Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Research paper

Carbon Nanofibers Loaded with Carbon Nanotubes and Iron Oxide as Flexible Freestanding Lithium-Ion Battery Anodes



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ARTICLE INFO

Article history: Received 17 April 2017 Received in revised form 15 September 2017 Accepted 15 September 2017 Available online 18 September 2017

Keywords: Electrospinning Iron oxide Carbon nanotube Lithim ion battery Anode

ABSTRACT

We demonstrate the fabrication of flexible electrospun carbon nanofibers (CNFs) containing uniformly distributed carbon nanotubes (CNTs) and iron oxide (FeO_x) nanoparticles (NPs) as a composite material for lithium-ion battery (LIB) anodes. The uniform incorporation of CNTs and FeO_x NPs within the CNFs was confirmed by transmission electron microscopy. Embedding even a small amount of CNTs (0.1 wt%) in the CNFs increased the LIB performance by a factor of two compared with pure CNFs. The specific capacity was also increased, by 25%, when an iron source (iron (III) acetylacetonate) was added at a concentration of 2 wt%. The FeO_x-CNT/CNF electrode maintained a capacity of 1008 mAh·g⁻¹ at a current density of 100 mA·g⁻¹ after 100 cycles. Further, the high-performance anode material was freestanding, flexible, and lightweight. This makes it suitable for next-generation LIBs, which must deliver high power over long periods while also being light and flexible.

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1. Introduction

Extensive research efforts are focused on producing lithium-ion batteries (LIBs) with higher energy and power densities and longer operational lifetime. Carbon-based materials that have relatively low potential with respect to lithium are usually employed as anode materials in LIBs. However, they fall short in terms of performance due to their limited rate capability and the modest lithium storage capacity of graphite [1]. Although graphene has been widely investigated as a substitute material, it also suffers from the drawback that aggregation of graphene sheets through van der Waals interactions lowers the surface area and reduces the lithium storage capacity [2,3].

Metal oxides such as Fe_2O_3 , NiO, Cu_2O , and SnO_2 have shown significant potential for use in batteries and are being studied widely, as they are nontoxic and abundant in nature [4]. Fe_2O_3 as an anode material for LIBs has a high theoretical capacity of 1007 mAh·g⁻¹ [5]. However, disadvantages of Fe_2O_3 include low electrical conductivity and poor capacity retention, owing its

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https://doi.org/10.1016/j.electacta.2017.09.086 0013-4686/© 2017 Elsevier Ltd. All rights reserved. microstructure and/or the tendency of Fe_2O_3 nanoparticles to aggolomerate. Efforts have been made to fabricate composite materials by uniformly distributing Fe_2O_3 nanoparticles in a matrix of a carbon material, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), or carbon black [6,7]. CNTs have been employed to enhance the lithium storage capacity as well as conductivity. Single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) have been reported to have conductivities as high as $10^6 \text{ S} \cdot \text{m}^{-1}$ and $10^5 \text{ S} \cdot \text{m}^{-1}$, respectively [8].

Lithium insertion and storage in MWCNTs occurs at three different potentials: first, at potentials lower than 0.5 V (versus Li/Li⁺). Li is intercalated between the graphene layers; then at 0.5–1.6 V, lithium enters the nanocavities; and finally, at 1.5–3.0 V, lithium reacts with surface oxygen [9]. The inner cores of the CNTs can provide space for lithium storage. However, in the case of pure CNTs, access to the inner parts of the CNTs is highly restricted. To improve access to the inner cores of CNTs, methods such as electron irradiation and chemical oxidation, among others, have been used to form pores in CNTs, increasing the number of sites available for lithium diffusion. Eom et al. reported that the lithium storage capacity of CNTs can be enhanced by etching, while Oktaviano et al. suggested that it could be increased by drilling [10,11]. In addition, Fe₂O₃-CNT hybrid materials have been reported to exhibit enhanced lithium storage capacity [12].



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The use of CNTs and Fe₂O₃ together to form a composite is advantageous because the resilient network of the CNTs can buffer the volume expansion of Fe₂O₃ while also improving the cycling stability. In addition, the conductivity of Fe₂O₃ is improved upon combination with CNTs. This also ensures stable electrochemical kinetics. The CNTs may prevent the drifting or agglomeration of metal oxide nanoparticles, thus ensuring that the active reaction sites are maintained. Adding Fe₂O₃ onto or into a carbon nanofiber matrix was reported to enhance the charge storage capacity [13]. The use of CNTs with CNFs was shown to enhance the mechanical properties of CNF [14]. Electrospun CNFs are easy to prepare and can be directly used as a conductive electrode material after carbonization [15]. The prior reports described above led us to expect that adding both Fe₂O₃ and CNTs into CNFs could produce a composite material with a high capacity and stability and good capacity retention properties.

Zhou et al. [6] prepared a composite consisting of 5–10 nm diameter Fe_2O_3 nanoparticles anchored on flexible SWCNT membranes for use as a LIB anode. The material showed a specific capacitance of 1243 mAh·g⁻¹ at a current density of 50 mA·g⁻¹. Filling of CNTs with Fe_2O_3 has also been attempted. Yu et al. [16] tried to fill CNTs with Fe_2O_3 nanoparticles via a chemical vapor deposition process. Further, Gao et al. [17] reported the fabrication of hybrid Fe_2O_3/CNT composites by a hydrothermal process. Zhao et al. [18] used a hydrothermal method to produce Fe_2O_3 -decorated SWCNTs with a "nanohorn" morphology. Yan et al. produced Fe_2O_3 nanoparticles on functionalized CNTs through a two-step process. However, their capacity decreased from 272 to 182 mAh·g⁻¹ after 50 cycles at a current density of 100 mA·g⁻¹.

The coupling of CNFs with CNTs has also been attempted previously [21,22]. However, to the best of our knowledge, there has been no report on the coupling of iron oxide with a CNT/CNF composite, which is the focus of this study. CNTs and iron oxide can be readily incorporated into or onto CNFs by electrospinning. A post-spinning annealing treatment removes the binder from the CNFs, producing a freestanding film that can itself act as the current collector, reducing the overall mass of the system by eliminating the need for a separate current collector [23].

2. Materials and Methods

2.1. Fabrication of FeO_x-CNT/CNF composite

First, 0.05 g and 0.75 g of polyacrylonitrile (PAN, M_w = 150 kDa, Sigma-Aldrich) were each separately dissolved in 4.5 g of N,Ndimethylformamide (DMF, 99.8%, Sigma-Aldrich) by stirring at 60 °C for 24 hours, to make concentrations of 1 wt% and 9 wt% PAN/ DMF. Then, 0.1 wt% of MWCNTs (purity >90%, XNM-HP-1500, XinNano Materials Inc. Taiwan) was added to the 1 wt% PAN solution, and the solution was stirred for an additional 24h to ensure that the CNTs were dispersed uniformly. Higher PAN concentrations hampered the dispersion of CNT. Thus, the additional 9 wt% PAN is added after dispersing the CNT in 1 wt% PAN solution. The 0.1 wt% of CNT was observed to be optimal for maintaining a stable dispersion; higher CNT concentrations led to agglomeration. Note that the CNT used here is in as received form without any further treatment to improve the dispersibility of the CNT. Then, iron (III) acetylacetonate ((FeAcAc), Fe(C₅H₇O₂)₃, Sigma-Aldrich) was added to the CNT/PAN-DMF solution, and the mixture was stirred for 12 h at 25 °C to completely dissolve the FeAcAc. The mixture was then tip-sonicated for 30s to ensure homogenous dispersion of the CNTs in the solution. The CNT and FeAcAc weight percents stated here are relative to PAN/DMF solution. The proportion of the CNTs in all the solutions was kept constant by varying the metal concentration, as shown in Table 1, to determine

Table 1 Precursor composition

recursor	composition.	

CNT/FeAcAc [wt%]
0.0: 0
0.1: 0
0.1: 2
0.1:4

the optimized concentrations of FeAcAc and CNT for ensuring good electrochemical performance, in terms of capacity, stability, and capacity retention.

Next, NFs were produced by the electrospinning process [24]. The setup used consisted of a syringe, needle, grounded collector, and high-voltage power supply. The precursor solution (Fig. 1a) was delivered using a syringe (Fig. 1b) at an optimized flow rate of $250 \,\mu\text{L}\,\text{h}^{-1}$, which yielded a stable Taylor cone at the end of the needle. The electrospun NFs were collected on a drum collector held 15 cm away from the needle. Mats of different colors were formed, depending on the concentration of the FeAcAc salt (Fig. 1 c). The synthesized mats were stabilized by heating in air at a rate of 5 °C min⁻¹ to 280 °C and holding them at that temperature for 30 min. The stabilized mats were annealed again in a tube furnace at a temperature of 700°C for 2 h in flowing argon. The temperature of the furnace was raised from room temperature to 700 °C at a rate of 3 °C min⁻¹ in order to carbonize the stabilized NFs. After carbonization, the mats turned black (Fig. 2) and became highly conductive.

2.2. Characterization

The surface morphologies of the composite mats were analyzed by field-emission scanning electron microscopy (FE-SEM, S-5000, Hitachi, Ltd.), transmission electron microscopy (TEM, JEM 2100F, JEOL Inc.) and elemental mapping by energy-dispersive X-ray spectroscopy (EDX) within the TEM. The structural properties of the mats were characterized by X-ray diffraction (XRD) analysis (SmartLab, Rigaku). A confocal Raman spectrometer (Jasco, NRS-3100) was used to analyze the defects in the CNFs in the mats. Finally, X-ray photoelectron spectroscopy (XPS) measurements (Theta Probe Base System, Thermo Fisher Scientific Co.) were performed to evaluate the chemical states of the constituent elements on the surfaces of the composite mats. N₂ adsorption and desorption isotherms were measured to determine the surface area of composites using a volumetric adsorption apparatus (Tristar 3000, Micromeritics). The sample was pretreated at 70 °C for 48 h under high vacuum ($< 10^{-6}$ Torr) before commencing adsorption studies.

2.3. Electrochemical tests

The carbonized mats were highly flexible and freestanding and could be punched to directly produce working electrodes. The mats showed good flexibility and could be bent without breaking, as shown in Fig. 2. The punched electrodes (14 mm in diameter) were used to form CR2032 coin-type half-cells, which were subjected to electrochemical tests. A metallic Li sheet was used as the reference electrode, and a microporous polymer separator (Celgard 2400, Celgard, Chungbuk, South Korea) was placed between the two electrodes. A solution of 1 M LiPF₆ in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (1:1:1 by volume) (PuriEL, Soulbrain, Seongnam, South Korea) was used as the electrolyte. Galvanostatic discharging/charging was performed between 0.005 and 3 V at 25 °C using a WBCS3000 battery cycling system (WonATech, Seoul, South Korea). The cells were subjected to rate tests at different current densities (10 cycles each



Fig. 1. Schematic illustration of (a) preparation of FeAcAc-MWCNT solution, (b) electrospinning using a drum collector, and (c) photographs of CNT/CNF and FeO_x-CNT/CNF mats.



Fig. 2. Flexibility at large bending angles of FeO_x-CNT/CNF composite mats, (a) carbonized mats (b) punched electrodes.

at 100 mA·g⁻¹, 200 mA·g⁻¹, 500 mA·g⁻¹, and 1000 mA·g⁻¹). This was followed by an additional 60 cycles at 100 mA·g⁻¹. Long-term cycling tests were conducted at a current density of 100 mA·g⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed on the coin cells using a potentiostat (Versa-STAT-3, Princeton Applied Research, USA). The Nyquist plots of the cells were obtained using a small sinusoidal perturbation (amplitude of 10 mV) over a frequency range of 100 kHz to 10 mHz.

3. Results and Discussion

SEM images of the pristine CNFs and the CNT/CNF composites (Fig. 3a and b) show that they have smooth surfaces. Further, the morphology of the CNT/CNF composite is the same as that of the pristine CNFs, indicating that the CNTs were well embedded in the CNFs. When the FeAcAc salt was introduced into the CNT/CNF composite, the surface roughness increased, as shown in Fig. 3c

and d. The CNTs were also more exposed to the outer surface owing to the higher conductivity of the precursor solution and dispersion of CNTs in the solvent [25]. In all cases, the fibers are continuous and have CNTs distributed uniformly along them. The diameter of the individual fibers was determined by measuring an average of 100 NFs for each case. The fiber diameters for cases 1, 2, 3, and 4 were 380, 555, 295, and 293 nm, respectively.

TEM was employed to determine the distribution of CNTs and FeO_x particles in the CNFs. Fig. 4a shows that the CNTs are well embedded in the CNFs and are preferentially aligned along the axis of the fibers. The high resolution image of the area marked with the red circle in Fig. 4a is shown in Fig. 4b, illustrating the alignment of the CNTs in the fiber. The FeO_x particles were visible as well-dispersed dark spots on the CNFs in the TEM images (Fig. 4c). However, no crystalline FeO_x phase was observed in the HRTEM image (Fig. 4d); this indicates that the FeO_x phase is amorphous. Carbon may also be present in the amorphous FeO_x phase. These



Fig. 3. SEM images of various samples: (a) pristine CNFs (case 1) (b) CNT/CNF composite (case 2, FeAcAc = 0 wt%), (c) FeO_x-CNT/CNF composite (case 3, FeAcAc = 2 wt%), and (d) FeO_x-CNT/CNF composite (case 4, FeAcAc = 4 wt%).



Fig. 4. (a), (c) Low-resolution TEM images of CNF, (b),(d) high resolution TEM images (circles in (d) showing 1- amorphous carbon, 2- amorphous FeOx and 3- twisted CNT), and (e) results of elemental mapping for composite corresponding to case 3 (i.e., FeOx-CNT/CNF composite with FeAcAc = 2 wt%).

results are consistent with XRD analysis, discussed below. A few of the CNTs in the CNFs are twisted, as can be seen from Fig. 4d. This twisting of the CNTs has been reported to provide increased lithium storage sites [26]. The elemental maps (Fig. 4e) confirm that Fe and O are homogeneously distributed in the CNFs.

XRD analyses were performed to investigate the crystal structures of the various samples. Fig. 5a shows the XRD patterns of the CNFs, the CNT/CNF composite, and the FeO_x-CNT/CNF

composites with different concentrations of FeAcAc. The pristine CNFs exhibit a broad peak at 21.4° , which is related to the turbostratic graphitic phase of carbon formed by carbonization of PAN. When CNTs are added to the CNFs, this peak appears at 21.5° ; this is also attributable to a turbostratic/disordered carbon phase. When the FeAcAc is added, peaks related to turbostratic carbon remain at 21.4° and 21.8° in the spectra of the samples corresponding to cases 3 and 4, respectively. However, the XRD



Fig. 5. (a) XRD patterns and (b) Raman spectra of various samples.

patterns of the composites do not contain any distinct peaks related to iron oxide, confirming that FeO_x is present in the composites in an amorphous form. The XRD pattern of the pristine CNTs is provided in the Supporting Information (Fig. S1).

Raman spectroscopy was employed to obtain further insights into the structural changes induced by the addition of FeAcAc. As can be seen from Fig. 5b, all the spectra show peaks centered at 1330 and 1570 cm⁻¹, corresponding to disordered carbon (D) and graphitic carbon (G), respectively. The ratio of the intensities of the D and G bands (I_D/I_G) of carbon is indicative of the degree of graphitization. The I_D/I_G ratio of the CNFs (case 1) was 1.04, suggesting that the CNFs have substantial amorphous content. When CNTs were added to the CNFs (case 2) an additional peak was observed, at 2650 cm⁻¹. This peak is attributed to the 2D mode of the CNTs (Supporting Information Fig. S2). The I_D/I_G ratio of the CNT/CNF composite was lower (\sim 0.86) than that of the CNFs. This suggested that the density of the defects in the CNT/CNF composite was lower owing to the graphitic nature of the CNTs (see Fig. S2). Further, in the case of the FeO_x-CNT/CNF composites, the presence of FeO_x resulted in the I_D/I_G ratio being 1.0 and 1.12 for cases 3 and 4, respectively. This implied that more defects were generated after the incorporation of FeO_x into the CNT/CNF composite [12]. Thus, the difference in the I_D/I_G ratios of the CNT/CNF and FeO_x-CNT/CNF mats indicates that addition of FeAcAc in the CNT/CNF matrix generated structural defects. These defects are highly desirable as they can aid the insertion of Li ions into the CNTs [19,27]. Raman spectra from 100–1000 cm⁻¹ are presented in Fig. S3. The weak Fe-O peaks observed there correspond to multiple iron oxide phases. Their low intensity suggests that much of the iron oxide may be present in amorphous form.

The oxidation states of the constituent elements on the surface of the FeO_x-CNT/CNF composite (case 3) were characterized by XPS survey measurements after Ar⁺ etching to remove surface oxides and any adsorbed species. The XPS peaks denote the specific energy states of the electrons in the *s* or *p* orbitals of the respective atoms. Fig. 6a confirms the presence of Fe, O, C, and N, based on the corresponding peaks that appear at their respective band energy positions. The N detected in survey spectrum of the sample is from polyacronitrile (PAN) used to prepare the carbon nanofibers. The Fe2*p* core spectrum (Fig. 6b) shows two broad peaks, at 710.9 and



Fig. 6. Results of XPS measurements of FeO_x-CNT/CNF composite (case 3): (a) survey, (b) Fe2p, (c) C1s, and (d) O1s spectra.

724.3 eV; these correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The spin-orbit splitting of the 2p bands is 13.4 eV. The Fe $2p_{3/2}$ peak at 710.9 eV can be deconvoluted into three peaks located at 709.1, 710.9 and 712.9 eV. Charge-transfer-related satellite peaks are indicative of the actual oxidation state of iron. For Fe²⁺, the satellite peak appears at a lower binding energy of 714.9 eV, whereas the satellite peaks for Fe³⁺ appear at 717.2 eV [28–30]. The Fe $2p_{1/2}$ peak at 724.3 eV was deconvoluted as 722.6, 724.9 and 726.8 eV [28,31,32]. Note that the spectrum does not show any evidence of a Fe $2p_{3/2}$ peak near 707 eV, which would be characteristic of metallic (zerovalent) iron. In the C1 s spectrum (see Fig. 6c), the peaks at 284.3, 285.2, 286.1, 287.7 and 288.5 eV correspond to C=C sp², C-C sp³, C-O, C-N/C=N and C=O bonds, respectively [33]. Further, in the O1 s spectrum (see Fig. 6d), the peak at 529.6 eV is attributable to the formation of Fe-O bonds, while the two shoulder peaks located at 531.25 and 532.72 eV are related to the Fe-O-H or oxygen in the oxidized CNTs and the surface -OH moieties, respectively. A high resolution spectrum near the N1 s peak is shown in Fig. S4 and demonstrates the chemical states of nitrogen incorporated from the nitrile groups of PAN.

Fig. 7 shows galvanostatic discharge/charge curves for the various samples for the 1st, 2nd, and 100th cycle. The curves were obtained for voltages of 0.005-3V (versus Li⁺/Li) at a current density of 100 $m\bar{A} g^{-1}$. In all the cases, there is a large and irreversible loss in capacity after the first cycle, owing to the decomposition of the active material in the electrolyte and the formation of a solid electrolyte interface (SEI) layer. The curves have a smooth slope between 0.8 and 2.5 V, which can be attributed to the initiation of the Li-ion insertion process. The discharge/charge capacities of the samples corresponding to cases 1 and 2 after the first cycle are \sim 994/708 and 1627/1059 mAh·g⁻¹, respectively. The addition of CNTs increased Li storage capacity by a factor of \sim 1.5, as shown by the curves for the first 2 cycles. This increase in the storage capacity is attributed to the increase in the surface area observed by Brunauer-Emmett-Teller (BET) analysis (see Fig. S5 and Table S1). Thus, storing of Li ions is enhanced and the electronic conductivity is improved by the incorporation of CNTs. When FeO_x was added, an extended plateau was observed at 0.83–0.88 V (see Fig.7c-d), indicating the conversion of the metal ions into metal particles. For both case 3 and case 4, an elongated tail is observed for N = 1. The sample corresponding to case 3 shows a specific capacity of 1789 mAh $\cdot g^{-1}$ at a current density of 100 $mA \cdot g^{-1}$. Thus, the CNTs in the FeO_x-CNT/CNF composite resulted in a high initial coulombic efficiency owing to the improved buffering of the volume expansion of the FeO_x nanoparticles in the case of this morphology (Fig. 4). However, the elongated tail disappeared for case 4, with the sample showing a specific capacity of only 1316 $mAh \cdot g^{-1}$ at the same current density. The higher capacity of the sample corresponding to case 3 can be attributed to the lower degree of agglomeration of the FeO_x particles, which results in the improved accommodation of volume changes. Further, for N=2, the capacity was reduced, most likely owing to the formation of a thick SEI layer, which lowers the electron transfer rate at electrode/ electrolyte interface. Thus, the high discharge/charge capacity and retention rate of the sample corresponding to case 3 can be ascribed to the excellent morphology of the composite material, as evidenced by TEM images (Fig. 4). Fig. 7 shows clearly that the specific capacity increases rapidly for voltages higher than 1 V and that no plateau is formed. This phenomenon also indicates that the SEI layer is formed during the first cycle. However, as the number of cycles increases, the case 3 sample shows identical discharge characteristics up to voltages of 1V and at lower voltage range. Further, the decline in the discharge capacity of case 4 may be attributed to two phenomena, namely, the agglomeration of the FeO_x particles and/or the formation of the SEI layer. The restructuring of the SEI laver could be related to the formation of cracks in it, owing to the repeated expansion/contraction of the FeO_x nanoparticles. It is worth noting, that, for case 4, the slope of the discharge curves (N=1 and 100) for voltages higher than 1 V are similar, while for case 3, the discharge curve for voltages greater than 1V remains almost constant, indicating that neither the agglomeration of the FeO_x particles nor crack formation in the SEI layer occurs. This supports the conclusion that the sample corresponding to case 3 was prepared with the optimal FeAcAc



Fig. 7. Discharge/charge curves for (a) case 1, (b) case 2, (c) case 3, and (d) case 4 at 100 mA \cdot g⁻¹.

concentration, yielding the best specific capacity retention rate even after long-term cycling (N = 100), as shown in Fig. 8a .

The cycling performance of the samples corresponding to cases 1-4 at a current density of 100 mA \cdot g⁻¹ are shown in Fig. 8a. Owing to the absence of the CNTs and FeO_x, the sample corresponding to case 1 (i.e., the pristine CNFs) shows a specific capacity of only 354 $mAh \cdot g^{-1}$ after 100 cycles, which is only 50% of the reversible capacity after the second cycle (N=2). Thus, the sample provides nearly the theoretical capacity of CNF if we assume that one Li-ion interacts with six atoms of the carbon, which could deliver 372 $mAh \cdot g^{-1}$. The sample corresponding to case 2 (i.e., the CNT/CNF composite) delivers a reversible capacity of 812 mAh \cdot g⁻¹ after 100 cycles, retaining 81% of the reversible capacity after the second cycle (N=2). We attribute this increase in capacity to the enhancement in Li storage because of the CNTs embedded in the CNFs. Additionally, as reported by Jung et al. [34] CNT could show a theoretical capacity of 1116 mAh \cdot g⁻¹, which explain the capacity increase of the CNT/CNF sample. The initial high capacity value of case 3 which incorporates both CNT and FeO (theoretical capacity is 1116 and 746 mAh \cdot g⁻¹ respectively) is attributed to the formation of SEI layer. Also, case 3 exhibits the highest initial reversible capacity (1183 mAh·g⁻¹ at N = 2). Further, the capacity of this sample is 1008 mAh·g⁻¹ after 100 cycles, with the sample retaining 85% of its reversible capacity after the second cycle (N=2). We attribute the higher capacity observed in case 3 to the synergistic impact of CNF-CNT-FeO_x, high surface area, and intercalation of Li-ion in the composites. The high specific capacity, near the theoretical capacity could be due to extracapacity gained from the intercalation of Li-ions [35]. Furthermore, due to high surface area (Fig. S5c), case 3 has shown excellent and stable capacity retention. When the FeAcAc concentration was increased to 4 wt%, the reversible capacity after 100 cycles was 692 mAh \cdot g⁻¹, which is 70% of the capacity after the second cycle. This decrease may be due to the aggregation of the FeO_x particles during the cycling process and disruption of the SEI by their volume change. Thus, the capacity values of the case 3 sample were the highest, due to the synergistic effects of the FeO_x particles and the CNTs. The initial coulombic efficiencies of the samples corresponding to cases 1, 2, 3, and 4 were 68, 65, 70, and 74%, respectively. In all cases, the coulombic efficiency increased to 98-99% after the 3rd cycle.

To test the rate capacities of the samples, the cells were discharged/charged for 10 cycles each at current densities of 100–1000 mA·g⁻¹. Fig. 8b shows the rate capabilities of the various samples. Increasing the current to 1000 mA·g⁻¹ results in polarization of the electrolyte/electrode interface. Hence, the overall capacity drops in all cases. The reversible capacities of the case 3 composite were 1789, 915, 654, and 526 mAh·g⁻¹ at 100, 200, 500, and 1000 mA·g⁻¹, respectively. Even though, initially, case 4 and case 3 sample had similar capacity at N = 31-34, the case

3 sample was less susceptible to the polarization effect at higher current density (1000 mA·g⁻¹) and provided a reversible capacity of 584 mAh·g⁻¹ after N = 40 cycles. This superior performance of case 3 at all current densities is clearly observed from Fig. S6. The galvanostatic discharge/charge curves at various current densities for all samples at N = 1, 10 (100 mA·g⁻¹), 20 (200 mA·g⁻¹), 30 (500 $mA \cdot g^{-1}$) and 40 (1000 $mA \cdot g^{-1}$) are presented in Fig. S6. When the current density was reset to 100 mA \cdot g⁻¹, a specific capacity of 1022 $mAh \cdot g^{-1}$ was observed, indicating that this composite shows highly stable cycling performance. The higher rate capability of the FeO_x-CNT/CNF composites can be ascribed to the uniformly distributed CNTs and FeO_x particles; the CNTs provide an efficient electron transport pathway and improve the lithium storage capacity. When FeO_x is added to the CNT/CNF, the storage capacity of the composite increases, particularly at higher current densities, owing to the small size of the FeO_x particles and because of the defects formed in the CNTs, as evidenced by the Raman spectra.

Thus, the CNT/CNF composite shows a modest storage capacity, which can be increased by the inclusion of a small amount of FeO_x. Further, the specific capacity of case 3 sample is comparable to those of other similar materials reported recently (see Table 2). The values for some of the materials [18,36,37] are higher; however, in those cases, multiple steps were needed for electrode fabrication. Further, those materials required the use of a binder and current collector. The added mass of the current collector can be an issue during actual device use. Zhou at al [6]. and Yang et al. [38] reported freestanding binder-free films consisting of Fe₂O₃ and CNTs. However, their approaches are relatively expensive because they are based on chemical vapor deposition.

We performed EIS measurements and analyses to elucidate the electrochemical kinetics of the various samples. The Nyquist plots of the fabricated cells before the cycling tests as determined by EIS are shown in Fig. 9a and b. A semicircle is present in the high-tomedium frequency regime for all the samples. A semicircular arc in the Nyquist plot indicates that a coherent redox reaction occurs at the electrode/electrolyte interface. The impedance values for all samples are listed in the table shown in Fig. 9d; these were obtained by fitting the measurement data to the Randles equivalent circuit using the software ZSimpWin. The intercept of the real impedance in the high-frequency region corresponds to the solution impedance (R_s) at the electrode/electrolyte interface, which was estimated to be 0.08, 0.071, 0.23, and 0.27 Ω for the samples corresponding to cases 1, 2, 3, and 4, respectively. The solution impedance of the case 2 sample is lower, indicating that its electronic conductivity is higher and its diffusion pathway for Li ions is shorter, owing to the CNT/CNF network present. The diameter of the semicircle in the mid-frequency region represents the charge-transfer resistance (R_{ct}) . A constant phase element (CPE) was used owing to the presence of a depressed semicircle in



Fig. 8. (a) Long-term cycling performance at 100 mA·g⁻¹ and (b) Rate capability for voltages of 0.005–3.0 V.

Table	2

Comparison of specific capacities of previously reported Fe₂O₃-CNT composites and that of FeO_x-CNT/CNF composite fabricated in present study.

Composition	Electrode prepared	First Discharge capacity [mAh·g ⁻¹]	First reversible capacity $[mAh \cdot g^{-1}]$	Reversible capacity (N th) [mAh·g ⁻¹]	Current rate $[mA \cdot g^{-1}]$	Refs.
Fe ₂ O ₃ /graphene/ CNT	Vacuum filtration $_{a,d}$	1657	1011	716(120)	50	[12]
Fe ₂ O ₃ /CNT	Nanoparticles ^{c,d}	1400	1050	764(60)	200	[17]
Fe ₂ O ₃ /CNT	CVD ^{a,b}	1100	590	392(800)	3000	[38]
Fe ₂ O ₃ /MWCNT	Nanoparticles ^{c,d}	870	580	515(50)	100	[19]
Fe ₂ O ₃ /CNT/ Graphene	Solution method ^{c} ,	1910	984	812(100)	74	[36]
Fe ₂ O ₃ /CNT	CVD/ oxidation ^{a,b}	2097	1400	801(90)	500	[6]
Fe ₂ O ₃ /CNT/C	Nanospindles ^{c,d}	1060	680	820(100)	500	[37]
Fe ₂ O ₃ /SWCNT	Nanohorns ^{c,d}	1400	925	950(75)	150	[18]
Fe ₂ O ₃ /CNT	Template method _{c,d}	2081	1000	768(40)	35	[16]
FeO _x /CNT/CNF	Electrospinning a,b	1789	1269	1008(100)	100	Present

a – without binder, b – without current collector (CC), c- with binder, d-with current collector.



Fig. 9. (a) Nyquist plots of various samples before being tested, (b) magnified Nyquist plots, (c) MATLAB rendered TEM image, (d) Randle's equivalent circuit and impedance values.

the spectra. The charge-transfer impedance of the case 3 and case 4 samples (123 and 143 Ω) were very similar to those of the case 2 (CNT/CNF) and case 1 (CNFs) samples, which had charge-transfer impedances of 120 Ω and 122 Ω , respectively, indicating that the FeO_x particles and CNTs were uniformly distributed in the composite fibers, as was also observed from the TEM analysis of

the case 3 sample (see Fig. 9c, the colored image was obtained by post-processing the original TEM image in MATLAB to better visualize the FeO_x particles near the top of the image). Further, a small semicircle (i.e., a lower impedance) is indicative of enhanced reaction kinetics, that is, of an improved rate of uptake and removal of Li ions. Although the CNT/CNF composite is a conductive

material and showed the lowest impedance, it was unable to store a large amount of Li ions, as carbon provides only one electron per C atom. In contrast, FeO_x can react with multiple Li ions. Further, the impedances of the case 1, case 2, and case 3 samples are similar. A straight line in the lower-frequency regime is representative of the Warburg impedance (W), which is associated with solid-state diffusion of Li ions in the active materials of the electrode. The impedance response of the case 3 sample is the straightest, suggesting that the diffusion of solid-state Li ions was the fastest in this sample. Thus, we conclude that the case 3 sample showed the best electrochemical performance, as also evidenced by the results of the long-term cycling and rate capability measurements.

4. Conclusions

We have fabricated FeO_x-CNT/CNF nanocomposite mats using electrospinning to buffer the volume expansion of FeO_x and ensure high coulombic efficiency through the high conductivity provided by the CNTs. The fabricated mats were freestanding and highly flexible and exhibited excellent cycling stability over 100 cycles. The incorporation of FeO_x and CNTs with 2 wt% FeO_x-CNT/CNF resulted in superior rate performance (580 mAh·g⁻¹ at 1000 mA·g⁻¹), owing to the uniform distribution of the CNTs and FeO_x particles on the CNFs. The electrospinning technique employed in this study to prepare the FeO_x-CNT/CNF composite mats is a costeffective and simple one, and the thus-fabricated flexible composite mats should find wide use as electrode materials in flexible high-performance Li-ion batteries.

Acknowledgement

This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (2016M1A2A2936760), NRF-2013M3A6B1078879, NRF-2017R1A2B4005639, and NRF-2016R1A2B3009481.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017.09.086.

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