductivity, these metal oxides possess an exceptional chemical stability, high specific capacitance, as well as high density of active surface sites. Particularly, nanoscale MnO_2 is highly attractive due to its assistive pseudo-capacitive behavior, and faradaic interaction with sodium ions, which enables for fast and reversible ion intercalation/de-intercalation [32-34]. To the best of our knowledge, the effect of MnO_2 morphology on the electrode electrochemical performance and its effect on capacitive deionization performance has not been studied before. Moreover, simultaneous use of G and MnO_2 nanomaterials to exploit the advantageous features of high surface area and conductivity with the pseudocapacitive and faradaic surface activity, respectively, is not fully explored in CDI applications [35, 36]. In this work, we propose a facile one-pot hydrothermal synthesis strategy to control the morphology of $\alpha\text{-MnO}_2$ NPs grown on G nanocomposites by varying the concentration of manganese oxide precursors. A structure-to-performance correlation, which is of great significance for material optimization, is established through a series of complementary physical and electrochemical characterizations.

2 Experimental Section

2.1 Materials

Aqueous hydrogen peroxide H_2O_2 (30 wt.%), poly(vinylidene) fluoride (PVDF), N,N-dimethylformamide (DMF), potassium permanganate (KMnO_4), aqueous hydrochloric acid (HCl , 37 wt.%), sulfuric acid (H_2SO_4 , 98%), acetone, ethanol and graphite flakes were received from Sigma Aldrich and all used reagent are analytical grades and were used without further purification.

2.2 Hydrothermal synthesis of MnO_2/G nanocomposites

Few layers of G sheets were prepared from natural graphite flakes via a simple mechanochemical ball milling as previously reported by Bharath et al. [37, 38]. Then, 500 mg of the mechanochemically exfoliated G was suspended in 45 mL of double distilled water by probe sonic dispersion for 3h. Consequently, 0.1, 0.2 and 0.3 M of KMnO_4 was dissolved in 50 ml of G dispersion (5 mg/mL) separately with vigorous magnetic stirring for 2 h. Afterwards, the above mixed solutions were transferred in a Teflon-lined stainless-steel autoclave and the temperature

was maintained at 140 °C for 6 h. The obtained precipitate was collected and washed with deionized water for several cycles, followed by acetone. Finally, the hybrid nanocomposites were dried in a vacuum oven at 70 °C for 12h. In this work, the samples prepared with the different molar concentrations of KMnO_4 , namely, 0.1, 0.2 and 0.3 M, are tagged as $\text{MnO}_2/\text{G-1}$, $\text{MnO}_2/\text{G-2}$ and $\text{MnO}_2/\text{G-3}$, respectively. Also, GO was prepared via the modified Hummers method [39] for comparison studies.

2.3 Characterization

The synthesis of nanocomposites was assessed and confirmed through electron transmission and scanning microscopy using HR-TEM (JEOL, JEM-3000F) and field emission scanning electron microscopy (FE-SEM, FEI-JEOL JSM 7610-F) with energy dispersive spectroscopy (EDS). The crystalline structure of the nanocomposites was examined through powder X-ray diffraction (XRD) on a D8 X-ray diffractometer (Bruker AXS, German) using $\text{Cu } K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) and Raman spectra using a JY-1058 Raman spectrometer equipped with a 520 nm laser source. The chemical composition and functional groups of the nanocomposites were qualitatively measured through Fourier transform infrared spectroscopy (FTIR) analysis (Bruker IFS 66 v/s IR spectrometer) and X-ray photoelectron spectroscopy (XPS, PHI 5702 spectrometer) equipped with a monochromatic $\text{Al } K\alpha$ X-ray source. The SSA (m^2/g) and pore size of the obtained nanocomposites were estimated using nitrogen adsorption-desorption measurements in a 3Flex Micromeritics instrument. Prior to the measurements, approximately 150 mg of the sample was degassed under vacuum (10^{-6} mbar) at 250 °C for 12 h.

2.4 Electrodes fabrication and Electrochemical analysis

The morphological dependent electrochemical properties of the $\text{MnO}_2/\text{G-1}$, $\text{MnO}_2/\text{G-2}$ and $\text{MnO}_2/\text{G-3}$ nanocomposites were studied via cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis. The working electrodes were fabricated starting with mixing the active materials, PVDF and carbon black with a mass ratio of 5: 15: 80, all dispersed in DMF. Then the obtained slurry was coated on nickel foam and then dried at 50 °C for 6 h. All CV and EIS measurements were carried out in a three-electrode system with Ag/AgCl as a standard reference electrode, platinum wire as counter electrode, and prepared nanocomposites as the working electrode. The CV measurements were carried out in a voltage range of -0.2 to 0.8 V, using different scan rate ($10\text{--}100 \text{ mV s}^{-1}$). In this study, 1.0 M of NaCl was used as

electrolyte solution. Moreover, Equation (1) was used to determine the specific capacitance of the electrodes; where, C_s is specific capacitance (F/g), $\int IdV$ is the integrated area of the CV curve (A.V), and ΔV is potential window (V), v is potential scan rate (V/s) and m is the mass of electrode material (g). The EIS spectra of the resulting electrodes were obtained using the same electrode system in 1.0 M of NaCl solution at the frequency range between 100 kHz to 0.01 Hz.

$$C_s = \frac{\int IdV}{2v\Delta V.m} \quad (1)$$

2.5 CDI experiments

The CDI experiments were conducted in batch-mode with a continuously recycling system consisting of a peristaltic pump, CDI unit cell, current recorder and conductivity meter. In each experiment, NaCl salt dissolved in distilled water to obtain a 100 mg L⁻¹ solution with a conductivity of about 206 $\mu\text{S cm}^{-1}$. The size of the electrodes was 110×55 mm², and 0.12 mm in thickness. In these experiments, G was used as a cathode material while the anode was constructed with the prepared MnO₂/G-1, MnO₂/G-2 or MnO₂/G-3 nanocomposites. The anode and cathode were separated by a 3-mm thick spacer and assembled. A 50 mL of NaCl solution with flow rate of 10 mL min⁻¹ was continuously pumped using a peristaltic pump into the CDI cell and the effluent was continuously recirculated to the feed tank. An optimum applied voltage of 1.2 V was applied to the electrodes [25-28].

The NaCl electrosorption capacity (q , mg/g) of the electrode was estimated by the following equation (2); where C_0 and C_e (mg/L) represent the initial and final NaCl concentration, V (L) is the solution volume, and m (g) is the weight of active material.

$$\text{Salt removal capacity (mg/g)} \quad q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

3 Results and Discussion

3.1 Nucleation-growth mechanism

The optimization of nanomaterial synthesis is of greatest prominence for the quality of the final product, and for their potential applications in various fields. To achieve this goal, nanomaterials synthesis parameters, such as precursor concentration, temperature and time have been exploited at various stages by several recent studies [33-34]. Indeed, precursor concentration is an important parameter, which dictates the size and shape of the nanomaterials. Fig.1 schematically

shows the associations between the nucleation and growth rates and the concentration of the KMnO_4 precursor. Desired KMnO_4 concentration in the 0.1-0.3 M range was dissolved to the G dispersion for the formation of MnO_2/G -1, MnO_2/G -2 and MnO_2/G -3 nanocomposites herein. Generally, two kinds of growth mechanisms can be associated with the formation of MnO_2 on G surfaces such as, the spontaneous reduction of MnO_4^- towards MnO_2 on the G matrix via oxidizing exterior carbon and the redox reaction between Mn^{2+} and the oxidants (such as MnO_4^- and H_2O_2) on the G sheet, respectively [40, 41]. Specifically, in this formation process, spontaneous reduction reactions were occurred on the G matrix, resulting towards MnO_2 NPs formation on the surface of G under hydrothermal conditions applied. The formation of the MnO_2 NPs can be illustrated as per the following reaction equation:

This equation illustrates the redox reaction taking place on the G matrix. Specifically, the latter serves as sacrificial reducing mediator and converts aqueous MnO_4^- into MnO_2 , leading to uniformly grown MnO_2 NPs. Moreover, various molar concentration of the precursor may have influence on the shape and size of MnO_2 , which is grown on G sheets. From the structural and morphological studies, it is confirmed that the crystallite size and shape of MnO_2 both depend on the concentration of permanganate as can be seen below in Fig.2. When the concentration of the permanganate increases above the equilibrium concentration, the nucleation started on G matrix. Probably, nucleation occurs when the permanganate concentration reaches to minimum required saturation which generates the critical free energy of formation [42, 43]. Consequently, manganese nuclei are formed on the G surface and growth occurs simultaneously under hydrothermal conditions (140 °C). Meanwhile, the nucleation rate increases very rapidly as the concentration of permanganate increases further from 0.1 to 0.3 M. The rate of the manganese oxide nuclei formation increases with increasing the precursor concentrations. In addition, a higher population of manganese crystallites are produced during hydrothermal reaction, which leads to larger particle size of MnO_2 on G surface [44]. This study demonstrates the vital role of the precursor concentration in controlling the morphology of the MnO_2 NPs.

Fig.1 Nucleation growth mechanism of MnO₂/G-1, MnO₂/G-2 and MnO₂/G-3 nanocomposites.

Fig.2 FE-SEM microphotographs of G (a), MnO₂/G-1 (b,c), MnO₂/G-2 (d-f) and MnO₂/G-3 (g-i), EDS spectrum of MnO₂/G-1 (j) and mapping of MnO₂/G-1 (k).

The detailed growth process of MnO₂ nanoparticles on G nanocomposites with different loadings of manganese was further confirmed through FESEM micrographs as presented in Fig.2(a-k). FESEM image in Fig.2 (a) shows uniform dispersion of ball milled exfoliated G sheets, which

contains few layers of carbon sheets. Fig.2(b-i) show the representative FESEM images obtained for the MnO_2/G nanocomposites, synthesized with varying the molar ratio (0.1 to 0.3 M) of manganese precursors, at different magnifications. The result indicates that all the samples are composed of prawn-like MnO_2 nanostructures being uniformly dispersed on the surface of G sheets but the sizes of MnO_2 NPs depend on the molar ratio of manganese precursors. FESEM micrograph image of MnO_2/G -1 nanocomposite in Fig.2(b) shows the agglomeration-free individual G sheets with uniformly distributed prawn-like MnO_2 on the surface of G sheets. Fig.2(c) shows a higher magnification of the prawn-like MnO_2 from this sample, with typical size of ~60 nm. The increased molar concentration of permanganate ions to 0.2 M increases the density of prawn-like MnO_2 nanoparticles on G matrix and also increases the nanoparticle size up to ~74 nm, as shown in Fig.2(d-f). Further, higher density of prawn-like MnO_2 nanoparticles with a size of 83 nm were grown on G by increasing the molar concentration of permanganate ions up to 0.3 M, as shown in Fig.2(g-i). This study confirms that increasing the molar concentration of manganese precursor from 0.1 to 0.3 M increases the diameter and density of the MnO_2 NPs on G sheet. The higher precursor concentration produces a higher number of manganese oxide nuclei, and enhances the grain growth. Therefore, sizes of the MnO_2 nanoparticles can be tuned by adjusting the concentration of the precursor in the synthesis solution. The EDX spectrum in Fig. 2(j) confirms the presence of carbon (C), oxygen (O) and manganese (Mn) as dominant elements. Fig. 2(k) shows an elemental mapping of the MnO_2/G -1 nanocomposite where it confirms the elements of C, O, and Mn are uniformly distributed, supporting the presence of MnO_2 and G in the nanocomposites.

Fig.3 TEM images, at different magnification, for MnO₂/G-1 (a-c), MnO₂/G-2 (d-f), and MnO₂/G-3 (g-i), SAED pattern of MnO₂/G-1 (j), MnO₂/G-2 (k), and MnO₂/G-3 (l), EDS spectra of MnO₂/G-1 (m), MnO₂/G-2 (n), and MnO₂/G-3 (o) nanocomposites.

Moreover, based on the TEM images, SAED and EDS (Fig. 3(a-o)) confirmation of the morphology, crystallinity and elemental composition of the samples is possible. In particular, Fig. 3(a-c) show the TEM images of the MnO₂/G-1 nanocomposite with different magnifications, which reveal that agglomeration-free growth with less population of nanoparticles obtained in the particular sample. High-magnification TEM image in Fig.3(c) clearly indicated that the incomplete prawn-like morphology of MnO₂ nanoparticles grown on surfaces and edges of G sheets due to insufficient number of nuclei formation. While, increase the molar concentration of manganese to 0.2 M resulted to sufficient number of nuclei involved towards the complete formation of prawn-like morphology with dense number of MnO₂ nanoparticles grown on G sheets as shown in Fig.3(d-e). Moreover, Fig.3(g-i) show the different magnification TEM images of MnO₂/G-3 nanocomposites. A single two-dimensional (2D) G sheet is well decorated by a large quantity of MnO₂ nanoparticles, and the outlines of both the G and prawn-like MnO₂ nanoparticles can be clearly observed. The diameter of the MnO₂

nanoparticles increases with increasing the molar concentration of manganese to 0.3 M. Also, Fig.3(i) shows the formation of agglomerated MnO_2 nanoparticles with larger diameter are grown on G sheet due to aggregation of large number of manganese nuclei. Also, the analysis of the crystalline structure through the selected area electron diffraction (SAED) patterns shown in Fig.3(j-l), confirms the formation of crystalline MnO_2 and G phases. The SAED pattern of all the samples, shows faint rings with bright spots which are representative of semi-crystalline MnO_2 nanomaterials. The diffraction rings can be indexed to (110), (221), and (521) crystal planes of tetragonal MnO_2 and (002) of G sheets, which are well-matched with the XRD analysis [45, 46]. Furthermore, the EDS spectra in Fig.3(m-o) show that the obtained $\text{MnO}_2/\text{G-1}$, $\text{MnO}_2/\text{G-2}$, and $\text{MnO}_2/\text{G-3}$ nanocomposites are composed of C, O, Mn and a small amount of Cu observed due to TEM grid used.

Representative X-ray diffraction (XRD) patterns of G, $\text{MnO}_2/\text{G-1}$, $\text{MnO}_2/\text{G-2}$, and $\text{MnO}_2/\text{G-3}$ nanocomposites are shown in Fig.4(a-d). According to Fig.4(a), two characteristic diffraction peaks at 26.4° and 42.7° , can be observed for G, corresponding to the (002) and (100) planes of G. Furthermore, the diffraction peaks in the XRD patterns (Fig.4 (b-d)) of the MnO_2/G nanocomposites with different molar loadings of MnO_2 samples can be found at $2\theta = 14.78^\circ$, 18.57° , 31.37° , 36.45° , 38.22° , 41.67° , 49.98° , 58.11° , 60.01° , and 67.31° diffraction angles corresponding to the (110), (200), (310), (400), (211), (301), (411), (600), (521), and (002), planes, respectively of the standard tetragonal $\alpha\text{-MnO}_2$ (JCPDS card PDF file no.44-0141) phase.[46, 47]. Average crystallite size of the oxide phase in the case of $\text{MnO}_2/\text{G-1}$, $\text{MnO}_2/\text{G-2}$, and $\text{MnO}_2/\text{G-3}$ nanocomposites was calculated to be 32, 42 and 61 nm, respectively, using the Debye-Sherrer's equation. Specifically, different molar concentrations of permanganate plays an important role in the formation of larger crystallite sizes with good crystallinity, in agreement with the SEM and TEM studies. This observation from the XRD patterns confirms that various crystallite sizes of MnO_2 nanoparticles can be effectively grown on the G matrix by adjusting the molar content of the manganese oxide precursor through the simple hydrothermal process.

Fig.4 XRD patterns of (a) G, (b) MnO₂/G-1, (c) MnO₂/G-2 and (d) MnO₂/G-3 nanocomposites.

Fig.5 (a) Raman spectra of (a) GO, (b) G, (c) MnO₂/G-1, (d) MnO₂/G-2 and (e) MnO₂/G-3 nanocomposites.

Raman spectroscopy is broadly used to characterize the structure of carbo-based nanocomposites. The Raman spectrum of a reference GO sample, as illustrated in Fig.5(a), shows the presence of D and G bands at 1350 and 1590 cm^{-1} , respectively. The D band is associated to the defect level of sp^3 (carbon-oxygen moieties) and the G band is the sp^2 (C=C) aromatic carbon structure which is a mainly degenerate phonon mode of the E_{2g} symmetry at the Brillouin zone center [48, 49]. The Raman spectrum in Fig.5 (b) recorded for the pristine G prepared in this work, shows three intense peaks at 1350, 1590 and 2715 cm^{-1} corresponding to the D, G and 2D vibration modes, respectively. The observed 2D intense band is attributed to single-layer and bilayer stacked carbon sheets, respectively, and is usually due to the two second-order phonons with opposite momentum in the highest optical branch adjacent to the K point of the Brillouin zone [45]. Previous studies reported that planetary ball milled G sheets contain few layers of carbon and evidence that prepared G consist of a less disordered sp^2 (C=C) aromatic structure [5, 49]. Moreover, Fig.5 (c-e) show the Raman spectra of the various MnO_2/G nanocomposites, which consist of three prominent G characteristic peaks at 1350, 1590 and 2715 cm^{-1} corresponding to the D, G and 2D bands, respectively, and two other intense peaks at 426 and 607 cm^{-1} that can be attributed to the bending modes of O-Mn-O and A_{1g} spectroscopic species originating from breathing vibrations of MnO_6 octahedra, respectively [50]. Moreover, the intensity ratio (I_D/I_G) of the samples shows the defect level of the carbon structures. Especially, broad with higher intensity of G band leads to lower disorder structure of G. The intensity ratios (I_D/I_G) of 1.02, 0.97, 0.98, 1.10, and 1.24 correspond to GO, G, MnO_2/G -1, MnO_2/G -2 and MnO_2/G -3, respectively. The higher intensity ratio ($I_D/I_G=1.02$) recorded for the GO compared with that of the G ($I_D/I_G=0.97$), indicates the presence of localized sp^3 defects in the sp^2 (C=C) network upon oxidation of the graphite [51]. Furthermore, MnO_2/G with different manganese concentrations of 0.1, 0.2 and 0.3 M reveal a higher intensity ratio than G. In addition, intensity ratio of the nanocomposites increases with increasing the molar ratio of permanganate from 0.1 to 0.3, which is an indication of high concentration of MnO_2 nanoparticles present on the G sheets.

Fig.6 (a) FTIR spectra of (a) GO, (b) G, (c) MnO₂/G-1, (d) MnO₂/G-2 and (e) MnO₂/G-3 and (f) MnO₂ nanoparticles. The bands at 2330 and 2360 cm⁻¹ correspond to adsorbed CO₂.

Figures 6 (a-f) show the FTIR spectra of (a) GO, (b) G, (c) MnO₂/G-1, (d) MnO₂/G-2 and (e) MnO₂/G-3 and (f) MnO₂ nanoparticles. Fig.6(a) shows the FTIR spectra of GO which exhibit two intense peaks at 1727 cm⁻¹ and 1510 cm⁻¹ corresponding to the stretching vibrations of carboxylic (C=O) and epoxy (C-O) groups, respectively [37, 38]. The FTIR spectrum of G in Figure 1(b) shows a sharp intense peak attributed at 1636 cm⁻¹ associated with the stretching vibration of C=C. Also, FT-IR spectrum of GO and G shows the sharp intense peaks at 3437 and 1636 cm⁻¹, which correspond to the bending modes of H₂O associated with KBr used for the preparation of the FTIR pellets. The FTIR spectra of all the nanocomposites exhibit intense peaks at 510 and 617 cm⁻¹ corresponding to the stretching vibrations of Mn-O and Mn-O-Mn bonds, respectively [35, 47].

The surface chemical environment of the samples was studied using XPS. The survey spectra of the MnO₂/G-2 nanocomposite is shown in Fig.7 (a) and shows the characteristic photoelectron and X-ray induced Auger peaks of Mn, O and C. The Mn 2p core level spectrum (Fig.7(d)) exhibits the Mn 2p_{3/2} peak at 642.2 eV and the Mn 2p_{1/2} peak at 653.9 eV. These binding energies, peak shape and spin-orbit splitting of 11.7 eV are very consistent with MnO₂ powder and nanowires recorded by other authors [31,51]. The O 1s peak (Fig. 7(c)) shows a strong intense peak at 529.6 eV, together with a lower intensity peak at 531.1 eV and shoulder at 532.9

eV corresponding O^{2-} , OH^- and adsorbed H_2O respectively. The C 1s core level spectrum, Fig.7(b), exhibits a strong peak at 284.5 eV, associated with sp^2 hybridized C bonding with further peaks/shoulders at higher binding energies, attributable to different C-O species, found both on MnO_2 and G surfaces [51,52]. The XPS spectra are in good agreement with the TEM, XRD, Raman and FTIR results.

Fig.7 (a) XPS survey spectra of $MnO_2/G-2$ and the core level XPS spectra of (b) C 1s, (c) O 1s and (d) Mn 2p.

3.2 Electrochemical studies

The morphological dependent electrochemical properties of the obtained nanocomposites were studied deeply through CV and EIS analysis. Fig.8(a) shows the CV profiles of the pure α - MnO_2 and all composite-based electrodes at a scan rate of 10 mV/s in a 1.0 M NaCl solution. All the electrodes show a good rectangular and symmetric CV curves, suggesting ideal electrochemical double-layer capacitance behavior. Moreover, the impact of MnO_2 loading on surfaces of G and their electrochemical behavior can be shown in Fig.8 (a).

Fig.8 (a) CV curves of α -MnO₂, α -MnO₂/G-1, α -MnO₂/G-2, and α -MnO₂/G-3 in 1 M NaCl at 10 mV s⁻¹, (b) CV curves of α -MnO₂/G-2 electrode in 1 M NaCl solution at different scan rates from 10 to 100 mV s⁻¹, and (c) the specific capacitance for α -MnO₂/G-2 versus the scan rate.

Specifically, α -MnO₂/G-2 based electrode shows a larger encircled area of CV curve indicating higher specific capacitance with higher electrochemical performances. The specific capacitance of the samples was calculated from the eqn (1). Generally, the specific capacitance of the as-prepared electrodes is proportional to the areas of a CV curve. The specific capacitance was calculated to be 212, 178, 375 and 244 F/g for the α -MnO₂, α -MnO₂/G-1, α -MnO₂/G-2, and α -MnO₂/G-3, respectively. Among them, α -MnO₂/G-2 based electrode shows higher specific capacitance than other composite electrodes due to synergistic effect of the well-dispersed and high crystalline prawn-like MnO₂ with higher electrical conductivity of G. Various previous studies were already reported that the neat G sheets mainly contribute to the electrical conductivity and prevent the agglomeration of the individual nanoparticles. Specifically, α -

MnO₂/G-2 sample favors the agglomeration-free growth of uniformly dispersed prawn-like MnO₂ with high crystallinity increasing the electrochemically active sites population for effective redox reactions and enhancing the utilization ratio of individual MnO₂ nanoparticles compared to the rest of the samples. Fig.8(b) shows the α -MnO₂/G-2 CV curves at different scan rate of 10 to 100 mV/s. The CV curves are close to rectangular shape up to 70 mV/s scan rate, which is characteristic for good charge transmission at the electrode surface. Though, slight redox peaks of pseudocapacitance behavior in the case of MnO₂/G-2 based electrode can be attributed to the low scan rate (10 mV/s). The asymmetrical CV curves at higher scan rate of 100 mV/s can be attributed to the combined pseudocapacitive and EDLC feature which both contribute to the total capacitance [44]. The high CV currents at higher scan rate indicate low internal resistance of nanocomposites due to the homogenous dispersion of α -MnO₂ on G surface. Scan rate dependent specific capacitance was depicted in Fig. 8(c). The specific capacitance of the α -MnO₂/G-2 electrode slightly decreases with increasing the scan rate. At a higher scan rate, NaCl ions are not fully accessible to the interior surfaces of the active sites in the electrodes due to short diffusion time. However, in the case of lower scan rate most of the electrolyte ions are full inserted into the active redox sites due to longer diffusion/residence time [15, 16, 35, 47, 52]. This phenomenon would lead to a gradual decrease in the specific capacitance of the α -MnO₂/G-2 electrode with increasing the scan rate. However, the specific capacitance of the α -MnO₂/G-2 electrode at 100 mV/s remains at 123 F/g, which confirms the high specific capacitance and superior rate capability of the α -MnO₂/G-2 electrode. The improved electrochemical performance of α -MnO₂/G-2 as compared to other electrodes is due to morphology-controlled synthesis of MnO₂ nanoparticles on G sheets. Specifically, prawn-like morphology with uniform dispersion helps to enhance the intercalation/ de-intercalation behaviors of sodium ions from the electrolyte to α -MnO₂, resulting increase the pseudocapacitance performances than already available literatures.

Fig.9 Electrochemical impedance spectroscopy (EIS) spectra (Nyquist plots) of G, α - MnO_2 , α - $\text{MnO}_2/\text{G-1}$, α - $\text{MnO}_2/\text{G-2}$, and α - $\text{MnO}_2/\text{G-3}$ with the frequency range from 100 kHz to 0.01 Hz.

The electrochemical performances of the G, α - MnO_2 , α - $\text{MnO}_2/\text{G-1}$, α - $\text{MnO}_2/\text{G-2}$, and α - $\text{MnO}_2/\text{G-3}$ electrodes have been further studied by EIS with the frequency range from 100 kHz to 0.01 Hz. Fig.9 and inset Fig.9 show the Nyquist plots for all the nanocomposites and equivalent circuit, respectively. In the equivalent circuit (inset Fig.9), the symbols W, R_s , CPE and R_{ct} denote the Warburg impedance, contact resistance, capacitance of the double layer, and charge-transfer resistance, respectively. Theoretically, an ideal Nyquist impedance plot features a semicircle over the high frequency region and a linear part in the low frequency range [53]. The larger semicircle observed for the electrode corresponds to R_{ct} for the electrode, attributed to the poor electrical conductivity of the prepared electrodes. Meanwhile, vertical line in a low-frequency region, representing a nearly ideal supercapacitive behavior. Fig.9 shows the EIS spectra of α - MnO_2 , α - $\text{MnO}_2/\text{G-1}$, α - $\text{MnO}_2/\text{G-2}$, and α - $\text{MnO}_2/\text{G-3}$ which are composed of both a straight line in low frequencies and an approximate semicircle in high frequencies. Especially, in the low frequency region, the impedance plots of electrodes increase slightly and tends to become vertical lines, which are the features of ideal supercapacitive behavior. At the high frequencies, the impedance plots of α - MnO_2 , α - $\text{MnO}_2/\text{G-1}$, α - $\text{MnO}_2/\text{G-2}$, and α - $\text{MnO}_2/\text{G-3}$ exhibit different semicircle can be attributed to the different electrical resistivity of the electrode

materials. The equivalent series resistance (ESR) of G, α -MnO₂, α -MnO₂/G-1, α -MnO₂/G-2, and α -MnO₂/G-3 electrodes obtained from the intersection of the Nyquist plot at the x-axis is 0.1, 3.4, 1.2, 1.4, and 2.3 Ω , respectively. These results suggest that the G based α -MnO₂ nanocomposites possess low electrical resistivity than pristine α -MnO₂. These EIS studies confirm that the α -MnO₂/G-2 based electrode has low resistance with good ion response at high-frequency ranges while a controlled loading of MnO₂ on G can be tuned achieving an ultimate higher specific super capacitance than other reported electrodes [53]. EIS analysis highlight the merit of α -MnO₂/G-2 based electrode to meet the requirements of both low resistance and higher supercapacitance toward development of potential electrode for CDI applications.

Fig.10 (a) plots of conductivity vs. time, (b) electrosorption capacity vs. time, (c) CDI Kim-Yoon plots for G, α -MnO₂/G-1, α -MnO₂/G-2, and α -MnO₂/G-3 electrodes and (d) desalination-regeneration profile of the α -MnO₂/G-2 in a 100 mg L^{-1} NaCl at 1.2 V with a flow rate of 10 mL min^{-1} .

3.4 CDI performance studies

Carbon -based materials are the most commonly used electrode materials in CDI applications, has a moderate electrosorption capacity. Recent studies specify that the carbon cannot efficiently capture the Na ions due to insufficient electrochemical properties such as capacitance, charge and discharge properties and conductivity. Recently, a few MnO₂ based electrodes have been reported for high-performance CDI application, thus enabling proper Na⁺ adsorption, high structural stability, and large reversible capacity [24-27, 50]. The desalination performances of the α -MnO₂-G nanocomposites were examined through the HCDI system using G and MnO₂ based G composite as cathode and anode, respectively. The CDI performance of the fabricated electrodes such as G//G, G// α -MnO₂/G-1, G// α -MnO₂/G-2, and G// α -MnO₂/G-3 electrodes tested by a series of electrosorption experiments in 100 mg L⁻¹ NaCl with a flow rate of 10 mL min⁻¹ at 1.2 V. Fig.10 (a) depicts the CDI profiles of G//G, G// α -MnO₂/G-1, G// α -MnO₂/G-2, and G// α -MnO₂/G-3 electrodes. In this process G//G based electrodes assembly exhibits conventional CDI performance, i.e. salt ions are adsorbed when the voltage applied to 1.2V and the salt ions are desorbed when the voltage is turned in to 0 V (Fig 10(a)). As shown in Fig.10 (a), the solution conductivity decreases in the first 30 min, indicating the moderate adsorption of the salt ions and the calculated desalination capacity of the G//G system of 6 mg g⁻¹ in 100 mg L⁻¹ NaCl solution was received.

On the other hand, the HCDI concept was tested for the following electrode systems: G// α -MnO₂/G-1, G// α -MnO₂/G-2, and G// α -MnO₂/G-3. The composite-based electrodes are used as anodes to utilize the highly reversible desodiation; while the G electrodes are used as cathode, targeting the electro-sorption of Cl⁻ ions. During the desalination process the cations are intercalating while external bias passed to the anode. Then in the discharging process, the anodic electrode is oxidized and release already adsorbed cations from the anode into the electrolyte [24, 27]. The HCDI performance of the fabricated electrode assembly of G// α -MnO₂/G-1, G// α -MnO₂/G-2, and G// α -MnO₂/G-3 was tested by a series of CDI experiments in 100 mg L⁻¹ NaCl solution as shown in Fig.10(a). The conductivity of the NaCl solution decreases quickly once the voltage is applied to the hybrid electrodes system, and then plateau was reached within 50 min. The G// α -MnO₂/G-2 based electrode system reaches the lowest solution conductivity of 99.7 μ S cm⁻¹, compared to 118.7 and 145.3 μ S cm⁻¹ for the G// α -MnO₂/G-1, and G// α -MnO₂/G-3 electrodes, respectively. Fig.10(b) shows the electrosorption capacity of the present electrode

systems with time during the external bias current passed to the anode (charging process). The salt removal capacity (q) of the G// α -MnO₂/G-2 electrode reaches 29.5 mg/g which is higher than obtained capacity by G// α -MnO₂/G-1, and G// α -MnO₂/G-3 electrodes, the latter exhibiting desalination capacities of 17.5, and 25.3 mg g⁻¹, respectively.

In addition for the electrosorption capacity in this hybrid CDI, electrosorption rate is another important parameter to determine the CDI performances. The Kim-Yoon plot of all electrodes is shown in Fig.10(c). The CDI Kim-Yoon plot, in which the salt removal rate is plotted against to the electrosorption capacity, which was first proposed by Yoon et al [6]. Moreover, Kim-Yoon plot offers a visual depiction of the NaCl removal behaviour of the prepared various electrode materials and this can be an assessment tool for the deionization performance of the hybrid CDI device. The electrosorption capacity (q) at adsorption time (t , min) and corresponding electrosorption rate (v , mg g⁻¹ min⁻¹) were determined according to the following equations 5 and 6, respectively; Where C_0 and C_t are the initial and final conductivity ($\mu\text{S cm}^{-1}$), V is the volume of NaCl aqueous solution (L), m represents the active working materials (mg), and t is the time of electrosorption adsorption process (min).:

$$q = \frac{(C_0 - C_t) \times V}{m} \quad (5)$$

$$v = q/t \quad (6)$$

A comparison of the NaCl removal capacity and Kim-Yoon plots for electrosorption rate of the present CDI electrodes such as G//G, G// α -MnO₂/G-1, G// α -MnO₂/G-2, and G// α -MnO₂/G-3 are depicted in Fig.10(c) [54]. Specifically, G// α -MnO₂/G-2 electrodes exhibit the most upper and right region Kim-Yoon plot, indicative of the highest deionization capacity and fastest electrosorption rate among electrodes studied. The significance of this investigation confirms that the G// α -MnO₂/G-2 electrode integrates the merits of high adsorption capacity and fast deionization rate toward promising desalinization device. The high deionization capacity and fast electrosorption rate of the G// α -MnO₂/G-2 electrode can be associated with the combined capacitive behavior of EDLCs and pseudocapacitors, long charge/discharge ability and lower electrical resistivity. Especially, single layer G possesses EDLCs, and high conductivity, which is responsible for the fast electrosorption, and prawn-like α -MnO₂ nanoparticles contribute the pseudocapacitive which holding high specific capacitance is taking advantage of a fast and

reversible electrosorption of salt ions. In addition, monodispersed high crystalline prawn-like morphology helps to improve the contact between salt ions in the solution to the individual α - MnO_2 nanoparticles causes to improve the CDI performances. Furthermore, the desalination recycling stability of the electrode is performed to investigate the reversibility of G// α - MnO_2 /G-2 electrode during the electrosorption and desorption process. The cycle stability of the G// α - MnO_2 /G-2 electrode was tested in 100 mg L^{-1} NaCl solution over four successive electrosorption-desorption cycles as shown in Fig.10 (d). In each cycle, electrode reached the electrosorption/desorption equilibrium at every 50 min and the cycles were initiated by switching the polarity to the electrodes. Fig.10 (d) shows the variation of solution conductivity with four adsorption-desorption cycles. Noticeably, the CDI process of the G// α - MnO_2 /G-2 electrode can be repeated effectively. The high electrosorption capacity, fast electrosorption rate and reversibility of the α - MnO_2 /G-2 electrode can be used for constructing high performance inverted CDI device. After cycles, the electrosorption retention of the inverted CDI electrode retained over 98% showing better cyclic stability and this behavior can be linked to the well-dispersed prawn-like α - MnO_2 and G-based electrode enhancing intercalation/de-intercalation of the salt ions to the electrodes. Fig.11 demonstrates the schematic representation of the inverted CDI device functioning, which is based on the mechanism of sodium ion batteries (SIBs). The electrode components and the ion intercalation/de-intercalation mechanism of SIBs and inverted CDI are the same concept [55, 56].

Fig.11 Schematic representation of the functioning of CDI device.

Generally, CDI is composed of two electrodes, which serve as host frameworks for the insertion/de-insertion of salt ions in NaCl solution. In this hybrid CDI system, G used as the cathode and α -MnO₂/G-2 nanocomposites used as an anode, which is separated by ion exchange membrane that is a transport medium for ions in NaCl solution, as shown in Fig.11. During the reverse potential (external bias current passed through anode), the Na⁺ and Cl⁻ ions are extracted from the salt solution and inserted into respective opposite charged electrodes. The Na⁺ ions extracted from salt solution and inserted into the anode, while the external electron passes through the outer circuit. Also, an electron and Na⁺ ions combine to form a stable sodium atom ($Na^+ + e^- \rightarrow Na$) and intercalate with manganese lattice [56, 57]. The following reaction can be expressed for the intercalation of Na to the anode.

The high desalination capacity and high electrosorption rate confirms that the α -MnO₂/G based anode is capable of capturing sodium ions rapidly and reversibly through surface adsorption and surface redox reactions. The larger Na⁺ ions insertion can be attributed due to the synergetic effect of high pseudocapacitive prawn-like α -MnO₂ nanoparticles and high electrochemical conductivity of G. Also, G prevents the agglomeration of individual α -MnO₂ nanoparticles and also act as electron shuttling mediator to the outer circuit. Resultant, prawn-like α -MnO₂ nanostructures are giving possible interstitial sites for Na⁺ insertion and suitably sized pathways for Na⁺ diffusion [57]. Therefore, prawn-like α -MnO₂/G-based anode possesses a larger contact area with the salt solution which favors the transport kinetics of Na-ions and electrons. Meanwhile, Cl⁻ ions are migrating to the positively charged cathode side due to the electrostatic interaction between cathode surface and Cl⁻ ions into the salt solution. Therefore, consideration of the overall CDI performance, α -MnO₂/G-2 composite-based electrode is enabling to undertake rapid uptake of salt ions than other electrodes. On the other hand, switching the polarization to the electrodes, the MnO₂/G electrode is oxidized and cations in the MnO₂ structure are de-inserted to maintain charge balance as schematically presented in Fig.11. During this cycle, Na metallic atoms at the anode de-insert from the MnOONa structure by dissociation into a positive Na⁺ ion and a negative electron ($Na \rightarrow Na^+ + e^-$) [57]. The following reaction can be used for described the de-intercalation of Na⁺ ions process that takes place on the anode

Simultaneously, Cl^- ions desorb at the surface of G-based cathode when switching the polarization to the electrode. Compared with recently developed electrodes for CDI application, $\alpha\text{-MnO}_2/\text{G-2}$ nanocomposites possess very high desalination capacity, high adsorption rate and reversible electrochemical sorption toward high performance CDI device. Table1 summarizes the CDI performance of various carbon-based or manganese oxide-containing composites. The CDI performance of $\alpha\text{-MnO}_2/\text{G-2}$ nanocomposites stands at a high level among various carbon and carbon-based metal oxides electrodes. Notably, the electrosorption capacity of G// $\alpha\text{-MnO}_2/\text{G-2}$ hybrid system is relatively high as compared with other anode MnO_2 materials (14.9 mg/ g). Thus, it could be concluded that the $\alpha\text{-MnO}_2/\text{G-2}$ nanocomposite-based electrode is highly suitable for the development of high- performance CDI.

Table1. Comparison of specific capacitance and electrosorption capacity of different CDI electrodes

Electrode materials	Specific capacitance (F g^{-1})	Applied voltage (V)	Desalination capacity (mg g^{-1})	Reference
TiO_2 NF/activated carbon	380	1.2	17.7	[58]
Porous carbons and hierarchical ZnO nanocomposites	199	1.2	11.98	[59]
Nitrogen-doped hollow mesoporous carbon spheres	179	1.2	16.6	[6]
rGO-SnO ₂ nanocomposite	142	1.2	17.62	[60]
3D foam-like carbon nanoarchitectures	238	1.4	20.9	[61]
Sodium manganese oxide ($\text{Na}_4\text{Mn}_9\text{O}_{18}$)	300	1.2	31.2	[62]
$\text{Ti}_3\text{C}_2\text{-MXene}$	176	1.2	13	[63]
Starch Derived Porous Carbon Nanosheets	-	1.1	15.6	[64]
Carbon aerogel microsphere	83	1.2	5.62	[65]
MnO_2 as anode	-	1.4	14.9	[29]
Ag-Cu/G	128	1.2	16.81	[66]
Prawn-like $\alpha\text{-MnO}_2/\text{G}$ nanocomposites as anode	375	1.2	29.5	Present work

4. Conclusion

In summary, towards achieving high performance CDI electrode, the α -MnO₂/G nanocomposites were rationally synthesized using hydrothermal method. It was found that Mn precursor concentration in the 0.1 to 0.3 M range has direct influence on the size and shape of the MnO₂ on G sheets. Nucleation growth mechanism was driven by the formation of nanocomposites and obtained samples were characterized by different analytical tools. Specifically, 0.2 M of Mn (MnO₂/G-2) provided sufficient number of nuclei, which help in achieving complete formation of prawn-like morphology with dense number of nanoparticles uniformly grown on G sheets. In addition, the MnO₂/G-2 hybrid nanocomposite showed better specific capacitive performance (375 F g⁻¹ at 10 mV s⁻¹). Additionally, the performance of MnO₂/G-2 composite -based electrode on HCDI system was evaluated. It was found that its prawn-like morphology enhances the insertion/de-insertion of (Na⁺) from the salt solution, resulting in increase of the electro sorption capacity of 29.5 mg g⁻¹ in 100 mg g⁻¹ NaCl solution. The synergistic effects of the HCDI, by combining electrical double layer capacitive and pseudocapacitive behavior of MnO₂/G-2 nanocomposites, possess fast and reversible redox behavior towards development of an efficient CDI process. Therefore, this hybrid CDI device could be used as cost-effective, and high-performance desalination system.

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6. References

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