A high capacity MnFe$_2$O$_4$/rGO nanocomposite for Li and Na-ion battery applications†

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A porous MnFe$_2$O$_4$/reduced graphene oxide (rGO) nanocomposite with high storage capacity was prepared by a hydrothermal method. The MnFe$_2$O$_4$/rGO nanocomposite sample was characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and high resolution transmission electron microscopy. The electrochemical characteristics with lithium as well as sodium were studied using cyclic voltammetry and a battery cycle tester. In this work, apart from the lithium storage, the sodium storage ability of the spinel type MnFe$_2$O$_4$ as an anode is demonstrated for the first time. The prepared MnFe$_2$O$_4$/rGO composite with sodium alginate binder shows a highly stable capacity of 905 mA h g$^{-1}$ versus Li/Li$^+$ and 258 mA h g$^{-1}$ versus Na/Na$^+$ at 0.1 C rate. The enhancement in capacity and excellent cycleability of the MnFe$_2$O$_4$/reduce graphene oxide nanocomposite is due to constrained volume expansion during conversion reactions and enhancement of electrical conductivity.

1. Introduction

In recent times, there has been an incredible increase in the use of lithium ion batteries due to their practical applications in electronic devices, hybrid electric vehicles and all types of electric vehicles.1–5 In order to find an alternative to lithium energy storage systems, researchers have focused on sodium ion batteries. Sodium is very cheap and abundant in the earth’s crust, which makes it the most advantageous element for battery applications after lithium. Furthermore, its interaction chemistry is similar to lithium. These days, the most common anode materials used in secondary ion batteries are carbon materials. The drawback of using carbon materials as anodes is that they lead to a lower reversible storage capacity that cannot meet the growing demands of high storage capacity of secondary batteries.6 It has thus become imperative to develop an electrode material with low cost, long life, high storage capacity and safety.7–9 One of the promising materials having high performance as anode materials for secondary ion batteries is transition metal oxides (TMO). The TMO based materials has high capacity as compared with the commercially used graphite material (e.g., 1007 mA h g$^{-1}$ of Fe$_2$O$_3$; 890 mA h g$^{-1}$ of Co$_3$O$_4$; 755 mA h g$^{-1}$ of MnO; 717 mA h g$^{-1}$ for NiO).10,11 Also, binary metal oxides also called as spinel ferrites with the general formula MFe$_2$O$_4$ (M = Mn, Co, Ni, Zn or Mg) are very fascinating materials due to their interesting electrical and magnetic properties with high thermal and chemical stabilities.12 Manganese ferrite (MnFe$_2$O$_4$) one of the ferrite families is grown as various morphologies such as nanocrystals,13 nanocubes14 and hollow spheres.15 Manganese ferrite stores through the conversion reaction mechanism (MnFe$_2$O$_4$ + 8X$^-$ + 8e$^-$ → Mn + 2Fe + 4X$_2$O; X = Li & Na) and it has high theoretical capacity of 928 mA h g$^{-1}$, which is much higher than carbon anode (375 mA h g$^{-1}$).16 The TMO materials show poor electrochemical performances due to low electronic conductivity. To overcome this problem, doping of high electronic conducting carbon forms to achieve enhanced electrochemical properties is essential.

Besides, graphene based nanocomposites as anodes for rechargeable lithium ion batteries have been extensively investigated, such as graphene–metal composite,16 graphene–metal oxides17 and graphene–sulfur composites.18 The decoration of nanoparticles into the graphene sheets will generate a porous network, providing an outstanding electron-conducting and ion-transporting pathway.19,20 The theoretical capacity of graphene is 744 mA h g$^{-1}$, which is twice than that of graphite materials. In case of sodium ion battery, Fe$_2$O$_3$/graphene sheet composites,21 and MoS$_2$/carbon nanofibers etc., were used as anode materials.22 Thus, graphene based nanocomposite materials will have enhanced electrochemical performances, particularly charging/discharging process and rate capabilities. In present work, manganese ferrite incorporated in graphene sheets was prepared via solvolithothermal process. The prepared
materials were characterized using XRD, Raman, SEM and TEM techniques. The composite was further tested as anode for lithium as well as sodium ion battery applications and results showed that it exhibited high storage capacity and excellent cyclic stability.

2. Experimental

2.1 Synthesis of MnFe$_2$O$_4$/rGO composite

Graphene oxide is primary precursor to synthesis the reduced graphene oxide and manganese ferrite nanocomposite (MnFe$_2$O$_4$/rGO), which was prepared from natural graphite by a modified Hummer’s method.$^{24}$ Manganese ferrite nanocomposite was synthesized from our previous work.$^{25}$ In a typical procedure, 300 mg of graphene oxide, 3 mmol of manganese chloride (MnCl$_2$·4H$_2$O) and 6 mmol of ferric chloride (FeCl$_3$·6H$_2$O) were mixed and dissolved in an appropriate amount of ethylene glycol followed by ultrasonication for more than 2 h. Then the mixture was subjected to stirring by adding sodium acetate and polyethylene glycol about for a certain time. The product was dried in Teflon coated hydrothermal bomb and kept in hot-air oven at 200 °C for 10 h. Finally, after reaching to room temperature, the product was separated by centrifugation for several times in water and ethanol followed by drying at 60 °C.

2.2 Characterization

X-Ray diffraction patterns (XRD) were recorded on a Rigaku Miniflex using the Cu Kα radiation ($\lambda = 1.5406 \AA$) over 2θ range from 10–80°. The microscopic feature of the samples was characterized by field-emission scanning electron microscopy (SEM) (Hitachi S-4800) and high-resolution transmission electron microscopy (HR-TEM) with Energy Dispersive Spectrometer (EDS) (JEOL-2000EX, JEOL, Tokyo, Japan) operated at 120 kV. Raman measurements were carried out in the back scattered geometry using an (He–Ne laser) laser excitation source emitting at 514 nm with 20 mW power coupled with an ARAMIS (Horiba Jobin Yvon, France) micro-Raman spectrometer. Elemental analysis (EA) was carried out by using Thermo Scientific Flash 2000 Series element analyser. Thermogravimetric (TG) analysis was carried out on Q600 (TA Instruments, USA) at a heating rate of 5 °C min$^{-1}$ in air (200 ml min$^{-1}$).

2.3 Electrochemical measurement

Electrochemical studies of the synthesized MnFe$_2$O$_4$/rGO nanospheres were carried out in CR2032 type cells. The electrode composite consists of 70% active material, 20% Super P carbon and 10% Na-alginate in DI water solvent. The above mixture was grounded properly to form slurry. The slurry was centrifuged for several times in water and ethanol followed by centrifugation for several times in water and ethanol before use. The dried Cu-foil was cut into circular electrode disks. The electrode consisted of 70% active materials, 20% Super P carbon and 10% Na-alginate in DI water solvent. The above mixture was grounded properly to form slurry. The slurry was subjected to stirring and aging by adding ethylene glycol followed by ultrasonication for more than 2 h. Then the mixture was subjected to stirring by adding sodium acetate and polyethylene glycol about for a certain time. The product was dried in Teflon coated hydrothermal bomb and kept in hot-air oven at 200 °C for 10 h. Finally, after reaching to room temperature, the product was separated by centrifugation for several times in water and ethanol before use.

As shown in Fig. 2, the Raman spectra of as-prepared MnFe$_2$O$_4$/rGO nanocomposite consists of two parts, which correspond to (111), (220), (311), (400), (422), (333), (440), (533) and (622) crystal planes of MnFe$_2$O$_4$ in accordance with the standard JCPDS no. 74-2403. The peaks were broad indicating the nanocrystalline nature of the material. Under these experimental conditions, no other diffraction peaks were obtained, which indicates that the prepared material is of high purity.

For the reference, pure MnFe$_2$O$_4$ XRD patterns along with JCPDS data was shown in Fig. S1.$^6$ Raman spectroscopy is one of the techniques, to know the defects in the sp$^2$ carbon materials. As shown in the Fig. 2, the Raman spectra of as-prepared material MnFe$_2$O$_4$/rGO have peaks at 1340, 1595, 2680 and 2947 cm$^{-1}$ are assigned to D, G, 2D and D + G-bands respectively and a weak peak at 615 cm$^{-1}$ was assigned to the MnFe$_2$O$_4$ nanoparticles.$^5$
3.2 Morphological & thermo-gravimetric analysis

The surface morphology and particle size of the as-prepared MnFe₂O₄/rGO nanocomposite were further analyzed by FE-SEM and HR-TEM. From the FE-SEM images as shown in Fig. 3, it was observed that the MnFe₂O₄ nanoparticles were well decorated as homogeneous spherical particles onto the graphene sheets and the estimated cluster size was \( \sim 130 \text{ nm} \). Fig. 3c and d shows the SEM images of the MnFe₂O₄/rGO nanocomposite in different magnifications. From Fig. 3d, the MnFe₂O₄ nano-clusters were sandwich between graphene sheets, which is good evidence for the stable electrode operations during the conversion reaction. Structure of the MnFe₂O₄/rGO nanocomposite was further investigated by HR-TEM. HR-TEM images of pure porous MnFe₂O₄ nanostructures at different magnifications are shown in Fig. 4, which indicated the formation of agglomerated clusters made up off very small nano sized particles with \( \sim 120 \text{ nm} \) in diameter, which is close that observed from FE-SEM. The SAED patterns were recorded and Debye-Scherrer rings were obtained. These are shown in Fig. 4d and represented as \((111), (220), (311), (400), (422), (333), (440), (533)\) and \(622\) lattice planes, which are supported by the XRD analysis. Furthermore, from elemental analysis, the carbon content in this composite is 19 wt%. Hence it is confirmed from the above analysis that the solvothermal route offered a homogeneous synthesis of the composite.

Furthermore, thermo-gravimetric analyses of the composite were carried out in air to know the phase changes and decomposition details. MnFe₂O₄/rGO composite was heated to 1000 °C at a rate of 5 °C min⁻¹ and the corresponding TG and DTA curves for MnFe₂O₄/rGO composite is given in Fig. S2.† The TGA measurement identifies the weight loss of the materials from 35 °C to 1000 °C. The weight loss below 100 °C is ascribed to be desorption of physically adsorbed moisture. Furthermore, weight loss above 150 °C is due to decomposition of ethylene glycol, whereas from 500–800 °C, a plateau is observed which could be due to the partial decomposition of the sample to form monophasic MnFe₂O₄. After 750 °C, there is an abrupt decrease in weight (%), which could be due to burning of graphene. This temperature is slightly higher as it is in the form of composite with MnFe₂O₄. From Fig. S2,† the loading percentage of graphene was calculated from TGA of MnFe₂O₄/rGO. As observed, the decomposition of graphene starts after 750 °C with a corresponding weight loss of 21% (calculated from the difference in weight% in the declination of the weight (%) curve on the left y-axis after 750 °C). Thus taking into consideration the weight loss due to absorbed moisture, EG molecules and graphene, the loading of MnFe₂O₄ is 79%.

3.3 Electrochemical analysis

The cyclic voltammetry of MnFe₂O₄/rGO versus Li & Na for twenty cycles between 3 to 0.002 V at a scan rate of 0.2 mV s⁻¹ are shown in Fig. 5a and b respectively. From Fig. 5a, in the first cycle, a large cathodic peak located around 0.5 V vs. Li/Li⁺ can be associated with the reduction reactions of Fe³⁺ and Mn²⁺ with Li and the formation of Li₂O during the first discharge process. In the subsequent cathodic scans, MnFe₂O₄/rGO nanoclusters show a cathodic peak and anodic peak at 0.7 V and 1.6 V vs.
Li/Li$^+$ and can be attributed to the reductive reaction of Fe$_3$O$_4$ and MnO to Fe and Mn metal, respectively. The MnFe$_2$O$_4$/rGO composites show all redox reaction peaks for MnFe$_2$O$_4$ nanoparticles. After the first cycle, the intensity of redox peaks remains constant which indicates the electrode stability. From Fig. S1, the cyclic voltammogram of pure MnFe$_2$O$_4$ intensity of peaks changes with cycle numbers, which indicates lower stability against lithium. Fig. 5b shows the CV profile for MnFe$_2$O$_4$/rGO composites versus Na/Na$^+$. In Fig. 5b, the observed anodic peaks at 1.6 and 1.85 V correspond to oxidation of Fe$^{0}$ to Fe$^{3+}$ and Mn$^{0}$ to Mn$^{2+}$. The broad cathodic peak centered at 0.75 V is attributed to the reduction reactions of Fe$^{3+}$ and Mn$^{2+}$ with Na and the formation of Na$_2$O during the discharge process.

The MnFe$_2$O$_4$/rGO was showing good rate capability and cycling stability due to the 2D graphene structure which will provide the conductive path for electron transportation and also it will accommodate the volume expansion while charging/discharging. Furthermore, alginate binder has better adhesive nature with the current collector and anode material during conversion reaction. The alginate binder effect on one of the spinel transition metal oxide has been demonstrated in our previous reports. Hence, the capacity fading is minimized in the lithium ion battery fabricated with MnFe$_2$O$_4$/rGO anode and alginate binder. This is reflected in the discharge capacity retention up to few numbers of cycles.

Fig. S4a and b† show the voltage profile and charge/discharge capacity vs. cycle number plots for the pure MnFe$_2$O$_4$ electrode at 0.1C rate. From Fig. S4a, pure MnFe$_2$O$_4$ electrode delivers discharge capacity of 990 mA h g$^{-1}$ at first discharge. The capacity fading is observed when the number of cycle is increasing. A deep fall in the discharge capacity from the initial value to 405 mA h g$^{-1}$ in the 30th cycle is observed. This lower cyclic stability is reflected the previous mentioned CV results. The observed low stable cyclability in pure MnFe$_2$O$_4$ electrodes versus Li is might be due to low electronic conductivity and nano sized particles in cluster dissolution in electrolyte while charging-discharging.

The cycleability and charge discharge curves for the MnFe$_2$O$_4$/rGO versus Li/Li$^+$ material are shown in Fig. 6. From Fig. 6, the MnFe$_2$O$_4$/rGO has delivered stable capacity of 905 mA h g$^{-1}$ at 0.1C rate for 30 cycles with excellent coulombic efficiency. The MnFe$_2$O$_4$/rGO composites presented the extra 1st discharge capacity, is due to the reversible formation and decomposition of polymeric gel-like films on the active particles. The significance of our MnFe$_2$O$_4$/rGO composite was its increased capacity at 0.1C and cyclic stability compared to recently reported Co$_3$O$_4$@graphene composites, Fe$_3$O$_4$/rGO, and NiFe$_2$O$_4$ nanoparticles. The enhancement of electrochemical properties of MnFe$_2$O$_4$/rGO versus Li/Li$^+$ is can be due to the better electronic conductivity network. The discharge profile versus sodium was shown in Fig. 7. From Fig. 7a, the MnFe$_2$O$_4$/rGO vs. Na/Na$^+$ has delivered stable capacity of 258 mA h g$^{-1}$ at 0.1C rate for 50 cycles. Furthermore, we are the first group who demonstrated MnFe$_2$O$_4$/rGO composite as an anode for sodium ion batteries. From Fig. 6 and 7, two things are clearly observed when the MnFe$_2$O$_4$/rGO composite is using as anode for Li and Na-ion batteries. First, the shape difference in charge–discharge curves. The charge–discharge curves of MnFe$_2$O$_4$/rGO versus Li/Li$^+$ has shows one voltage plateau at 0.8 V, but MnFe$_2$O$_4$/rGO versus Na/Na$^+$ charge–discharge curves does not shows any plateau region. Second, capacity difference, MnFe$_2$O$_4$/rGO compos is high Li storage capacity than Na capacity. The above mentioned two differences between Li and Na-ion batteries are may be due to the low ionic diffusivity of Na-ion.

The voltage vs. cycle number and discharge profile for the battery fabricated with MnFe$_2$O$_4$/rGO at different current rates are shown in Fig. 8a–d respectively. From Fig. 8a and b, discharge capacity of the anode versus Li/Li$^+$ decreases to 720, 580, 320, 160 and 60 mA h g$^{-1}$ when current rate increased to 1C (920 mA g$^{-1}$), 2C (1840 mA g$^{-1}$), 5C (4600 mA g$^{-1}$) and 10C (9200 mA g$^{-1}$), respectively. From Fig. 8c and d, discharge capacity of the anode versus Na/Na$^+$ with different current rates are 98 mA h g$^{-1}$ (920 mA g$^{-1}$), 58 mA h g$^{-1}$ (1840 mA g$^{-1}$), 22 mA h g$^{-1}$ (4600 mA g$^{-1}$) and 8 mA h g$^{-1}$ (9200 mA g$^{-1}$). The high rate capability and good reversibility are due to the good electronic conductivity, higher surface area and excellent adhesive properties of 2D graphene and alginate binders. The cross linking hydrocarbon chain and swelling nature of alginate binder, maintains good electrical contact between the current collector and anode material upon continuous conversion.

Xuefeng et al., successfully demonstrated reaction mechanism of MnFe$_2$O$_4$/graphene composites versus Li/Li$^+$ using ex
Here, first time the path of reaction mechanism of MnFe$_2$O$_4$/graphene composites versus Na/Na$^+$ during discharging and charging was observed by using ex situ TEM for the 1st discharge and 1st charge electrodes. Fig. 9a and b shows the ex situ TEM image and SAED patterns for the 1st discharge MnFe$_2$O$_4$/rGO composite electrode versus Na/Na$^+$. From Fig. 9a and b, the retention of morphology and the interplanar distance are derived by measuring the distance between bright rings about the center. The obtained, inter planar distance values are matched to the Miller indices of pure Fe, Mn and Na$_2$O. The ex situ TEM results for the fully charged MnFe$_2$O$_4$/rGO composite electrode are shown in Fig. 9c and d. In Fig. 9c, the morphology is totally changes from nanoclusters to tiny metal oxide particles which are bounded in graphene network. SAED patterns of fully charged electrode in Fig. 9d and it is observed that the formation of Fe$_2$O$_3$ and MnO at charge state. Hence, it is proved that the Fe, Mn metals and sodium oxide formed at discharge state and the formation of Fe$_2$O$_3$ and MnO at charged state. Furthermore, we have taken ex situ XRD for the 1st discharge and 1st charge electrodes, but it is very hard to find corresponding peaks in X-ray diffraction. The XRD patterns for 1st discharge and 1st charge electrodes along with their JCPDS data are shown Fig. S3.† Hence, it is confirmed that formation of Fe$_2$O$_3$ and MnO at charged state using ex situ TEM results, which the direct evidence for conversion reaction mechanism as is proposed in earlier section.
semicircle, $R_{\text{SF-CT}}$) resistance values could be estimated from fitted data and presented in Table 1. The value of $R_{\text{SF-CT}}$ increasing and decreasing during discharging and charging might be due to the solid electrolyte interface (SEI) formation/partial dissolution/re-formation.

Fig. 10c and d, shows the two distinct semi-circles, which are belongs to the $R_{\text{SF}}$ and $R_{\text{CT}}$ and varying during the charging and discharging states versus Na. From Fig. 10c and d, it is observed that the values of $R$ at OCV (initial point of discharging state) and 3 V (final point of charging state) are almost equal. Hence, it is confirmed that the SEI between electrolyte and MnFe$_2$O$_4$/rGO composite is stable during the discharging and charging. Furthermore, nano-sized porous structures with 2D graphene network offer good charge transfer kinetics due to their high surface to volume ratio.

### 4. Conclusions

Spinel manganese ferrite/reduce graphene oxide (MnFe$_2$O$_4$/rGO) nanocomposite was synthesized from natural graphite by a modified Hummer's method. XRD and Raman results confirmed the formation of MnFe$_2$O$_4$/rGO phase and structure respectively. Micro structural analysis was done using SEM and HRTEM, which showed the uniform dispersion of ferrites in graphene sheet network. The MnFe$_2$O$_4$/rGO composites delivers a high stable maximum discharge capacity of 905 mA h g$^{-1}$ vs. Li/Li$^+$ and 258 mA h g$^{-1}$ vs. Na/Na$^+$ at 0.1C rate. Here, Na-alginate binder provided a strong interaction between active material and current collector; further graphene sheets gave the enough void space for the volume expansion during the conversion reaction, act as a barrier to avoid active material dissolution and also it will enhance the electrical conductivity of nanocomposite. Results demonstrated that the MnFe$_2$O$_4$/rGO composite material with alginate is a potential anode material for next generation rocking chair battery applications.

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