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Enhanced Electrochemical Performances of Mn$_3$O$_4$/Heteroatom-Doped Reduced Graphene Oxide Aerogels as an Anode for Sodium-Ion Batteries

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Abstract: Owing to their high theoretical capacity, transition-metal oxides have received a considerable amount of attention as potential anode materials in sodium-ion (Na-ion) batteries. Among them, Mn$_3$O$_4$ has gained interest due to the low cost of raw materials and the environmental compatibility. However, during the insertion/de-insertion process, Mn$_3$O$_4$ suffers from particle aggregation, poor conductivity, and low-rate capability, which, in turn, limits its practical application. To overcome these obstacles, we have successfully prepared Mn$_3$O$_4$ nanoparticles distributed on the nitrogen (N)-doped and nitrogen, sulphur (N,S)-doped reduced graphene oxide (rGO) aerogels, respectively. The highly crystalline Mn$_3$O$_4$ nanoparticles, with an average size of 15–20 nm, are homogeneously dispersed on both sides of the N-rGO and N,S-rGO aerogels. The results indicate that the N-rGO and N,S-rGO aerogels could provide an efficient ion transport channel for electrolyte ion stability in the Mn$_3$O$_4$ electrode. The Mn$_3$O$_4$/N- and Mn$_3$O$_4$/N,S-doped rGO aerogels exhibit outstanding electrochemical performances, with a reversible specific capacity of 374 and 281 mAh g$^{-1}$, respectively, after 100 cycles, with Coulombic efficiency of almost 99%. The interconnected structure of heteroatom-doped rGO with Mn$_3$O$_4$ nanoparticles is believed to facilitate fast ion diffusion and electron transfer by lowering the energy barrier, which favours the complete utilisation of the active material and improvement of the structure’s stability.

Keywords: sodium-ion batteries; Mn$_3$O$_4$ nanoparticles; N-rGO aerogel; N,S-rGO aerogel; electrochemical performances

1. Introduction

Because of the rising demand for lithium-ion (Li-ion) batteries, the scarcity of lithium sources, and the expected steep rise in lithium prices, there is an urgent need for innovative and low-cost battery systems [1]. The most researched new battery technologies use the same insertion and extraction chemistry as Li-ion batteries, such as potassium-ion (K-ion) and sodium-ion (Na-ion) batteries, despite the fact that the electrode materials needed to be reconfigured [2]. In large-scale energy storage, Na-ion batteries have gained considerable interest owing to the availability and natural resources of sodium [3–8]; moreover, they appear to be a better alternative to Li-ion batteries. Unfortunately, because of the large radius (1.02 Å), high atomic mass (23 g mol$^{-1}$), and low redox potentials (2.71 V vs. SHE) for Na-ion, most examined electrodes, especially the anode, are not ideal hosts for Na-ion insertion [9–12]. In addition, because Na has a higher chemical activity than Li, the...
production, transportation, and application of Na-ion batteries may be more difficult [13,14]. Furthermore, severe volume changes caused by repeated cycling of the anode materials contribute to the failure of the battery by causing cracks and loss of electrical contact. To improve battery performances, nanoscale materials are frequently used owing to their ease of stress release and high resistance to structural defect formation [15,16].

To date, various materials have been explored, and transition-metal oxides, such as MnO$_x$ [17,18], FeO$_x$ [19,20], and Co$_3$O$_4$ [21], have drawn increasing attention owing to their high theoretical capacities. Notably, previous studies have demonstrated that Mn and Mn-based compounds can alloy with Na and perform well as Na-ion battery anodes [15,22,23]. Mn$_3$O$_4$ is one of the promising anode materials and has a high theoretical capacity (937 mAh g$^{-1}$) because of its conversion reaction mechanism, natural availability, low cost, and environmental friendliness [24]. So far, the Na-ion storage behaviour in Mn$_3$O$_4$ nanostructures has been investigated [25] and possesses similar problems to other transition-metal oxides. The volume changes during the repeated insertion/de-insertion process of Na-ions lead to the substantial aggregation of particles and may affect the mechanical stability of the electrode materials [26,27]. Jiang et al. [28] were the first to report the Na-ion storage performances of Mn$_3$O$_4$ thin film synthesised via electrostatic-spray deposition, which exhibits poor cycling performances. The capacity deterioration during cycling is explained by the formation of a porous reticular structure in the grids. To ensure the large capacity of Mn$_3$O$_4$ electrode accompanied by high reversibility [29], the internal structure of Mn$_3$O$_4$ needs to be modified to compensate for the volume changes by adopting various strategies, such as synthesise multifunctional nanostructures [25] and nanocomposites [30], and by hybridising with carbon-based materials, such as mesoporous carbon [31], graphene [32], reduced graphene oxide (rGO) [33], and carbon nanofibres [34]. Because of the unique layered structure, high specific area, superior conductivity, and excellent electrical properties, graphene-based matrices or their derivatives (e.g., rGO) have been used to improve the charge transfer and reduce the agglomeration of transition-metal oxide electrodes [35]. Such a combination could be an effective way to improve the electrochemical performances of the batteries by shortening the Na-ion diffusion pathway, improving electroactivity, and relieving volume variation [29,36]. Wang et al. [25] reported that encapsulating Mn$_3$O$_4$ nanotubes in porous graphene sheets can improve the structural integrity and electrical conductivity of the electrodes, with a satisfactory discharge capacity and cyclability of up to 55 cycles. Nonetheless, aggregation or restacking between rGO layers will drastically reduce the active sites and influence the Na-ion transfer rate, which results in low reversible capacity [37]. Doping rGO with heteroatoms, such as nitrogen (N) [38,39] and sulphur (S) [40], could enhance the electronic conductivity and ameliorate the physicochemical functions of the rGO. It has been demonstrated that N-doping can significantly increase the electronic conductivity and Na-ion storage capacity of the electrode because of the introduction of N-doped defects and functionalised groups [41–44]. On the other hand, S-doping could increase the interlayer distance to promote the insertion/de-insertion of Na-ions owing to their larger covalent radius (102 pm) than carbon (77 pm) [43,45]. In addition, codoping with multiple heteroatoms can enhance the performance of rGO through synergistic interactions between heteroatoms [46]. However, the content of S in the doping materials could also be hindered by the incorporation of the graphene network because of the oversized atomic radius of S (180 pm) [47].

In this work, the Mn$_3$O$_4$/nitrogen (N)- and Mn$_3$O$_4$/nitrogen, sulphur (N,S)-rGO aerogels were prepared via the hydrothermal method using NH$_3$ and L-cysteine as a source of nitrogen and nitrogen, sulphur elements, respectively. Upon treatment of graphene oxide (GO) with NH$_3$ and L-cysteine, GO was not only reduced to graphene but also simultaneously doped with N and N$_x$S-atoms. The Mn$_3$O$_4$/N- and Mn$_3$O$_4$/N,S-rGO aerogels have a promising reversible discharge capacity of 370 and 281 mAh g$^{-1}$, respectively, up to 100 cycles at a current density of 0.1 A g$^{-1}$. These nanocomposites also possess excellent cycling stability and better rate capability. In fact, when compared with
other methods, the current method has the advantages of simplicity, friendliness, reliability, and cost-effectiveness. The promising capacity and cyclability demonstrated by the Mn$_3$O$_4$/heteroatom-doped rGO aerogel in our work add to the body of knowledge available to other researchers attempting to forecast the prospects of these composites for the development of Na-ion batteries.

2. Materials and Methods

2.1. Synthesis of the Mn$_3$O$_4$/N- and Mn$_3$O$_4$/N,S-rGO Aerogels

GO was obtained using a typical Hummers method [48]. Mn$_3$O$_4$ was synthesised according to the previous work [49]. For the synthesis of the Mn$_3$O$_4$/N-rGO aerogel, 90 mg GO and 63 mg Mn$_3$O$_4$ were ultrasonically dispersed in 18 mL deionised (DI) water for 1 h, and then 4 mL ammonia (NH$_3$, Sigma-Aldrich, St. Louis, MO, USA) was slowly added into the mixture. The mixture was transferred into a Teflon-lined (125 mL) stainless-steel autoclave and heated at 180 °C for 12 h. Finally, the black hydrogel suspensions were freeze-dried to collect the Mn$_3$O$_4$/N-rGO aerogel. The same procedure was performed to prepare the N,S-rGO aerogel; however, NH$_3$ was replaced with L-cysteine (Sigma-Aldrich, St. Louis, MO, USA) as a nitrogen/sulphur source and denoted as Mn$_3$O$_4$/N,S-rGO aerogel.

2.2. Physical Characterisation

The structural phases of the obtained samples were determined via X-ray diffraction (XRD; Rigaku Miniflex II, Tokyo, Japan). The amount of Mn$_3$O$_4$ in the heteroatom-doped rGO aerogel was confirmed using a thermogravimetric analyser (TGA, Perkin Elmer, Waltham, MA, USA) within the temperature range of 30 °C–800 °C at a heating rate of 10 °C min$^{-1}$ in air. The morphology of these samples was observed via scanning electron microscopy (SEM; JOEL, Akishima, Tokyo, Japan) (JSM-6360L) and transmission electron microscopy (TEM; TECNAI G2 20 S-TWIN FEI, FEI Company, Lincoln, NE, USA). Fourier transform infrared spectroscopy (FTIR) was recorded on IR Tracer-100, Shimadzu, Kyoto, Japan. Raman spectra were collected via Raman spectroscopy (Renishaw, Gloucestershire, UK (532 nm radiation)) extended with 0.1% power laser measurement. Surface composition analysis was further conducted via X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD XPS, Kratos, Manchester, UK).

2.3. Electrochemical Measurements

The active materials, carbon black (Sigma-Aldrich, >99.5%, St. Louis, MO, United States) and polyvinylidene fluoride (PVDF, Sigma-Aldrich, St. Louis, MO, United States) (weight ratio, 75:20:5), were dissolved in N-methyl-2-pyrrolidone (NMP). The slurry was then coated onto a copper (Cu) foil and dried at 100 °C overnight. CR2032 coin-type cells were fabricated in an argon-filled glovebox (Unilab, MBRAUN, Garching, Germany, H$_2$O, O$_2$ < 0.1 ppm) using sodium metal (Sigma-Aldrich, 99.9% trace metal base, St. Louis, MO, United States), glass fibre (GF/D Whatman) separator, and electrolyte (1 M NaClO$_4$ (98%, Sigma-Aldrich) in propylene carbonate (99.7%, Sigma-Aldrich, St. Louis, MO, United States) with the addition of 5 wt.% fluoroethylene carbonate (99%, Sigma-Aldrich, St. Louis, MO, United States). The electrochemical performances of the nanocomposites were studied using a Neware battery analyser. Cyclic voltammetry (CV) was conducted using an electrochemical workstation (CHI 700E).

3. Results and Discussion

Scheme 1 presents the synthesis of the Mn$_3$O$_4$/heteroatom-doped rGO aerogel using GO through hydrothermal, followed by freeze-drying. Upon heating, GO was converted to rGO, and simultaneously, through the $\pi$–$\pi$ interactions, hydrogen bonding, coordination, and electrostatic interactions, the GO layers could self-assemble into three-dimensional (3D) networks. Concurrently, the presence of NH$_3$ and L-cysteine introduced the doping of N-atom and N,S-atoms on the rGO layer, respectively. Strong cross-links, which are the
building blocks of the 3D rGO network, were produced as a result of this process and acted as an effective conductive network for ion and electron transportation [30].

Scheme 1. Schematic representation of the synthesis procedure of the Mn$_3$O$_4$/heteroatom-doped rGO aerogel.

The thermal stability (in air) of all samples was determined via TGA. The TGA curve (Figure 1) shows two weight loss stages for all samples, except for pristine Mn$_3$O$_4$, and the evaporation of physically and chemically adsorbed water was adequately attributed to the weight loss at temperatures above 100 °C. Between 150 °C and 600 °C, the N-rGO and N,S-rGO aerogels demonstrated the decomposition and disintegration of nitrogen and sulphur-containing functional groups, followed by decarboxylation and elimination of hydroxyl functionalities, respectively [50]. For a temperature less than 500 °C in air, rGO is often entirely burnt to CO$_2$ [51]. For the Mn$_3$O$_4$ nanoparticles, no weight loss was observed in the temperature range of 100 °C to 500 °C. As the temperature approached 540 °C, the weight began to increase, which could be attributed to the transformation of Mn$_3$O$_4$ to Mn$_2$O$_3$ [30,33]. Therefore, the amounts of Mn$_3$O$_4$ in the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels were estimated to be 63 and 60 wt.%, respectively.
The phase purity and structure of the synthesised N-rGO aerogel, N,S-rGO aerogel, pure Mn$_3$O$_4$, Mn$_3$O$_4$/N-rGO aerogel, and Mn$_3$O$_4$/N,S-rGO aerogel were analysed via XRD. The disordered configuration of loosely packed graphene sheets of the N-rGO and N,S-rGO aerogels was disclosed by the enormous broad peak at approximately 24°–25°, corresponding to the graphite (002) plane (Figure 2) [52,53]. Because of the relatively low diffraction intensity of the N-rGO and N,S-rGO aerogels compared with Mn$_3$O$_4$ prominent peaks, the diffraction peaks of these aerogels were less evident in the XRD patterns of the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels [54]. Both Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels corresponded to the planes of tetragonal crystallinity in Mn$_3$O$_4$ (JCPDS card no 240734), hence indicating the presence of pure Mn$_3$O$_4$ without any noticeable impurities. The crystallite size of Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels were 12.7 and 17.4 nm, respectively, calculated using Scherrer’s Equation. These results supported the formation and dispersion of Mn$_3$O$_4$ nanoparticles on the network surface of the N-rGO and N,S-rGO aerogels.

Figure 3 presents the SEM images for all samples. The N-rGO (Figure 3a) and N,S-rGO (Figure 3b) aerogel samples exhibited a typical well-defined and interconnected 3D network structure of rGO aerogel with a pore structure smaller than 1 μm. Such structures could provide an open channel for the access of electrolytes and minimise volume changes during the charge and discharge processes [55]. It is clearly demonstrated that Mn$_3$O$_4$ agglomerated in a size of 0.5–1.1 μm, which is an aggregate of individual Mn$_3$O$_4$ nanoparticles, anchored uniformly on the porous N-rGO (Figure 3c) and N,S-rGO (Figure 3d) aerogel layers. This suggests an effective assembly between the Mn$_3$O$_4$ nanoparticles and rGO aerogel sheets during the hydrothermal treatment. Moreover, pristine Mn$_3$O$_4$ nanoparticles with a particle size of 0.5–1.0 μm are beneficial in that they provide more active sites for the electrochemical reaction [56,57]. Therefore, the synergistic effect between the small-sized Mn$_3$O$_4$ and heteroatom-doped rGO aerogel could have a
tremendous effect on the electrochemical properties, especially the cyclability and rate capability of the batteries.

Figure 2. XRD patterns of Mn₃O₄, N-rGO aerogel, N,S-rGO aerogel, Mn₃O₄/N-rGO aerogel, and Mn₃O₄/N,S-rGO aerogel.

Figure 3. SEM images of (a) N-rGO aerogel, (b) N,S-rGO aerogel, (c) Mn₃O₄/N-rGO aerogel, (d) Mn₃O₄/N,S-rGO aerogel, and (e) pristine Mn₃O₄.
Further characterisation of the morphology and structure of the Mn₃O₄/N-rGO and Mn₃O₄/N,S-rGO aerogels was carried out using high-resolution transmission electron microscopy (HRTEM). A typical crumpled structure of rGO and interconnected and cross-linked random rGO layers construct a 3D framework with open-pore structures (Figure 4a,b). The heteroatom-doped rGO aerogels exhibited a thin lamellar structure with distinct edges, overlaps, and curve profiles. Furthermore, the N-rGO and N,S-rGO aerogels had more wrinkled surfaces because of structural defects caused by heteroatom doping. Figure 4g shows the TEM image of Mn₃O₄. From Figure 4c,d, it can be seen that the Mn₃O₄ nanoparticles are uniformly dispersed over the surface of the rGO layers, with 15–20 nm average diameters of Mn₃O₄ nanoparticles (measured from the distribution histogram (inset)). The HRTEM images (Figure 4e,f) show that each Mn₃O₄ nanoparticle has a distinct lattice fringe, confirming the crystalline nature of Mn₃O₄ in the heteroatom-doped rGO aerogel. The HRTEM images indicate that the distinct interlayer d-spacing is 0.25 nm, which corresponds to the (211) plane of the tetragonal phase of the Mn₃O₄ nanoparticles. These results suggested that the Mn₃O₄ nanoparticles have a strong connection and network with the heteroatom-doped rGO aerogels, which is in accordance with the SEM images.

The disordered degree of the heteroatom-doped rGO aerogels was characterised via Raman spectroscopy and is presented in Figure 5. Typical broad peaks corresponding to the D and G bands at 1359 and 1600 cm⁻¹, respectively, were observed in the heteroatom-doped rGO aerogels. The G band reflected the radial C-C stretching of ordered sp²-linked carbon atoms, whereas the D band indicated the defects or irregularities on the graphene edges [58,59]. Furthermore, the intensity ratio of the D and G bands (I_D/I_G) for the N-rGO aerogel was 0.95, whereas it was 0.98 for the N,S-rGO aerogel. After the nitrogen and sulphur doping, defects were introduced to the rGO aerogel layers [60,61], where the I_D/I_G ratios of the Mn₃O₄/N-rGO and Mn₃O₄/N,S-rGO aerogels increased to 0.98 and 1.00, respectively. Two peaks at 658 and 369 cm⁻¹ were observed in the Mn₃O₄/N-rGO and Mn₃O₄/N,S rGO aerogels, respectively [62,63]. These strong peaks corresponded to the Mn-O breathing vibration of Mn²⁺ ions and thus demonstrated that Mn₃O₄ is successfully attached to the rGO layer [64,65]. Additionally, the peaks at 2450 cm⁻¹ were associated with the second-order two-phonon mode 2D band. It is worth noting that the Raman spectrum associated with Mn₃O₄ in the Mn₃O₄/N-rGO and Mn₃O₄/N,S-rGO aerogels was shifted to a low wavenumber in comparison with the pristine Mn₃O₄, indicating the electronic coupling between Mn₃O₄ and heteroatom rGO aerogel.

Figure 6 presents the FTIR spectra of the Mn₃O₄/N-rGO and Mn₃O₄/N,S-rGO aerogels to further support the presence of heteroatom in the rGO aerogel, as well as the Mn₃O₄ nanoparticles in the nanocomposites. The peak positioned at 1730, 1363, and 1215 cm⁻¹ corresponded to the stretching vibration C=O of carboxylic groups, O-H deformation, and C-O stretching vibration from epoxy groups, respectively, indicating that GO was successfully converted into rGO [66,67]. The peak located at 1099 and 2451 cm⁻¹ associated with the absorption band of C=S and S-H stretching vibration, respectively, was observed in the N,S-rGO and Mn₃O₄/N,S-rGO aerogels and, thus, confirmed the presence of S atom on the surface of N,S-rGO aerogel samples [68]. In addition, the C-N stretching vibration band located at 1416 cm⁻¹ could be assigned to the characteristic band of nitrogen doping. For the Mn₃O₄ nanoparticles, the strong peaks at 528 and 621 cm⁻¹ were attributed to the Mn-O stretching of the tetrahedral and octahedral sites in Mn₃O₄ [30]. As a result, Mn-O, C-N, C=S, and N-H linkages confirmed that Mn₃O₄ nanoparticles were successfully integrated into the heteroatom rGO layers.
Figure 4. TEM images of (a) N-rGO aerogel, (b) N,S-rGO aerogel, (c) Mn$_3$O$_4$/N-rGO aerogel (inset: particle-size distribution), (d) Mn$_3$O$_4$/N,S-rGO aerogel (inset: particle-size distribution), and (g) Mn$_3$O$_4$ nanoparticles and HRTEM images of (e) Mn$_3$O$_4$/N-rGO aerogel and (f) Mn$_3$O$_4$/N,S-rGO aerogel.

The disordered degree of the heteroatom-doped rGO aerogels was characterised via Raman spectroscopy and is presented in Figure 5. Typical broad peaks corresponding to the D and G bands at 1359 and 1600 cm$^{-1}$, respectively, were observed in the heteroatom-doped rGO aerogels. The G band reflected the radial C-C stretching of ordered sp$_2$-linked carbon atoms, whereas the D band indicated the defects or irregularities on the graphene edges [58,59]. Furthermore, the intensity ratio of the D and G bands ($I_D/I_G$) for the N-rGO aerogel was 0.95, whereas it was 0.98 for the N,S-rGO aerogel. After the nitrogen and sulfur doping, defects were introduced to the rGO aerogel layers [60,61], where the $I_D/I_G$ ratios of the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels increased to 0.98 and 1.00, respectively. Two peaks at 658 and 369 cm$^{-1}$ were observed in the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels.
Figure 5. Raman spectra of N-rGO aerogel, N,S-rGO aerogel, Mn₃O₄ nanoparticles, Mn₃O₄/N-rGO aerogel, and Mn₃O₄/N,S-rGO aerogel.

Figure 6. FTIR spectra of N-rGO aerogel, N,S-rGO aerogel, Mn₃O₄ nanoparticles, Mn₃O₄/N-rGO aerogel, and Mn₃O₄/N,S-rGO aerogel.
The XPS technique was used to obtain further insight into the chemical states of elements on the surface of the samples. Figure 7 presents the XPS spectra of the Mn$_3$O$_4$/N,S-rGO and Mn$_3$O$_4$/N-rGO aerogels, respectively. From the survey scan XPS spectra, the presence of nitrogen (Figure 7a) and nitrogen–sulphur (Figure 7b) is noticeable, which agrees well with the FTIR results. For the Mn$_3$O$_4$/N-rGO aerogel, the atomic percentage of the N was 11.54%, whereas, for the Mn$_3$O$_4$/N,S-rGO aerogel, the atomic percentages of the N and S were 4.12% and 2.76%, respectively. Both nanocomposites exhibited an Mn 2p$_{3/2}$ at 642 eV, Mn 2p$_{1/2}$ at 653 eV, Mn 3s at 771 eV, an O 1s peak at 531.6 eV, a C 1s peak at 284.5 eV, and N 1s peak at 399.3 eV. For O 1s (Figure 7c,d), the XPS spectra could be deconvoluted into four peaks located at 527, 531, 533, and 534 eV, which correspond to Mn-O, C-O-Mn, C=O, and surface adsorbed oxygen, respectively. The C 1s (Figure 7e,f) could be fitted into three different peaks, which corresponded to the signal of C-C (283.5 eV) and C=O (287 eV) for both nanocomposites, C-O, C-S, and C-N (285.4 eV) for the Mn$_3$O$_4$/N,S-rGO aerogel, and C-O and C-N (284.6 eV) for the Mn$_3$O$_4$/N-rGO aerogel. Thus, it further confirmed the presence of N and S-atoms in the nanocomposites [24]. Figure 7g,h present the N 1s region, where the binding energies located at 397, 399, and 403 eV were assigned to pyridinic N, pyrrolic N, and graphitic N, respectively. The presence of pyridinic N, graphitic N, and pyrrolic N at the defect or edge sites was favourable to improving the Na-ion transport and sodium storage capacity [69]. As can be seen from Figure 7i, the S 2p spectra positioned at 163.8, 164.9, and 168.9 eV are assigned to S 2p$_{3/2}$, S 2p$_{1/2}$, and SO$_x$, respectively, indicating the existence of Mn-S [70,71]. The curve fitting of the high-resolution Mn 2p spectrum for the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels is presented in Figure 7j. The peak located at 640–652 eV and 651–655 eV could be assigned to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively, indicating the existence of the Mn species, implying the possible presence of Mn$_3$O$_4$ in the nanocomposites [72]. The splitting widths of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ were 12.2 and 11.4 eV for the Mn$_3$O$_4$/N,S-rGO and Mn$_3$O$_4$/N-rGO aerogels, respectively, and were in accordance with other earlier reports [73], which further demonstrated that the Mn$_3$O$_4$ nanoparticles have formed in the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels.
Figure 7. XPS spectra for the survey spectrum of (a) Mn$_3$O$_4$/N,S-rGO aerogel and (b) Mn$_3$O$_4$/N-rGO aerogel, O 1s spectra of (c) Mn$_3$O$_4$/N,S-rGO aerogel and (d) Mn$_3$O$_4$/N-rGO aerogel, C 1s spectra of (e) Mn$_3$O$_4$/N,S-rGO aerogel and (f) Mn$_3$O$_4$/N-rGO aerogel, N 1s spectra of (g) Mn$_3$O$_4$/N,S-rGO aerogel and (h) Mn$_3$O$_4$/N-rGO aerogel, (i) S 2p spectra of Mn$_3$O$_4$/N-rGO aerogel and Mn$_3$O$_4$/N,S-rGO aerogel and (j) deconvoluted spectra of Mn 2p of Mn$_3$O$_4$/N-rGO aerogel.

To evaluate the sodium storage performances of the samples, the CV and galvanostatic charge/discharge testing have been conducted in a half-cell within the potential range of 0.01–3.00 V. As can be seen from Figure 8a, all samples exhibit a strong cathodic peak at 0.85 V in the first cycle and could be ascribed to the reductions of Mn$_3$O$_4$ to MnO as well as the formation of Na$_2$O, which is attributed to the decomposition of the electrolyte according to Equation (1)

\[
\text{Mn}_3\text{O}_4 + 2\text{Na}^+ + 2\text{e}^- \rightarrow 3\text{MnO} + \text{Na}_2\text{O} \tag{1}
\]
To evaluate the sodium storage performances of the samples, the CV and galvanostatic charge/discharge testing have been conducted in a half-cell configuration. The CV curves of (a) Mn$_3$O$_4$ nanoparticles, (b) Mn$_3$O$_4$/N-rGO aerogel, and (c) Mn$_3$O$_4$/N,S-rGO aerogel at a scanning rate of 0.1 mV s$^{-1}$. The peaks at 0.45 to 0.01 V could be attributed to the reduction of MnO to metallic Mn (Equation (2)) and solid electrolyte interphase (SEI) layer formation on the electrode surface of the electroactive material.

\[
\text{MnO} + 2\text{Na}^+ + 2e^- \rightarrow \text{Mn} + \text{Na}_2\text{O} \quad (2)
\]

During subsequent cycles, the CV curves nearly overlapped, indicating that the Mn$_3$O$_4$/heteroatom rGO aerogel was reversible during the insertion/de-insertion process of Na$^+$ ions [74]. The tiny peaks at 0.1 V and the broad peak at 0.8 V in the anodic process corresponded to Na$^+$ extraction into the graphitic carbon layers, which was the inverse process of Na$^+$ intercalation. When compared with Li-ion batteries, the CV peaks in Na-ion batteries were broader and weaker. This may be due to the larger radius of Na$^+$ than Li$^+$ and the slower Na$^+$ intercalation between graphitic carbon layers [75,76]. Contrary to the Mn$_3$O$_4$/N-rGO aerogel (Figure 8b), the Mn$_3$O$_4$/N,S-rGO aerogel (Figure 8c) exhibited a pair of small redox peaks at 1.6 and 1.8 V, which could be attributed to the sulphur embedded in the porous N,S-rGO aerogel during the Na-ion insertion/de-insertion process [77]. The CV curves exhibited good reversibility, leading to good cycling stability for longer cycles, and the overall sodium storage mechanism between Mn$_3$O$_4$ and Na$^+$ is expressed in Equation (3).

\[
\text{Mn}_3\text{O}_4 + 8\text{Na}^+ + 8e^- \leftrightarrow 3\text{Mn} + 4\text{Na}_2\text{O} \quad (3)
\]

Figure 9 presents the typical discharge/charge profiles of Mn$_3$O$_4$ and the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels electrodes for selected cycles at a current density of 0.1 A g$^{-1}$. The subsequent CV curves are different from the first sodiation, and the discharge plateau for the Mn$_3$O$_4$/N-rGO and Mn$_3$O$_4$/N,S-rGO aerogels is much longer than the pristine one, indicating that more Na-ions can be inserted into these nanocomposites [78]. Furthermore, no distinct plateau is observed, which is consistent with the CV results.
Figure 9. Charge/discharge profiles at selected cycles for (a) Mn$_3$O$_4$ nanoparticles, (b) Mn$_3$O$_4$/N-rGO aerogel, and (c) Mn$_3$O$_4$/N,S-rGO aerogel.

The cycling stability of all electrodes is presented in Figure 10a. The initial discharge capacities of Mn$_3$O$_4$, Mn$_3$O$_4$/N-rGO aerogel and Mn$_3$O$_4$/N,S-rGO aerogel were measured to be 522, 1950, and 884 mAh g$^{-1}$, respectively. In the second cycle, the discharge capacities were 336, 470, and 425 mAh g$^{-1}$ for Mn$_3$O$_4$, Mn$_3$O$_4$/N-rGO aerogel and Mn$_3$O$_4$/N,S-rGO aerogel, respectively. The irreversible capacity loss was mainly due to the irreversible formation of the SEI layer. Interestingly, the Mn$_3$O$_4$/N-rGO aerogel maintained its discharge capacity at 374 mAh g$^{-1}$ after 100 cycles with an 80% retention rate. Contrarily, the Mn$_3$O$_4$/N,S-rGO aerogel and Mn$_3$O$_4$ exhibited much lower discharge capacities of 281 mAh g$^{-1}$ (68% retention rate) and 185 mAh g$^{-1}$ (55% retention rate) after 100 cycles. For the few initial cycles, the porous structure of rGO aerogel promoted the formation of excessive SEI layers, resulting in a lower initial Coulombic efficiency [79]. Overall, the average Coulombic efficiency of all electrodes was almost 99%. Nevertheless, the Mn$_3$O$_4$/N,S-rGO aerogel electrodes demonstrated much lower discharge capacity, presumably because of the large atomic radius of S, as well as the large crystallite size than that of Mn$_3$O$_4$/N-rGO aerogel electrodes.
capacities of 203, 166, 145, 135, 128, and 156 mAh g\(^{-1}\) at various current densities of 0.2, 0.4, 0.6, 0.8, 1.0, and returning to 0.2 A g\(^{-1}\). The minimal drop in capacities with increased current densities indicated a higher degree of reversible Na-ion insertion/de-insertion owing to their expanded interlayer spacing [80]. The improved cycle and rate performance of Mn\(_3\)O\(_4\)/heteroatom-doped rGO aerogels may be due, in part, to the 3D porous structure, which may minimise the electron and ion transport path.

The specific capacity and cyclability of the Mn\(_3\)O\(_4\)/N-rGO aerogel and Mn\(_3\)O\(_4\)/N,S-rGO aerogel were improved, which benefitted from the synergistic effect of the heteroatom doping and porous structure of the rGO, as well as the small particle sizes of Mn\(_3\)O\(_4\). The rGO sheets as well as the porous structure in the conductive network of

Figure 10. (a) Cycling performances and Coulombic efficiencies of up to 100 cycles at a current density of 0.1 A g\(^{-1}\) and (b) rate capability at different current densities for Mn\(_3\)O\(_4\), Mn\(_3\)O\(_4\)/N-rGO aerogel, and Mn\(_3\)O\(_4\)/N,S-rGO aerogel.

In addition to their high discharge capacity and good cycling stability, the Mn\(_3\)O\(_4\)/N-rGO and Mn\(_3\)O\(_4\)/N,S-rGO aerogel electrodes exhibited remarkable rate performance, as presented in Figure 10b. The Mn\(_3\)O\(_4\)/N-rGO aerogel electrode exhibited discharge capacities of 203, 166, 145, 135, 128, and 156 mAh g\(^{-1}\) at various current densities of 0.2, 0.4, 0.6, 0.8, 1.0, and returning to 0.2 A g\(^{-1}\). The minimal drop in capacities with increased current densities indicated a higher degree of reversible Na-ion insertion/de-insertion owing to their expanded interlayer spacing [80]. The improved cycle and rate performance of Mn\(_3\)O\(_4\)/heteroatom-doped rGO aerogels may be due, in part, to the 3D porous structure, which may minimise the electron and ion transport path.

The specific capacity and cyclability of the Mn\(_3\)O\(_4\)/N-rGO aerogel and Mn\(_3\)O\(_4\)/N,S-rGO aerogel were improved, which benefitted from the synergistic effect of the heteroatom doping and porous structure of the rGO, as well as the small particle sizes of Mn\(_3\)O\(_4\). The rGO sheets as well as the porous structure in the conductive network of
the Mn$_3$O$_4$/heteroatom rGO aerogels provided an efficient electron and ion transport path, thereby decreasing the internal resistance to enhance the reaction kinetics and resulting in a high specific capacity and rate capability [81–83]. Poor electrical conductivity and large volume expansion in transition-metal oxide electrodes during the Na-ion insertion/de-insertion processes are among the constraints in the development of these materials for Na-ion battery applications. Here, the rGO sheets are more likely to provide sufficient elastic buffer space for the transition-metal oxide to accommodate the volume expansion/contraction and prevent the electrode from cracking or crumbling during the charge/discharge processes. In addition, the presence of the rGO aerogel could effectively enhance the electrical conductivity of the nanocomposites [84]. Meanwhile, Mn$_3$O$_4$ nanoparticles anchored on rGO can prevent the restacking of the rGO layers, preserve their high active surface area and maintain the channels for Na-ion diffusion, which is advantageous for increasing the Na storage within the nanocomposites [85]. Doping the rGO aerogels with nitrogen and codoping nitrogen/sulphur improves the physicochemical properties of the rGO component [43]. The incorporation of these heteroatoms into the rGO aerogels could facilitate the charge transfer between adjacent carbon atoms [86–88], thus improving the electrical conductivity and electrochemical activity of the rGO itself. The defects created by N-doping and functionalised groups may increase the electrical conductivity, and the larger covalent radius of S compared with Na may increase the interlayer spacing to facilitate Na-ion insertion/de-insertion within the electrode. All the aforementioned characteristics contributed to the improvements in the specific capacity and cycling ability of the Mn$_3$O$_4$/heteroatom-doped rGO aerogels. This strategy can be used as one of the approaches for mitigating the large volume change and poor electrical conductivity, which is associated with bare transition-metal oxide anodes.

4. Conclusions

In summary, the Mn$_3$O$_4$/heteroatom-doped rGO aerogels have been successfully synthesised via a hydrothermal route, followed by a freeze-drying process using NH$_3$ and L-cysteine as nitrogen and nitrogen–sulphur sources, respectively. The aerogel structure built well-interconnected heteroatom-doped rGO layers, and the Mn$_3$O$_4$ nanoparticles distributed on the rGO layers prevented the graphene layers from restacking again. The 3D structure provides a large active surface area and eases electron diffusion and Na-ion transportation. Both the N- and N,S-doped rGO aerogels with Mn$_3$O$_4$ exhibited high specific capacity, excellent cycling stability, and rate capability than the pristine Mn$_3$O$_4$. The heteroatom-doped rGO aerogel acts as a robust structure to accommodate the volume expansion of Mn$_3$O$_4$ nanoparticles and enables reversible Na-ion insertion/de-insertion. Our work demonstrates that N- and N,S-doped rGO aerogels can efficiently improve the Na storage capacity of Mn$_3$O$_4$ and offer a useful strategy for synthesising high-yield anode materials. Considering the simple step of the preparation process and the excellent cycling stability of the samples, the Mn$_3$O$_4$/heteroatom-doped rGO aerogel can be considered a potential candidate and provide an opportunity to explore these materials for the next generation of Na-ion batteries.

Author Contributions: Conceptualization, N.F.M.Y. and N.H.I.; methodology, N.F.M.Y., M.F.M.D., S.R.M. and N.A.H.; formal analysis, N.F.M.Y.; writing—original draft, N.F.M.Y.; visualization, N.F.M.Y., N.H.I. and M.F.M.D.; validation, N.H.I., M.F.M.D., S.R.M. and N.A.H.; investigation, N.H.I.; writing—review and editing, N.H.I., M.F.M.D., S.R.M. and N.A.H.; supervision, N.H.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundamental Research Grant Scheme (FRGS; FRGS/1/2018/S T G07/ U M T/02/3; VOT 59520).

Data Availability Statement: Not applicable.

Acknowledgments: Ministry of Higher Education Malaysia is acknowledged for financial support through the Fundamental Research Grant Scheme (FRGS; FRGS/1/2018/STG07/UMT/02/3).
Conflicts of Interest: The authors declare no conflict of interest.

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