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Abstract

Nitrogen-doped carbon coated Co₃O₄ nanoparticles (Co₃O₄@NC) with high Na-ion storage capacity and unprecedented long-life cycling stability are reported in this paper. The Co₃O₄@NC was derived from a metal – organic framework ZIF-67, where the Co ions and organic linkers were, respectively, converted to Co₃O₄ nanoparticle cores and nitrogen-doped carbon shells through a controlled two-step annealing process. The Co₃O₄@NC shows a porous nature with a surface area of 101 m² g⁻¹. When applied as an anode for sodium ion batteries (SIBs), Co₃O₄@NC delivers a high reversible capacity of 506, 317, and 263 mA h g⁻¹ at 100, 400, and 1000 mA g⁻¹, respectively. A capacity degradation of 0.03% per cycle over 1100 cycles was achieved at a high current density of 1000 mA g⁻¹. The outstanding Na-ion storage performance can be ascribed to the nitrogen-doped carbon coating (NC), which facilitates the capacitive reaction, minimizes the volume changes of Co₃O₄, and also enhances the electronic conductivity. This work sheds light on how to develop high-performance metal oxide@NC nanocomposites for SIBs

Keywords

performance, co₃o₄, nitrogen, doped, carbon, derived, metal, organic, superior, framework, sodium, ion, storage

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Superior sodium-ion storage performance of Co_3O_4 @nitrogen-doped carbon: derived from a metal–organic framework†

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Nitrogen-doped carbon coated Co_3O_4 nanoparticles (Co_3O_4 @NC) with high Na-ion storage capacity and unprecedented long-life cycling stability are reported in this paper. The Co_3O_4 @NC was derived from a metal–organic framework ZIF-67, where the Co ions and organic linkers were, respectively, converted to Co_3O_4 nanoparticle cores and nitrogen-doped carbon shells through a controlled two-step annealing process. The Co_3O_4 @NC shows a porous nature with a surface area of $101 \text{ m}^2 \text{ g}^{-1}$. When applied as an anode for sodium ion batteries (SIBs), Co_3O_4 @NC delivers a high reversible capacity of 506, 317, and 263 mA h g^{-1} at 100, 400, and 1000 mA g^{-1} , respectively. A capacity degradation of 0.03% per cycle over 1100 cycles was achieved at a high current density of 1000 mA g^{-1} . The outstanding Na-ion storage performance can be ascribed to the nitrogen-doped carbon coating (NC), which facilitates the capacitive reaction, minimizes the volume changes of Co_3O_4 , and also enhances the electronic conductivity. This work sheds light on how to develop high-performance metal oxide@NC nanocomposites for SIBs.

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Introduction

Sodium ion batteries (SIBs) have drawn enormous attention for applications in large-scale energy storage such as smart grids, due to their low cost and the wide natural availability of Na.^{1–3} Similar to lithium ion batteries (LIBs), Na-ion storage normally occurs *via* three types of reactions: insertion, alloying, and conversion. Among these reactions, the conversion type generally involves a multi-electron reaction, which contributes to high capacity and consequently attracts great research attention. The conversion reactions, however, are accompanied by large volume changes during the sodiation/desodiation, which result in agglomeration or pulverization, and thus capacity decay and poor cycle life.^{1,4} In addition, the poor electron conductivity of the matrix leads to unsatisfactory rate capability.⁵ A great deal of effort is obviously necessary to improve the electrochemical performance of conversion-type reactions.

One highly effective way to improve the cycling and rate performance of conversion-type materials is to coat the metal oxides with carbon materials,^{6,7} which can effectively

accommodate the volume changes and improve the electronic conductivity. Incorporation of heteroatoms into carbon can not only provide more active sites, but also enhance the chemical wettability.^{8–10} Nitrogen, with higher electron negativity and a similar atomic diameter to carbon, is a highly attractive doping candidate for carbon.^{11–13} Reducing the particle size to the nanoscale is another common approach to improve the electrochemical performance, since it can effectively shorten the diffusion distance and provide more contact surfaces between the electrolyte and electrode.^{14,15} The combination of a heteroatom-doped carbon coating and nanostructure is therefore a sound strategy to develop high-performance hybrid composites for SIBs.

Metal–organic frameworks (MOFs), composed of metal ions and interconnected organic linkers, feature tunable porosities and versatile functionalities.^{16–18} Using MOFs as templates to prepare electrochemically active materials (porous carbons, metal oxides, metal oxide/carbons, *etc.*) has been rapidly explored for LIBs.^{19–26} For example, highly N-doped porous carbon (derived from ZIF-8) showed a capacity of 2132 mA h g^{-1} after 50 cycles at 100 mA g^{-1} in LIBs.¹¹ Spindle-like Fe_2O_3 (derived from MIL-88Fe) anodes exhibited excellent rate capability in Li/ Fe_2O_3 half cells.²⁷ The successful applications of MOFs in LIBs have recently aroused attention in SIBs.²⁸

In contrast to the previous methods, where either metal ions or organic linkers were used to obtain pure metal oxide or carbon products,^{20–24} we report a method to produce metal oxide@nitrogen doped carbon core–shell structures where both metal oxides and organic linkers of the MOF precursor are fully

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utilized. Herein, ZIF-67 is selected as a dynamic template, since the organic linkers in ZIF-67 contain both N and C, a great source of NC; its metal ions Co^{2+} can be converted to Co_3O_4 . When applied as an anode for SIBs, this unique $\text{Co}_3\text{O}_4@\text{NC}$ exhibits outstanding electrochemical performance with a high capacity (506 mA h g^{-1} at 100 mA g^{-1}), and an ultra-long cycling stability (a capacity degradation of 0.03% per cycle during 1100 cycles at 1000 mA g^{-1}). This outstanding electrochemical performance can be attributed to the capacitive reaction and the full conversion between Co_3O_4 and Co. This approach can be easily transferred to develop other nanoscale metal oxides with N-doped carbon coatings for high-performance SIBs.

Experimental

Preparation of the $\text{Co}_3\text{O}_4@\text{NC}$ and the pure Co_3O_4

All chemicals were purchased from Sigma-Aldrich and used as-received without further treatment. The ZIF-67 precursor was synthesized according to the literature.^{29,30} Typically, to successfully convert the ZIF-67 to $\text{Co}_3\text{O}_4@\text{NC}$, two steps were involved. ZIF-67 powders were first placed in a tube furnace and calcined at 550°C for 2 h under Ar protection. The resultant sample was marked as Co@NC. The as-prepared Co@NC sample then underwent a controlled oxidization process by being held at 150°C for 12 h in air. For comparison, ZIF-67 derived pure Co_3O_4 was also synthesized. To obtain the pure Co_3O_4 , the Co@NC intermediate was further calcined at 350°C in air for another 3 h.

Characterization

X-ray diffraction (XRD, GBC eMMA, Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$), X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA-LAB 2201XL, Al $K\alpha$ X-ray radiation), Fourier transform infrared spectroscopy (FTIR, Shimadzu prestige-21), thermogravimetric analysis-differential scanning calorimetry measurements (TGA-DSC, Mettler Toledo TGA/DSC1), Raman spectroscopy (JobinYvon HR800 Raman spectrometer with a 10 mW helium/neon laser at 632.8 nm excitation), and nitrogen adsorption-desorption isotherms (NOVA 2200e, Quantachrome Instruments) were used to determine the structure or composition. Scanning electron microscopy (SEM, JEOL JSM7500FA), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HR-TEM, JEOL JEM-2010FEF) were adopted for morphological and structural investigations.

Electrochemical measurements

The electrochemical performances were evaluated by using standard 2032 type coin cells. The working electrodes were fabricated with 80 wt% active materials, 10 wt% acetylene black (Super-P), and 10 wt% sodium carboxymethyl cellulose (CMC) in deionized water to form a slurry. The slurry was then cast onto copper foil and dried in a vacuum oven at 80°C overnight. A sodium disc was used as the counter and reference electrodes. The electrodes were separated by a glass fiber. 1 M NaClO_4 in

propylene carbonate (PC) with the addition of 2 wt% fluoroethylene carbonate (FEC) was used as an electrolyte. The cells were assembled in an argon filled glovebox with oxygen and water content below 1 ppm. Galvanostatic charge-discharge tests were carried out on a battery testing system (Shenzhen NEWARE Battery, China) with the voltage between 0.01 and 3.00 V. Electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetry (CV) were performed on a Biologic VMP-3 electrochemical workstation. The capacities were calculated based on the active materials.

Results and discussion

The MOF derived $\text{Co}_3\text{O}_4@\text{NC}$ is synthesized through a controlled two-step oxidation as illustrated in Fig. 1. ZIF-67 consists of Co^{2+} ions bonded with the N in 2-methylimidazole (organic linkers) (Fig. 1a). During the first step calcination the cobalt ions were converted into ultra-small metallic Co particles (Fig. 1b). Meanwhile, the organic linker was carbonized to NC that wraps the Co particles (Co@NC). By annealing Co@NC at 150°C in air for 12 h, the central Co particles were gradually oxidized to Co_3O_4 ,³¹ while the NC shell survived at this relatively low temperature. The final sample (Fig. 1c) maintains the polyhedral outline of the precursor and is composed of core-shell $\text{Co}_3\text{O}_4@\text{NC}$ subunits.

The formation of the ZIF-67 precursor was confirmed by its X-ray diffraction (XRD) pattern (Fig. 2a) and Fourier transform infrared (FTIR) spectrum (Fig. S1, ESI†). A temperature of 550°C was chosen to anneal the ZIF-67 in Ar, since it demonstrated a dramatic weight loss between 500 and 650°C (TGA curves, Fig. S2†). The first-step annealing led to the formation of metallic Co, which was subsequently converted to Co_3O_4 when heated at 150°C in air for 12 h (Fig. 2a). XPS (Fig. 2b–e) reveals the presence of C, N, O, and Co in the resultant sample. The high-resolution XPS spectrum of Co 2p reveals two major peaks at 778.8 and 794.0 eV, and the 15.2 eV energy difference between the Co 2p peaks is indicative of spinel Co_3O_4 .³² The presence of satellite peaks (marked as Sat. in Fig. 2c) further confirms the well-defined Co_3O_4 structure.³³ The C 1s spectrum (Fig. 2d) indicates the presence of carbon, whose absence in the XRD pattern is due to its amorphous nature. Two types of nitrogen are observed in the N 1s spectrum (Fig. 2e), pyridinic and pyrrolic N at 399.1 and 400.6 eV, respectively. The presence of carbon in $\text{Co}_3\text{O}_4@\text{NC}$ is also evidenced by the characteristic D and G bands in the Raman spectrum (Fig. 2f). The carbon content of $\text{Co}_3\text{O}_4@\text{NC}$ is confirmed by using TGA curves (Fig. S3,† performed in air). The weight loss between 250 and 370°C is associated with the combustion of NC. Therefore, the carbon content in $\text{Co}_3\text{O}_4@\text{NC}$ was evaluated to be about 26 wt%. The nitrogen content in carbon is 15.4% according to the elemental analysis report. Elemental content (Co, C, N) is given in Table S1.†

The morphologies of the samples were characterized by scanning and transmission electron microscopy (SEM and TEM). The ZIF-67 precursors are in the form of polyhedron with smooth surfaces, and the typical particle size is $\sim 180 \text{ nm}$ (Fig. 3a and b). The $\text{Co}_3\text{O}_4@\text{NC}$ particles inherit the contour of

Fig. 1 Illustration of the formation of $\text{Co}_3\text{O}_4\text{@NC}$. Scanning electron microscope (SEM) images of (a) ZIF-67 precursor, (b) Co@NC intermediate, and (c) $\text{Co}_3\text{O}_4\text{@NC}$. The subunit composition, consisting of a Co_3O_4 core and a NC shell, is illustrated in (d).

Fig. 2 (a) XRD patterns of ZIF-67, Co@NC , and $\text{Co}_3\text{O}_4\text{@NC}$; (b) XPS survey spectrum of $\text{Co}_3\text{O}_4\text{@NC}$; high resolution XPS spectra of (c) Co 2p, (d) C 1s, and (e) N 1s of the $\text{Co}_3\text{O}_4\text{@NC}$; (f) Raman spectra of Co_3O_4 and $\text{Co}_3\text{O}_4\text{@NC}$ composites.

ZIF-67, but shrink to ~ 100 nm (Fig. 3c). The $\text{Co}_3\text{O}_4\text{@NC}$ polyhedron is composed of closely packed nanoparticles (NPs) that form a rough surface (Fig. 3d), which can also be observed in Co@NC and pure Co_3O_4 (derived from ZIF-67, ESI, Fig. S4†).³⁴ The polyhedral morphology of the particles and the existence of subunits can be seen more clearly under TEM (Fig. 3e and f). A core-shell structure is clearly demonstrated for $\text{Co}_3\text{O}_4\text{@NC}$ in the high-resolution TEM image (Fig. 3f), where ~ 5 nm Co_3O_4 is the core and 2–3 nm NC is the shell. The lattice fringe spacing of $2.8 \text{ \AA}$ is related to the (220) planes of spinel Co_3O_4 . The contrast profile of the NC shell displays a d -spacing of $3.8 \text{ \AA}$, which corresponds to the C (002) planes (inset of Fig. 3f).³⁴ This could be beneficial since carbon materials enable more effective sodiation/desodiation when the interlayer distance is larger than $3.7 \text{ \AA}$.³⁴ The bright dots in the dark field TEM image (Fig. 3g) are Co_3O_4 NPs, and the dark part is interconnected NC.

The corresponding energy dispersive spectroscopy (EDS) mappings (Fig. 3h) show that all the elements are uniformly distributed.

Fig. 3 SEM images of (a and b) ZIF-67 precursor; (c and d) as-obtained $\text{Co}_3\text{O}_4\text{@NC}$ at different magnifications. TEM images of (e and f) $\text{Co}_3\text{O}_4\text{@NC}$ at different magnifications. A and B in (f) represent the Co_3O_4 core and the NC shell, respectively. The contrast profile in inset (f) is obtained from the NC shell from the region highlighted by a double-sided arrow. (g) Dark-field TEM image of a $\text{Co}_3\text{O}_4\text{@NC}$ polyhedron, and (h) the corresponding elemental mappings for C, N, O, and Co.

The surface area and pore size distribution can greatly affect the electrochemical performance. The nitrogen sorption isotherms of this $\text{Co}_3\text{O}_4@\text{NC}$ sample (Fig. 4) show a typical type-IV hysteresis loop, confirming its mesoporous nature which facilitates the contact between the electrode and electrolyte. The Brunauer–Emmett–Teller (BET) surface area of the $\text{Co}_3\text{O}_4@\text{NC}$ is $101 \text{ m}^2 \text{ g}^{-1}$. The decreased surface area, from ZIF-67 ($664 \text{ m}^2 \text{ g}^{-1}$)³⁵ to $\text{Co}_3\text{O}_4@\text{NC}$ ($101 \text{ m}^2 \text{ g}^{-1}$), was likely caused by the carbonization of organic linkers. The majority mesopores of the $\text{Co}_3\text{O}_4@\text{NC}$ are $\sim 5 \text{ nm}$ in diameter that can be assigned to the pores in the shells, while the larger pores from 20 to 60 nm are likely related to the pores between polyhedra.

The sodium-ion storage performance of the $\text{Co}_3\text{O}_4@\text{NC}$ was investigated by assembling it into standard 2032 half-cells. Discharge–charge curves (at 100 mA g^{-1}) of the Co_3O_4 and $\text{Co}_3\text{O}_4@\text{NC}$ electrodes are presented in Fig. 5a and b. The large capacity loss in the first cycle mainly arises from the decomposition of the electrolyte and the formation of the solid electrolyte interphase (SEI) film.^{47,48} The first cycle discharge and charge capacities of the $\text{Co}_3\text{O}_4@\text{NC}$ electrode (813 and 516 mA h g^{-1} , respectively) are much higher than those of the pure Co_3O_4 electrode (495 and 326 mA h g^{-1}). In the second cycle, the $\text{Co}_3\text{O}_4@\text{NC}$ electrode delivers a high capacity of 517 mA h g^{-1} , much higher than 331 mA h g^{-1} from Co_3O_4 . This result outperforms not only the reported Co_3O_4 anodes,^{44–46} but also a large number of other materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$, MoS_2 , Sn@C , and Fe_2O_3 .^{36,37,39,40,43,49,50} The higher capacity of $\text{Co}_3\text{O}_4@\text{NC}$ may derive from its defect rich structure and porous nature, which help to trap more Na^+ during the cycling. Additionally, the N doping provides more active sites for Na^+ storage and enhances the capacitive behaviour.¹¹ Thus, this $\text{Co}_3\text{O}_4@\text{NC}$ electrode exhibits a higher capacity. Another remarkable difference between the pure Co_3O_4 and the $\text{Co}_3\text{O}_4@\text{NC}$ is the reversible capacity contribution at a lower potential (0.25 – 0.01 V). Compared with the rapid decline of pure Co_3O_4 , the $\text{Co}_3\text{O}_4@\text{NC}$ electrode contributes a large capacity of $\sim 185 \text{ mA h g}^{-1}$ in this range, which is likely to be associated with the NC shell.^{34,51}

The $\text{Co}_3\text{O}_4@\text{NC}$ electrode also displays excellent cycling stability (Fig. 5c). A capacity of $\sim 373 \text{ mA h g}^{-1}$ was delivered at the end of 60 cycles (87.0% capacity retention), in contrast to the poor cycling stability of the Co_3O_4 electrode (74.3% capacity retention). Superior rate capability is exhibited in the $\text{Co}_3\text{O}_4@\text{NC}$ electrode (Fig. 5d), which shows an average capacity

Fig. 5 The first and second discharge–charge curves of (a) pure Co_3O_4 and (b) $\text{Co}_3\text{O}_4@\text{NC}$ composites at 100 mA g^{-1} . (c) Discharge and charge capacity of pure Co_3O_4 and $\text{Co}_3\text{O}_4@\text{NC}$ electrodes for the first 60 cycles at 200 mA g^{-1} . (d) Rate capability and (e) long-term cycling stability of $\text{Co}_3\text{O}_4@\text{NC}$ electrode.

of 317 , 276 , and 263 mA h g^{-1} at 400 , 800 , and 1000 mA g^{-1} , respectively. When the current density was reversed back to 100 mA g^{-1} , a capacity of 457 mA h g^{-1} was obtained, 92% of the initial capacity. A direct comparison of the capacity retention at each current density is given in Fig. S5.† Exceptional long-term cycling stability was observed for the $\text{Co}_3\text{O}_4@\text{NC}$ electrode. It delivers a high reversible capacity of 175 mA h g^{-1} after 1100 cycles at a high specific current density of 1000 mA h g^{-1} (Fig. 5e), with a capacity decay of only 0.03% per cycle. Such an outstanding cycling stability is comparable or even better than the best electrodes reported (Table 1), especially for conversion-based Na-ion storage. Conversion reactions are generally accompanied by large volume changes and structural disintegration, which lead to poor cycling stability. Compared with large particles, this hierarchical structure is known to alleviate the negative impact due to volume changes.^{29,52} Furthermore, the carbon coating serves as a buffer and helps to maintain structural integrity.^{53,54} The as-obtained metal oxide@NC therefore is responsible for the outstanding cycling stability.

The existence of capacitive behaviour is beneficial for the cycling stability and rate capability in both LIBs and SIBs. However, it has been rarely mentioned in Na/ Co_3O_4 based cells. The contribution of the capacitive reaction in the $\text{Co}_3\text{O}_4@\text{NC}$ electrode was investigated in this work. Cyclic voltammetry curves (CVs, after the first cycle) at various scan rates were collected (Fig. 6a). Two peaks, marked as A and B, appeared during the sodiation and desodiation processes. The power-law relationship used to calculate the capacitive effect is illustrated in eqn (1) and (2).⁵⁵ Herein, i is the current, v is the scan rate,

Fig. 4 (a) Nitrogen absorption–desorption isotherms, and (b) the corresponding pore size distribution curve of the $\text{Co}_3\text{O}_4@\text{NC}$ sample.

Table 1 Electrochemical performance comparison of the Co₃O₄@NC electrode with some typical anode materials for SIBs

Electrode	Current (mA g ⁻¹)	Capacity (mA h g ⁻¹)	Capacity retention	Ref/year
Li ₄ Ti ₅ O ₁₂ /C	35	168	96% after 50 cycles	36/2015
^a PEO–MoS ₂	50	148	66% after 70 cycles	37/2015
Sn@C	500	445	90% after 200 cycles	38/2014
Al ₂ O ₃ /SnO ₂ /CC	134	377	80% after 100 cycles	39/2015
Fe ₂ O ₃	100	386	73% after 200 cycles	40/2014
CuO	50	303	64% after 50 cycles	41/2013
^b Co ₃ O ₄ NPs	25	447	86% after 50 cycles	42/2014
Co ₃ O ₄ /3D rGO	25	523	90% after 50 cycles	43/2015
Co ₃ O ₄ bowl	890	290	22% after 10 cycles	44/2014
Meso-Co ₃ O ₄	455	~130	44% after 250 cycles	45/2014
^c Co ₃ O ₄ –MCNTs	34	293	36% after 15 cycles	46/2015
Co ₃ O ₄ @NC	1000	175	67% after 1100 cycles	This work

^a PEO: poly(ethylene oxide). ^b NPs: nanoparticles. ^c MCNTs: multiwall carbon nanotubes.

Fig. 6 (a) CV curves (after the first cycle) of the Na/Co₃O₄@NC half-cells at different scan rates, (b) $\log i$ vs. $\log v$ plots used to qualify the electrochemical reaction, (c) relationship between the peak current and the scan rate used to quantify the contribution of the capacitive reaction, and (d) quantitative contributions for each type of electrochemical behavior.

and a and b are adjustable values. When b is close to 0.5, the electrochemical reaction is dominated by a diffusion (or faradaic) process; when b approaches 1, the system features a surface-limited capacitive (or non-faradic) reaction. In the $\log i$ vs. $\log v$ plot (Fig. 6b), b is calculated to be 0.77 and 0.86 for the reduction (peak A) and oxidation (peak B), respectively, indicating combined faradaic and non-faradaic processes.

$$i = av^b \quad (1)$$

$$\log i = b \times \log v + \log a \quad (2)$$

To quantify the contributions from the faradaic and non-faradaic behaviour, eqn (3) was used,^{47,56} where k_1V is the capacitive component and $k_2V^{1/2}$ is the intercalation component. In the plots of $i/V^{1/2}$ vs. $V^{1/2}$ (Fig. 6c), the slope represents

constant k_1 , and the intercept stands for constant k_2 . The percentages of faradaic and non-faradaic reactions that occurred in the electrochemical process were extrapolated (Fig. 6d). The capacitive reaction became dominant during desodiation. The pseudo-capacitive reaction at the surface is conducive to high rate capability and long-term cycling stability.^{55,57} This explains the outstanding Na-ion storage performance of Co₃O₄@NC.

$$i = k_1v + k_2v^{1/2} \quad (3)$$

Electrochemical impedance spectroscopy (EIS) was used to confirm the existence of the capacitive process and to investigate the kinetics in the Co₃O₄@NC electrode (Fig. 7). All the Nyquist plots contain a depressed semicircle in the medium to high frequency range, followed by a straight line. Generally, the more vertical the straight line is, the more capacitive the behaviour is.⁵⁶ The phase angle of each electrode is in the following order: the cycled Co₃O₄@NC (~73°) > pristine Co₃O₄@NC (~59°) > pristine Co₃O₄ (~46°). Accordingly, the following conclusions can be drawn: (1) the capacitive process in Co₃O₄@NC mainly originates from the NC shell, since the pure Co₃O₄ demonstrates negligible capacitive behaviour (a phase angle of 46°, close to 45°). The N-containing functional

Fig. 7 (a) Electrochemical impedance spectroscopy of the pristine Co₃O₄, Co₃O₄@NC, and Co₃O₄@NC electrodes after 1100 cycles, tested in the fully charged state. Equivalent circuits of (b) the pristine cells and (c) the cycled cells.

groups (pyridinic and pyrrolic N) in the NC facilitate the capacitive properties.¹¹ (2) The capacitive behaviour in the $\text{Co}_3\text{O}_4/\text{NC}$ sample becomes more dominant with cycling. To calculate the resistance, the related equivalent circuits are given in Fig. 7b and c. Here, R_s , R_{CT} , R_{SEI} , CPE, and W_o represent the resistance related to the electrolyte, charge-transfer, and the SEI, the constant phase element(s), and the Warburg impedance associated with Na^+ diffusion, respectively. Compared to the pure Co_3O_4 ($R_{CT} = 376 \Omega$), the $\text{Co}_3\text{O}_4/\text{NC}$ shows a much smaller R_{CT} value of 164Ω . The reduced R_{CT} can facilitate the kinetics and consequently improve the rate capability.

CVs were collected to obtain more information on the electrochemical reactions (Fig. S7†). There is a pair of broad redox peaks at about 0.6/1.4 V, except for the first cycle. Previous reports vaguely attributed this to reversible reduction and oxidation between Co_3O_4 and metallic Co.⁴³ Herein, to gain a clearer understanding of the electrochemical mechanism, *ex situ* XRD and high resolution (HR)-TEM were carried out. Fig. 8a displays the typical discharge-charge profile of the $\text{Na}/\text{Co}_3\text{O}_4/\text{NC}$ half cells in the first cycle. The plateaus at ~ 0.6 V in the discharge process and ~ 1.4 V in the charge process are in agreement with the CV results. Accordingly, five points, A (initial), B (discharged to 0.6 V), C (discharged to 0.01 V), D (charged to 1.4 V), and E (charged to 3.0 V), were selected to study the structural evolution during the electrochemical reaction. The strong reflections of Cu in the *ex situ* XRD patterns (Fig. 8b) are from the current collector. During the discharge

process, the Co_3O_4 phase gradually disappeared while a new phase of CoO appeared when the cell was discharged to 0.6 V. In the fully discharged state, only reflections belonging to Cu were observed. The following charge process experienced the reverse trend, with the presence of both CoO and Co_3O_4 at 1.4 V, and then only Co_3O_4 at 3.0 V. The XRD patterns do not reveal the Na_2O phase, which may be ascribed to its poor crystallization and/or small particle size. *Ex situ* TEM images were also collected at the corresponding potentials in Fig. 8c. The TEM image of the pristine $\text{Co}_3\text{O}_4/\text{NC}$ electrode at A shows the typical lattice fringes with 4.7 Å spacing for the Co_3O_4 (111) planes, and 3.8 Å for the C (002) planes of the NC. When discharged to state B, an interlayer distance of 2.1 Å was observed, which is related to the CoO (200) planes. After further discharging to state C, elemental Co emerges, as evidenced by its (111) and (200) planes. The absence of Co from the XRD patterns may be due to its relatively poor crystallinity, and/or small particle size.⁴² The *d*-spacing of 3.2 Å is ascribed to the (111) planes of Na_2O .^{41,42} During the charge reactions, both CoO and Co_3O_4 were detected at state D, while at state E, Co_3O_4 was the dominant phase. The EDS mapping indicates the presence of Co, Na, O, C, and N in the full discharged state (Fig. 9). The observation of the CoO intermediate during the process agrees with a report on $\text{Li}/\text{Co}_3\text{O}_4$ half cells⁵⁸ and explains the existence of the shoulder peaks in the CVs. Importantly, after full discharge the $\text{Co}_3\text{O}_4/\text{NC}$ can maintain its outline, and the NC

Fig. 8 Structural evolution of the $\text{Co}_3\text{O}_4/\text{NC}$ electrode during the electrochemical reaction. (a) Typical galvanostatic charge-discharge curve. Points A, B, C, D, and E represent the pristine state, the discharged state at 0.6 V and 0.01 V, and the charged state at 1.4 V and 3.0 V, respectively. (b) *Ex situ* XRD patterns corresponding to these points, and (c) TEM images (top) and selected area electron diffraction (SAED) patterns (bottom) at the corresponding points.

Fig. 9 (a) Dark field TEM image, and (b–g) the corresponding EDS mappings of the $\text{Co}_3\text{O}_4@\text{NC}$ electrode in the fully discharged state.

shell (dark part) effect protects the Co_3O_4 NPs (bright dots) from aggregation.

Based on the above discussion, the excellent Na-ion storage performance of $\text{Co}_3\text{O}_4@\text{NC}$ can be attributed to the following reasons. First, the complete encapsulation of the Co_3O_4 NPs (~ 5 nm) in the NC shell prevents the aggregation and pulverization of these NPs during cycling (Fig. 3g and 9a). Second, the NC shell formed *in situ* can not only effectively accommodate the volume changes but also decrease the charge transfer resistance. The interconnected organic linkers in the MOF precursor would contribute to the formation of the NC shell with high integrity, which helps to maintain the structure during the sodiation/desodiation. Third, the electrochemical reactivity features a large capacity that is mainly contributed by the NC shells, which leads to high rate capability and outstanding long-term stability. Such capacitive behaviour has not been reported in Co_3O_4 -based SIBs.

Conclusions

In summary, $\text{Co}_3\text{O}_4@\text{NC}$ was synthesized using ZIF-67 as the precursor and a dynamic template to obtain the desired morphology. During a controlled two-step calcination process, the central metal ions were transformed into Co_3O_4 NPs (~ 5 nm). The organic linkers were carbonized to form interconnected nitrogen-doped carbon layers (2–3 nm) on these Co_3O_4 NPs. The resultant $\text{Co}_3\text{O}_4@\text{NC}$ exhibits excellent Na-ion storage performance with high capacity and ultra-long cycling stability, which can be ascribed to the existence of capacitive behaviour and the full conversion between Co_3O_4 and metallic Co during the sodiation/desodiation. *Ex situ* XRD and TEM measurements reveal the electrochemical process during the cycling. This work points to a strategy to effectively improve the performance of conversion based Na-ion anode materials by using N-doped carbon coated metal oxide ($\text{MO}@\text{NC}$), particularly those derived from MOFs.

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