**Cooperatively assembled nitrogen-doped ordered mesoporous carbon/iron oxide
nanocomposites for low-cost, long cycle life sodium-ion batteries**

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Single pot, multi-component assembly of resol (carbon source), Pluronic F127,
tetraethylorthosilicate (TEOS), dicyandiamide (nitrogen source) and iron nitrate (iron oxides
source) yields nitrogen-doped ordered mesoporous carbon/iron oxide nanocomposites on

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carbonization. Etching the silica derived from the TEOS generates micropores in the carbon framework. The incorporation of iron oxide and nitrogen doping of the carbon tends to decrease the surface area; at approximately 3.7 wt% nitrogen and 21 wt% iron oxide (OMC-3.7-21), the surface area decreases from 2162 m²/g for the undoped ordered mesoporous carbon (OMC) to 974 m²/g and the pore volume decreases from 1.62 cm³/g to 0.6 cm³/g due to deformation of the nanostructure by crystallization of γ -Fe₂O₃ nanoparticles and N-doping of the carbon. Despite the decreased surface area, the reversible capacity when used as anodes in a sodium ion battery is increased from 110 mAh/g (undoped OMC) to 275 mAh/g (OMC-3.7-21) due to high capacity from the γ -Fe₂O₃ nanoparticles and the improved capacity associated with nitrogen doping of carbon. These nitrogen-doped ordered mesoporous carbon/iron oxide nanocomposites exhibit good cycle stability with almost 99% capacity retention after 350 charge/discharge cycles. The combination of low-cost and excellent electrochemical performance makes these mesoporous nanocomposites promising anode materials for sodium-ion batteries.

1. Introduction

With growing concerns regarding global warming, tremendous efforts have been devoted to the development of clean and renewable energy sources [1]. However, many renewable energy technologies, such as wind and solar, rely on intermittent sources and thus requiring the integration of the renewable energy technology with efficient and inexpensive energy storage systems [2-4]. Although much effort on these energy storage systems has focused on lithium-ion batteries (LIBs) due to their high energy densities [5], the long term availability and the cost of lithium may serve to limit LIBs in the future for large-scale, stationary energy storage systems [6]. Sodium-ion batteries (SIBs) provide an alternative energy storage technology that bypasses

these availability and cost issues of LIBs due to the high natural abundance and low-cost of sodium sources [7, 8]. However, a significant drawback of SIBs is the reduced specific capacity compared to the lithium analog due to the larger ion size of Na^+ and its higher intrinsic mass per charge [9, 10]. This larger cation size also limits intercalation of Na^+ in graphite, which is the most common anode materials for commercial LIBs, leading to limited discharge capacity in the SIBs ($< 30 \text{ mAh/g}$) [11]. Non-graphitic carbon has an increased atomic spacing that allows improved Na^+ intercalation and enhanced reversible capacity of SIBs, such as ordered mesoporous carbon (OMC) with $\sim 33 \text{ nm}$ pores where the capacity is increased more than 4 fold ($\sim 130 \text{ mAh/g}$) in comparison to graphite, even after 100 discharge-charge cycles [12].

Additional improvements in battery performance can be realized by introducing additional functionality into the amorphous porous carbon. These changes could be used to impact the structure, such as combined hard and soft-templating to introduce micropores in the carbon framework for enhancing the surface area and decreasing the ion diffusion path length [13-15]. Alternatively, the OMC can be doped with heteroatoms (nitrogen, sulfur or phosphorous) to improve the electrical conductivity, pore surface wettability with the electrolyte, and/or enable additional capacitive charge storage. These properties associated with doping of the carbon lead to increased discharge capacity and longer cycle life for Na-ion batteries compared to that for batteries using pristine carbon electrodes [16-18]. Alternatively, composites involving generally low conductivity, but high theoretical capacity materials, such as metal oxides, with carbon can provide additional electrochemical performance through a combination of different charge storage mechanisms including intercalation, conversion reactions, and alloying [19-21]. Among these, iron oxide is one of the most promising metal oxides for sodium-ion batteries due to its availability, minimal toxicity, and high theoretical energy storage capacity ($\approx 1007 \text{ mAh/g}$) [22,

23]. However, the volumetric variation of iron oxides during ion insertion and extraction usually leads to poor cycling stability [24]. The combination of high surface area carbon and iron oxide nanoparticles can provide synergistic advantages for the generation of high capacity Na-ion battery anodes with improved cycle stability. For example, porous carbon composites with 45.5 wt% iron oxides exhibit high discharge capacity of 225 mAh/g at relatively low current density of 50 mA/g [25]. However, challenges associated with these high performance materials from a commercialization perspective involve the scalability of the synthesis route of the nanocomposites, cost of the precursors, and improvements in the rate performance.

Here we seek to extend the pioneering concepts associated with the design of high surface area, nitrogen doped ordered mesoporous carbon/iron oxide nanocomposites for Na-ion batteries through the development of a scalable fabrication method that utilizes low cost precursors in order to fulfill requirements for low-cost grid-scale energy storage. One route for low cost, high volumetric production is roll-to-roll (R2R) processing, which has been demonstrated for fabricating nanostructured materials and flexible devices for energy storage [26, 27]. Here, R2R processing is applied to the large-scale fabrication of nitrogen-doped OMCs with iron oxide nanoparticles using commercially available and relatively low cost precursors of resol (carbon source), Pluronic F127 (mesopore template), tetraethylorthosilicate (TEOS, for hard templating micropores in carbon wall), dicyandiamide (nitrogen source) and iron nitrate (iron oxide source). Although the introduction of the N-heteroatom and iron oxide nanoparticles decreases the surface area of the OMC, the OMC composites with the highest nitrogen (3.7 wt %) and iron oxide (21 wt %) loading examined still exhibit high surface area (974 m²/g) and a narrow pore size distribution. The performance of these OMCs as anodes in Na-ion batteries depends strongly on both N-doping and Fe₂O₃ content. The specific capacity increases from 94 mAh/g (undoped

OMC) to 245 mAh/g for the highest nitrogen and Fe₂O₃ content at a rate of 100 mA/g. These nanocomposites from low-cost precursors combined with scalable R2R processing could be excellent candidates for anode material in sodium ion batteries due to their high specific capacity and excellent cycling stability.

2. Experimental section

2.1 Materials

Pluronic F127 ($M_w = 12,600$ g/mol, PEO₁₀₆-PPO₇₀-PEO₁₀₆), ethanol (>99%), tetraethyl orthosilicate (TEOS, >98%), potassium hydroxide (>85%), phenol (>99%), formaldehyde (ACS reagent, 37 wt% in H₂O, contains 10–15% methanol as stabilizer), sodium hydroxide (NaOH), tetrahydrofuran (THF, >99%), iron nitrate nonahydrate (>98%), dicyandiamide (>99%), poly(vinylidene fluoride) (PVDF), N-methyl-2-pyrrolidone (NMP, 99.5% EMD), ethylene carbonate (EC, >99.9%), propylene carbonate (PC, >99.9%) and sodium perchlorate (NaClO₄, >98%) were all purchased from Sigma-Aldrich. All chemicals were used without further purification unless otherwise noted. The oligomer of phenolic resin (resol) was synthesized by base catalyzed (NaOH) condensation of phenol and formaldehyde following prior reports.[28] Copper foil (9 μm thick) and carbon black (TIMCAL, SUPER C45) were obtained from MTI Corporation. Polyethylene terephthalate (PET, 125 μm) sheet was purchased from Terphane Inc and used as a substrate for the R2R processing.

2.2 Fabrication of ordered mesoporous carbon and nitrogen-doped carbon/iron oxides

The undoped OMC was synthesized as the control material following reported procedures in the literature [29, 30]. Briefly, 16 g of Pluronic F127 was dissolved in 40 g of 0.2 M HCl and 160 g

of ethanol. After stirring for 30 min, 100 g of tetraethyl orthosilicate (TEOS), and 80 g of resol solution (50 wt % in ethanol) were added to the Pluronic solution. For the N-doped mesoporous carbon, different amounts of dicyandiamide (10g, 20g) were added to the Pluronic solution along with the resol and TEOS (same amount as for the undoped OMC). For the preparation of N-doped mesoporous carbon/iron oxide composites, the dicyandiamide was held constant (20 g) and either 8 g or 16 g of iron nitrate were added to the Pluronic solution in addition to the resol and TEOS. Irrespective of its composition, the multi-component solution was heated to 40 °C and stirred for 2 h in order to hydrolyze TEOS. A 400 µm thick wet-film was then obtained by doctor blade casting the solution on a thermally stabilized PET substrate at a moving velocity of 50 cm/min using roll-to-roll processing [31]. The residual solvent was removed by heating at 50 °C for 2 h. Subsequently, the film was crosslinked at 120 °C for 3 h [32]. The crosslinked film was peeled from the PET substrate and broken into pieces. The pieces were carbonized at 800 °C for 3 h under N₂ atmosphere in a large alumina boat (Anderman Ceramics, Inc.). The heating schedule for carbonization was 1°C/min to 600 °C and 5°C/min to 800 °C. The carbonized materials were subsequently etched in 3 M KOH in H₂O/ethanol (50/50; v/v) solution to remove the silica. These materials are denoted as OMC-*x* and OMC-*x-y*, where *x* is the wt% of nitrogen in the carbon framework as determined from elemental analysis and *y* is wt% of iron oxide nanoparticles as determined by thermal gravimetric analysis (TGA) in the porous composites.

2.3 Characterization

Transmission small-angle X-ray scattering (SAXS) was performed using a Rigaku MicroMax 002+ instrument with a 2D multiwire area detector and a sealed copper tube operating at 45 kV to generate CuK_α X-rays (wavelength = 0.154 nm). The scattering vector (*q*) was calibrated

using the primary peak of silver behenate at $q = 1.076 \text{ nm}^{-1}$. Two-dimensional X-ray patterns were obtained in the range of $0.12 < q < 2 \text{ nm}^{-1}$ and the domain spacing, d , was determined as $d=2\pi/q^*$. Powder X-ray diffraction (XRD, Bruker AXS D8 Discover) was used to determine the crystalline phase of iron oxide nanoparticles. Transmission electron microscopy (TEM, JEOL-1230) operating with an accelerating voltage of 120 KV was used to obtain bright field microscope images using a digital CCD camera. The average particle size of iron oxides was determined from multiple TEM micrographs using ImageJ (National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>). The pore textural properties were determined from N₂ adsorption-desorption isotherms (Micromeritics Tristar) for the mesoporous materials. The pore size distributions were calculated from the adsorption isotherms using the Barrett, Joyner and Halenda (BJH) model [33], while the surface area was determined using Brunauer Emmett and Teller (BET) analysis [34]. TGA (TGA-2950) was used to determine iron oxide loading in the composite by oxidation of the carbon in the air. Elemental analysis (Perkin Elmer 2400 series) was used to determine the concentration of nitrogen, carbon and oxygen in the OMCs.

2.4 Cell fabrication and electrochemical characterization

For battery fabrication, the anode was prepared by mixing the active material (OMC or OMC/iron oxide composites) with carbon black and PVDF at a weight ratio of 7:2:1 in NMP. A homogenous slurry was obtained by mixing with mortar and pestle, and subsequently cast on the copper foil using a doctor blade with a casting thickness of 25 μm . The cast electrode was dried in an oven at 100 °C for overnight. The dried electrode was punched into 5/16" circular discs with a loading of 0.8-0.9 mg/cm^2 . 2032 coin cells were assembled in an argon-filled glove box

with < 0.5 ppm of O₂ and H₂O. Na-metal was used as the counter electrode, Celgard 3501 as the separator, and 1M NaClO₄ in EC/PC (1:1 v%) as the electrolyte. Galvanostatic charge/discharge of the Na-ion batteries was performed using 8 Channel Battery Analyzer BST-8A (1 mA, MTI Corporation) with a potential window from 0.01 V to 3.0 V (vs Na/Na⁺). Cyclic voltammetry (CV) was performed using an electrochemical workstation (CHI608E) at a scan rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out using CHI608E over a frequency range from 100 kHz-0.1 Hz with a perturbation potential of 5 mV. The DC component of the potential was the open circuit voltage.

3. Results and Discussion

Nitrogen-doped ordered mesoporous carbon with iron oxide nanocomposites were synthesized in ca. 100 g batches by extension of one-pot multi-constituent (resol, Pluronic F127, TEOS, dicyandiamide and iron nitrate) co-assembly methods [35] with roll-to-roll (R2R) processing (as shown in Supplementary Material, Figure S1). The R2R process consists of a casting zone and two hot air blowers (effectively a convection oven) for the evaporation of residual solvent and subsequent crosslinking of resol. The amount of material generated by this roll-to-roll method can be easily controlled by the speed and the time that the line is run to generate anywhere from single grams to kilograms of ordered mesoporous materials with properties that are not dependent on the batch size. Resol, dicyandiamide and iron nitrate were the precursors for carbon, nitrogen [36], and iron oxides respectively; while Pluronic F127 was used as the structure-directing agent. TEOS leads to interconnected silica in the carbon framework [35, 37], which was etched to generate micropores to enhance the surface area. Table 1 summarizes the characteristics of the synthesized materials. From elemental analysis of the carbonized samples,

the N-content of the mesoporous carbon increased from 2.4 to 3.6 wt% as the mass ratio of dicyandiamide to resol increased from 0.25 to 0.5. Increasing the iron nitrate content from 8 g to 16 g in the initial casting solution results in the increase of iron oxide content from 10.8 wt% to 21 wt% in the mesoporous material, as determined from TGA analysis.

Table 1. Elemental composition and structure properties of the OMCs and porous composites.

	Nitrogen ^a (wt %)	Fe ₂ O ₃ ^b (wt %)	FeO _x particle size (nm)	surface area (m ² /g)	pore size (nm)	<i>d</i> - spacing (nm)	Pore volume (cm ³ /g)
OMC	0	0	N/A	2160	3.7	9.7	1.62
OMC-2.4	2.4	0	N/A	1820	3.5	9.4	1.43
OMC-3.6	3.6	0	N/A	1590	3.5	9.3	1.25
OMC-3.6-10.8	3.6	10.8	4.4 ± 0.7	1100	3.8	9.9	0.73
OMC-3.6-21	3.7	21	7.8 ± 2.1	970	3.9	10.3	0.60

^a based on nitrogen in the carbon framework

^b based on iron oxide nanoparticles in the porous composites

Figure 1A illustrates the small angle X-ray scattering (SAXS) profiles for the mesoporous materials. A primary diffraction peak is observed for all of the samples, but the primary peak position and the breadth of this peak are strongly dependent on the composition of the precursor solution. The undoped OMC shows four scattering peaks with ratios relative to q^* as 1: $\sqrt{3}$:2: $\sqrt{7}$ with *d*-spacing of 9.7 nm. This scattering pattern corresponds to a well-defined, highly ordered cylindrical (*p6mm*) morphology. Addition of dicyandiamide for N-doping leads to a shift in the primary diffraction peak to higher q associated with a decrease in the domain spacing from 9.7 nm (undoped OMC) to 9.4 nm (OMC-2.4) and 9.3 nm (OMC-3.6). Additionally, the intensity and resolution of the scattering peaks are degraded with only primary and second order peaks

resolved in the scattering patterns. With the incorporation of iron oxide nanoparticles in the N-doped mesoporous carbon, all of the higher order diffraction peaks are not observed in the SAXS patterns. The main diffraction peak is still preserved, but broadens significantly to almost a shoulder shape at the highest (21 wt%) iron oxide loading. The introduction of iron oxide into the mesoporous carbon results in an expansion of nanostructures [36] as evidenced by the shift of the primary peak to lower q .

Figure 1. (A) Small angle X-ray scattering profiles for the OMC composites with different content of nitrogen and iron oxides and (B) X-ray diffraction patterns of OMC-3.6-10.8 and OMC-3.7-21 to examine the crystal nature of the iron oxide nanoparticles.

Figure 1B shows the XRD profiles of the ordered mesoporous carbon/iron oxide nanocomposites. Only the (222) peak is very well resolved, but the positions of the broad, weak peaks correspond well with the expected diffraction pattern of $\gamma\text{-Fe}_2\text{O}_3$. The four diffraction peaks from OMC-3.7-21 can be assigned to the (220), (222), (400) and (511) reflections of $\gamma\text{-Fe}_2\text{O}_3$ (PDF card No. 89-5892). The intensity of diffraction peaks decreases and the width of peaks broaden for the lower iron oxide loading (OMC-3.6-10.8), which suggests crystallization may depend on the metal nitrate content and the subsequent size of the nanoparticle formed. Similar size effects have been reported for other metal oxide-carbon composites upon

carbonization [38]. Additionally, the broad peak at 43° - 44° is also consistent with some fraction of graphitic carbon (PDF card No. 75-1621) and Fe_2O_3 nanoparticles are known to promote graphitization [39, 40].

One challenge associated with quantitative analysis of the SAXS patterns in assessing the quality of the ordered structure is that the contrast of the system is changed with the addition of the iron oxide due to the higher X-ray contrast between the Fe_2O_3 nanoparticles and carbon than that between the pores and the matrix, which tends to decrease the intensity and resolution of the primary diffraction peak [41]. Figure 2 shows the TEM micrographs of functionalized OMCs. For the N-doped samples without iron oxides nanoparticles (OMC-2.4 and OMC-3.6), the stripe-like patterns indicate the presence of a highly ordered mesostructure, which is consistent with the SAXS profiles. This mesostructure is similar to that obtained without N-doping (Supplementary Material, Figure S2), but the center-to-center distance between the stripes decreases from 9.8 nm to 9.2 nm to 9.1 nm as the N-doping increases from 0 to 2.4 wt% to 3.6 wt%. For OMC-3.6-10.8 (Figure 2C) and OMC-3.7-21 (Figure 2D), the stripe pattern could still be observed, yet the mesostructure is only locally ordered. The dark spots in the TEM micrographs are the Fe_2O_3 nanoparticles, which are fairly uniformly distributed in the carbon framework. As the iron nitrate concentration in the precursor increases from 20 wt% to 40 wt% (relative to the solid resol), the size of the iron oxide nanoparticles increases from approximately 4.4 ± 0.7 nm (Figure 2C) to 7.8 ± 2.1 nm (Figure 2D). These TEM micrographs suggest that the decreased scattering intensity in the SAXS patterns for the OMCs (Figure 1A) with iron oxide nanoparticles is at least partially associated with a decrease in the long-range ordering of these systems. The mobility of Pluronics surfactants in highly concentrated solution is known to be reduced [42, 43], which provides an

explanation for the decrease in long-range ordering due to the high solids concentration leading to a kinetically trapped mesostructure during solution casting/drying process [44].

Figure 2. TEM micrographs of (A) OMC-2.4; (B) OMC-3.6; (C) OMC-3.6-10.8; and (D) OMC-3.7-21.

Battery performance can be significantly impacted by the surface area and pore size distribution of the active electrode materials [45], thus it is important to understand how the compositional changes impact these properties. Figure 3A illustrates the N_2 adsorption-desorption isotherms for the OMCs. All of the samples exhibit type-IV N_2 adsorption-desorption curves with H_1 hysteresis loop that is consistent with mesoporous materials with cylindrical channels [46]. The N_2 adsorption is significant at low p/p_0 , which is associated with the presence of micropores that are hard-templated by the silica from TEOS. This microporosity leads to high surface areas for these OMC materials. Without any doping, the BET surface area of the OMC is around $2160 \text{ m}^2/\text{g}$ (See Supplementary Material, Figure S3) and decreases with increasing N-

doping to 1820 m²/g and 1590 m²/g for OMC-2.4 and OMC-3.6, respectively. Concurrent with this change in surface area, the total pore volume decreased from 1.62 cm³/g (OMC) to 1.43 cm³/g (OMC-2.4) to 1.25 cm³/g (OMC-3.6). The average pore size decreases slightly with increasing N-doping content (Figure 3B), which is consistent with the decreased *d*-spacing determined from both SAXS and the TEM micrographs. The influence of the dicyandiamide (N-doping agent) on the assembly must be considered in order to explain this decreased pore size and *d*-spacing. The addition of the dicyandiamide may act to partially compatibilize the hydrophilic and hydrophobic segments of the Pluronic template, which will have a similar effect as a plasticizer on the assembly of a block copolymer to decrease chain stretching and thus tend to decrease the *d*-spacing and the pore size [47].

The introduction of iron oxide nanoparticles into the N-doped carbon framework further decreases the surface area to 1100 m²/g and 970 m²/g for OMC-3.6-10.8 and OMC-3.7-21, respectively. Similarly the pore volume decreases to 0.73 cm³/g to 0.60 cm³/g for OMC-3.6-10.8 and OMC-3.7-21, respectively. Unlike the N-doped mesoporous carbon, there is a slight increase in the average mesopore size with the addition of Fe₂O₃ nanoparticles from the iron nitrate precursor as shown in Figure 3B. This increased pore size is consistent with the increased domain spacing from SAXS profiles, which is likely due to: (1) the enhanced rigidity attained by iron oxides to decrease the pore shrinkage and (2) the partial penetration of iron nitrate into the micelle leading to an expansion in nanostructures [36]. Irrespective, the pore size only varies between 3.5 nm and 3.9 nm for all of the samples as listed in Table 1. Thus, the primary effect of the doping of the OMCs is to decrease both the surface area and the pore volume. For materials

with invariant chemistry, these changes in pore texture tend to be unfavorable for its performance as the active material in a battery electrode.

Figure 3. (A) N_2 absorption-desorption isotherms of N-doped OMCs with different nitrogen and iron oxide content and (B) their corresponding pore size distributions determined from the absorption isotherm. The isotherms are vertically shifted by $200 \text{ m}^2/\text{g}$, $150 \text{ m}^2/\text{g}$ and $100 \text{ m}^2/\text{g}$ for OMC-2.4; OMC-3.6 and OMC-3.6-10.8, respectively.

Figure 4 illustrates the rate dependent charge storage properties of the OMC-based materials when used as the active material in sodium ion battery anodes. The discharge capacity is enhanced by the inclusion of nitrogen functional group and iron oxide nanoparticles in the mesoporous carbon. At the lowest rate examined (25 mA/g), the neat undoped OMC shows a discharge capacity of 115 mAh/g , which is similar to a previous report using OMC with approximately 6 nm cylindrical pores as anodes for sodium-ion battery [12]. By introduction of $3.6 \text{ wt\%}$ nitrogen heteroatoms into the carbon framework, the capacity increases to approximately 135 mAh/g at 25 mA/g . The inclusion of nitrogen group enhances the discharge capacity at higher current density likely due to the improved wettability of pore surface with

electrolyte; for example, when the current density is 0.8 A/g, OMC-3.6 exhibits a discharge capacity of around 80 mAh/g, while the OMC is only able to deliver a discharge capacity of 25 mAh/g. Incorporating the iron oxide nanoparticles into the porous carbon matrix further improves the discharge capacity through the conversion reaction mechanism between iron oxide and sodium ions.

Figure 4. Discharge capacity of the undoped OMC ($\triangle$); OMC-3.6 ($\square$), OMC-3.6-10.8 ($\diamond$) and OMC-3.7-21 ($\circ$) at current densities ranging from 25 mA/g to 2.5 A/g.

For OMC-3.6-10.8 and OMC-3.7-21, the discharge capacity increases to 205 mAh/g and 275 mAh/g at 25 mA/g, respectively. Increasing the current density decreases the discharge capacity of OMC-3.7-21 due to the kinetically limited sodium ion diffusion in the electrodes at high charging-discharging rate. Notably, even at a high current density of 1.6 A/g and 2.5 A/g, OMC-3.7-21 is still able to deliver a reversible capacity of 134 mAh/g and 88 mAh/g. This high rate capacity of mesoporous carbon/iron oxides nanocomposites can be attributed to: 1) the introduction of micropores in the well-defined cylindrical walls for shortening diffusion path length of sodium ions and 2) the incorporation of nitrogen heteroatoms in the carbon framework

for enhancing the wettability of carbon walls with organic electrolytes that facilitates efficient diffusion of sodium ions upon cycling [48]. When decreasing the current density back to 25 mA/g, the discharge capacity of OMC-3.7-21 is able to recover to around 276 mAh/g.

The Na-ion insertion-extraction behavior was investigated by cyclic voltammetry (CV) at a scan rate of 0.5 mV/s between 0.005-3V vs Na/Na⁺ as shown in Figure 5(A) for OMC-3.7-21. A reduction peak (1.1 V) with a shoulder peak at slightly lower voltage was observed in the first anodic scan (See Supplementary Material, Figure S5). This is assigned to the formation of solid electrolyte interface (SEI) during the initial cycle as these features are not as prevalent in the subsequent cycles. There also are spikes in the current at high voltage for the CV curves in the 1st and 2nd cycle that disappear in subsequent cycles. This behavior is reproducibly observed with almost noise-like features in the first 1-2 CV curves. These spikes in the CV curves are attributed primarily to locally non-ideal wetting of electrode with electrolyte during the preparation of the cell. The application of potential can improve the wetting of the electrode to increase the accessible surface area, which explains why the spikes in current dramatically decrease after the first CV cycle. Additionally, impurities introduced during cell fabrication can be oxidized at high potentials. The consumption of these impurities through oxidization would also explain the disappearance of the spikes in the current at high voltage in the CV curves after several cycles.

Due to the SEI formation during the 1st cycles, the CV for the second cycle can more clearly illustrate several weak redox peaks at 0.6 V, 1.2 V (cathodic) and 0.75 V (anodic) vs. Na/Na⁺ as shown in Figure 5A. The peak at 1.2 V during the cathodic scan corresponds to Na⁺ insertion into the Fe₂O₃ to form Na_xFe₂O₃ while the weak anodic peak at 0.75 V corresponds to the

oxidation from Fe^0 to Fe^{+3} . [49, 50] The galvanostatic discharge/charge profiles of OMC-3.7-21 at 25 mA/g are shown in the Figure 5(B). During the initial discharge cycle, the OMC-3.7-21 delivered 406 mAh/g and in the following second cycle, the capacity decreases to around 248 mAh/g. This difference in the discharge capacity from first cycle is likely predominately from the decomposition of electrolyte to form the SEI as evidenced by CV curves (Figure S5). The discharge profile of OMC-3.7-21 after 20 cycles is almost identical to the second cycle, which suggests excellent cycle stability of this material in anode for sodium-ion battery, which is similar to the nearly invariant CV curves for the 2nd to 5th cycle (Figure 5A). No distinct plateau can be observed in the discharge profile, which is similar to previous reports using small iron oxide nanoparticles (<10 nm) in a carbon matrix [50-52]. The slope change at approximately ~1.2 V agrees well with the CV results. Overall, the reaction can be described as:

Figure 5. (A) Cyclic voltammograms of the first two cycles for OMC-3.7-21 between 0.005 and 3 V at a scan rate of 0.5 mV/s and (B) discharge/charge profiles of OMC-3.7-21 at selected cycle between 0.05 and 3 V at a current density of 25 mA/g.

To demonstrate the stability of the OMC-3.7-21-based sodium ion battery, the coin cells were cycled at 100 mA/g for over 350 cycles. In order to activate the cell and to generate a stable SEI layer, a current density of 25 mA/g was applied for the initial discharge-charge cycle. As shown in Figure 6, the OMC-3.7-21 exhibited a high reversible capacity of 213 mAh/g at the beginning of the discharge-charge cycling, but the capacity gradually increased to approximately 260 mAh/g after 150 cycles. This increase in the discharge capacity has been previously observed for other nanocrystalline metal oxide anodes [53, 54] and was attributed to a gradual amorphization of crystalline Fe_2O_3 from successive insertion and extraction of sodium ions [52, 53]. Amorphous metal oxide nanoparticles exhibit faster kinetics for redox reaction than its crystalline state [55]. The reversible capacity after 370 cycles is 220 mAh/g with Coulombic efficiency around 99.5%, which is slightly higher than its initial value (second cycle) of 213 mAh/g. These results suggest excellent cycle stability for OMC-3.7-21 as an anode for Na ion batteries. This stability can be attributed to (1) the nano-sized iron oxide particles through multi-constituent co-assembly method and (2) the embedding of iron oxides in the carbon matrix to prevent pulverization and loss of the active Fe_2O_3 . Table S1 (see Electronic Supplementary Material) provides a comparison of the electrochemical performance of this material to recently reported composite anode materials for Na-ion batteries. The discharge capacity of our cell based on OMC-3.7-21 is greater than previously reported metal oxide-carbon composites, but does not reach the high capacity (~ 300 mAh/g) of some recent, advanced Na-ion cells that include an alloying (Sb) component in the carbon for the anode material. However, the combination of the scalable syntheses method (roll-to-roll) and low-cost precursors for the fabrication of the OMC-3.7-21 provides an additional advantage to the cells in this work in terms of potential for application in sodium ion batteries.

Figure 6. Cycling performance of OMC-3.7-21 as anode for Na-ion battery at 100 mA/g

In order to better understand the good capacity performance, Figure 7 shows the initial electrochemical impedance spectroscopy (EIS) spectrum of the OMC-3.7-21 and the EIS spectrum after 200 cycles in order to provide the insight into the sodium ion diffusion process in these ordered mesoporous carbon/ Fe_2O_3 nanocomposites. The Nyquist plots are fit using an equivalent circuit consisting of R_b as the bulk resistance of the cell (electrical conductivity of electrolyte), R_{ct} and C_{dl} as the charge transfer resistance and relative double layer capacitance, respectively, and W as the Warburg impedance that is related to the sodium ion diffusion in the electrode. After 200 cycles, both the bulk resistance (R_b) and charge transfer resistance increase. This increase in the bulk resistance is similar to a recent detailed EIS study where the influence of electrolyte additives was examined [56], which suggests that the increase is due to the SEI formation. Thus, we attribute these increases in resistance to the formation of the SEI layer [57]. The ionic conductivity of the anode material (OMC-3.7-21) does not appreciably change after

200 cycles as evidenced by the same slope of the Nyquist plot at lower frequency compared to its initial state.

In order to understand the impact of electrode composition on the resistances in the cycle, the other three electrodes were also examined using EIS (Figure S6). The EIS spectra for all of the electrodes can be fitted with the same equivalent circuit, which enables direct comparison of the resistances. Interestingly, while the OMC-3.7-21 has the highest loading of non-conductive Fe_2O_3 nanoparticles, it exhibits the lowest total resistance among all the samples (See Supplementary Material, Table S2). We attributed the decreased resistance for OMC-3.7-21 to the partial graphitization of carbon framework (Figure 1B), which is catalyzed by the Fe [58]. Overall, the mesoporous carbon/iron oxide nanocomposites exhibit high specific capacity performance with excellent cycle stability as the anode material of sodium-ion batteries, which can be attributed to the presence of micropores in the mesoporous channels for facilitating the diffusion of sodium ions upon cycling, constrained volumetric variation of Fe_2O_3 nanoparticles in the porous carbon matrix, and enhanced electrolyte wettability in the carbon framework from the inclusion of nitrogen heteroatoms.

Figure 7. Electrochemical impedance spectroscopy of Na-ion battery using OMC-3.7-21 as anodes before cycling and after 200 cycles under current density of 100 mAh/g. The dashed line is the fit to the equivalent circuit.

4. Conclusion

Ordered mesoporous Fe₂O₃-doped carbon nanocomposites were fabricated from low-cost raw materials using multicomponent cooperative assembly with R2R processing. Nitrogen doping of carbon through inclusion of dicyandiamide in the precursor leads to improved performance of the mesoporous carbon as anodes in sodium ion batteries. Iron nitrate provides a low cost precursor for iron oxide to provide further enhancements in capacity for sodium ion batteries. The combination of N-doping (3.7 wt %) and Fe₂O₃ nanoparticles (21 wt %) more than doubles the gravimetric capacity in comparison to standard ordered mesoporous carbon (OMC). This ordered mesoporous Fe₂O₃-doped carbon nanocomposite also exhibits relatively good rate performance (134 mAh/g at 1.6 A/g) and the performance is stable over 350 discharge-charge cycles without any decrease in capacity. The combination of superior electrochemical performance and low-cost, scalable processing methods makes the N-doped ordered mesoporous carbon/iron oxides as promising candidates for anodes in sodium ion batteries.

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Graphical abstract