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Uniqueness of Co₃O₄/Nitrogen-Doped Carbon Nano-spheres Derived from Metal-Organic Framework: Insight of Superior Lithium Storage Capabilities Beyond Theoretical and Electrochemical Features in High Voltage Battery

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The uniqueness of Co₃O₄/N-doped-carbon nano-spheres derivated from metal-organic frameworks offers new choices of functional materials for lithium (ion) batteries applications.

Uniqueness of Co₃O₄/Nitrogen-Doped Carbon Nano-spheres Derived from Metal-Organic Framework: Insight of Superior Lithium Storage Capabilities Beyond Theoretical and Electrochemical Features in High Voltage Battery

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Abstract: Developing versatile strategy to create new structured materials with hetero-atomic doping has become one of the fascinating research topics owing to their fantastic properties, while the popular metal-organic-framework opens a promising avenue to design diverse architectures. Herein, an intriguing kind of spherical N-doped porous carbon (*i.e.*, N-C) particles containing numerous Co_3O_4 nanocrystals (*i.e.*, $\text{Co}_3\text{O}_4/\text{N-C}$) is introduced, in which the Zn-Co based Prussian blue analogue act as a sacrificial template and carbon source while the volatilization of zinc and oxidation of Co can produce rich pores and form highly active Co_3O_4 nanocrystals. The resultant $\text{Co}_3\text{O}_4/\text{N-C}$ particles has an extremely high lithium storage capacity of 1255 mA h g^{-1} and excellent rate capability even to the current of 2000 mA g^{-1} . The long cycle life over 500 cycles at 1000 mA g^{-1} with the high capacity of 798 mAh g^{-1} further demonstrates its prominent properties. Our kinetics analysis reveals that the high performances beyond theoretical mainly stem from the active Co_3O_4 nanocrystals, fast diffusion of lithium ions within the structure and pseudocapacitive behaviors; therefore it further demonstrates impressive stability and rate capabilities in lithium ion battery versus the cathode of lithium layered oxide even at high voltage conditions.

Introduction

Rechargeable lithium-ion batteries (LIBs) have dominated the energy market from portable electronics, stationary grid energy storage to electric vehicles,¹⁻³ but the enhancement of energy density remains a great challenge to meet the ever increasing demand.⁴⁻⁶ Apart from the excellent researches in Ni-rich and Li-rich layered compounds for higher capacity cathode,⁷⁻⁹ the replacement of graphite anode (*i.e.*, 372 mAh g⁻¹) with greater capacity silicon or metal (oxide) (*e.g.*, >700 mAh g⁻¹) also attract great attention.¹⁰⁻¹³ However, the case of utilizing metal (oxide) anode in practical applications is rarely reported because the problems of large irreversibility, serious capacity fading and unexpected safety issues.^{14, 15} Most of these fatal disadvantages result from the huge volumetric variation of metal (oxide) as the alloying or conversion process in the repeated (de-)lithiation.¹⁶⁻¹⁸ To address these problems in an effort, herein we introduce a new kind of spherical N-doped porous carbon particles encapsulating numerous metal oxide nanocrystals (*e.g.*, Co₃O₄/N-C) within the structure, where the predominant properties allow them demonstrating an extremely high lithium storage capacity and stability.

To date, numerous excellent researches focus on designing metal (oxide) and/or the composite of metal (oxide)-carbon with diverse morphologies and structures to overcome the aforementioned shortcomings and a great progress has been achieved.¹⁹⁻²¹ Particularly, the hetero-atomic doping (*e.g.*, N, P, F) endow the materials with more intriguing performances not only in battery but also in the applications of electrochemistry, catalysis, and sensors due to the improved physiochemical properties and increased active site (*e.g.*, defect, vacancy).^{22, 23} Inspired by these merits, developing versatile strategy to create new structured materials with hetero-atomic doping becomes one of the fascinating research topics, where the popular metal-organic frameworks (MOFs) behaviors as an ideal template to construct many kinds of new structured

materials because of their great features in morphology, porosity, high surface area and tunable architecture.²⁴⁻³⁰

Herein, we introduce the Zn-Co based Prussian blue analogue (*i.e.*, Zn-Co PBA)³¹ as a sacrificial template to synthesis a new porous Co₃O₄/N-C spheres. This is the first time to disperse ultrafine metal oxide (*e.g.*, Co₃O₄) nanocrystals within N-C spheres and then construct an intriguing porous and uniform Co₃O₄/N-C spheres, which is distinct from the multi-shelled hollow,³² pompon-like,³³ or mesoporous structured metal oxide.³⁴ The spherical structured N-doped carbon can offer more new choices for materials design flourishing as those of hollow or porous carbon,³⁵ carbon nanotubes³⁶ or fibers,³⁷ and graphene (oxide).³⁸ And also, the kinetic analysis of lithium storage process on porous Co₃O₄/N-C spheres was carried out to understand the electrochemical behaviors, and the greater stability was further proved in high voltage battery applications.

Experimental

Synthesis of Zn₃[Co(CN)₆]₂·nH₂O precursor

All chemicals were used directly without any further purification. In a typical synthesis, 0.5268 g of zinc acetate dihydrate (Zn(Ac)₂·2H₂O) and 1.6 g of polyvinylpyrrolidone (PVP) were dissolved in 80 mL water under ultrasonication to form transparent solution A. Then, 0.5318 g potassium hexacyanocobaltate (K₃[Co(CN)₆]) was dispersed in 80 mL deionized water to form solution B. Subsequently, solution B was added into solution A dropwise under vigorous stirring in an ice-water bath for 1 h. After that, the mixture was statically aged for 6 h. The product was collected by centrifugation and washed with deionized water several times and dried in vacuum at 60 °C overnight.

Preparation of Co₃O₄/N-C nanospheres

The spherical Zn₃[Co(CN)₆]₂·*n*H₂O precursor were thermally annealed at 800 °C for 2 h under 95% Ar/5% H₂ atmosphere with a ramping rate of 2 °C min⁻¹ to form Co/N-C intermediates. The product of Co₃O₄/N-C nanospheres were obtained after thermally treating the Co/N-C intermediates at 200 °C for 12 h in air. For comparison, pure Co₃O₄ nanospheres were prepared by annealing the Co/N-C intermediates at 500 °C for 5 h in air.

Characterizations

The crystallographic information was acquired by the power X-ray diffractometer (XRD, Bruker D8 Focus) at a scan speed of 2° min⁻¹ using Cu Kα radiation. The morphology of samples were characterized by the scanning electron microscopy (SEM) operating on a Hitachi S-4800 SEM analyzer at an accelerating voltage of 10 kV, while the structural characteristics, porosity and elemental mapping was observed by the transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and the energy dispersive X-ray spectrometry (EDS) analysis on a FEI G2 S-Twin instrument. The valence status of chemical component were collected using X-ray photoelectron spectrometer (XPS, ESCALABMKLL) with Al Kα radiation, that emits 1.4866 keV X-ray with corresponding wavelength of 8.53 Å. Thermogravimetric analysis was performed in air from 25 to 800 °C with a heating rate of 10 °C min⁻¹ by using an STA 449 Jupiter (NETZSCH) thermogravimetry analyzer.

Electrochemical measurements

The negative electrode of Co₃O₄/N-C was prepared as below. Typically, the active materials of Co₃O₄/N-C, carbon black and sodium carboxymethyl cellulose (CMC) binder in a weight ratio of 70:20:10 was mixed in aqueous solution first to form a slurry and then casted on the copper foil.

The electrode was dried in vacuum oven at 80 °C for 12 h and then punched into circular electrode. The positive electrode composes of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, Super P and PVDF binder with the mass ratio of 91:4:5, which were mixed in N-Methyl-2-pyrrolidone (NMP) to form slurry first and then casted on the aluminum foil. The casted electrode was dried in vacuum oven at 120 °C overnight and punched into circular electrode for battery assembly. The mass loading of negative and positive electrode are controlled at 8.85 mg cm^{-2} and 1.70 mg cm^{-2} respectively to guarantee the total capacity ratio (*i.e.*, N/P ratio of ~ 1.10) in battery.

The electrochemical performances of $\text{Co}_3\text{O}_4/\text{N-C}$ in half battery were tested using CR-2032 type coin cell, in which the battery has the configuration of lithium foil counter electrode | *Celgard* 2400 membrane separator | $\text{Co}_3\text{O}_4/\text{N-C}$ electrode using the electrolyte of 1.0M LiPF_6 in ethyl carbonate and diethyl carbonate (EC/DEC, 1:1 in volume). The cut-off voltage was set at 0.01 V-3.0 V. Note that the theoretical capacity of $\text{Co}_3\text{O}_4/\text{N-C}$ was calculated as below: $C_{\text{theory}} = C_{\text{Co}_3\text{O}_4} \times (\text{mass percentage of } \text{Co}_3\text{O}_4) + C_{\text{graphite}} \times (\text{mass percentage of carbon}) = 890 \text{ mAh g}^{-1} \times 69.1\% + 372 \text{ mA h g}^{-1} \times 30.9\% = 730 \text{ mAh g}^{-1}$. The lithium ion full battery has the configuration of $\text{Co}_3\text{O}_4/\text{N-C}$ anode | *Celgard* 2400 membrane separator | $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode using the modified electrolyte of 1.0 M LiPF_6 in EC/ EMC (3:7 by weight) with 2 wt% VC as additive. The cut-off voltage was set at 0.2-4.5 V. The negative electrode of $\text{Co}_3\text{O}_4/\text{N-C}$ was stabilized first in half battery for several cycles to compensate the irreversibility and then dis-assembled for assembling the lithium ion full battery. All the cells were assembled in glovebox filled with argon, in which the moisture and oxygen content was strictly controlled below 0.1 ppm. The cyclic voltammetry and electrochemical impedance spectrum measurements were conducted on the *BioLogic VMP3* electrochemical workstation. The galvanostatic charge-discharge curves was recorded using the *LAND CT2001A* multichannel battery testing system.

Results and discussion

Features of Synthetic Strategy and Architecture

Figure 1 demonstrates the schematic process. The $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precursor can be thermally polymerized first to form cross-linked organics and then was carbonized to nitrogen-doped carbon, in which the reduction of zinc ions to metallic zinc by carbonaceous materials and its followed volatilization (*i.e.*, mp 420 °C) can produce pores during the carbonation process. Simultaneously, the cobalt ions can be also reduced to Co and then oxidized in air to form Co_3O_4 nanocrystals, giving rise to Co/N-C intermediates and $\text{Co}_3\text{O}_4/\text{N-C}$ spheres respectively. The morphology variation was confirmed first by SEM in **Figure 2**. We find that the narrow size distribution of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precursor around 700-900 nm in **Figure 2a-a1** can be maintained from the uniform Co/N-C intermediates in **Figure 2b-b1** (~570 nm) to the spherical $\text{Co}_3\text{O}_4/\text{N-C}$ (**Figure 2c-c1**, ~610 nm) with a shrinking size of 500-700 nm (**Figure S1**). Three salient features exist in this $\text{Co}_3\text{O}_4/\text{N-C}$ nano-spheres: i) a high dispersion and uniform size distribution, which can facilitate their manipulation and applications (*e.g.*, electrode preparation for battery with a high tap density); ii) a new spherical N-doped carbon spheres rich of porosity rarely reported before; iii) embedded Co_3O_4 nanocrystals within the N-doped carbon spheres with higher electronic conductivity which can avoid any aggregation for diverse applications. Besides, the uniform Co/N-C intermediates and derivate of Co_3O_4 (~470 nm) from $\text{Co}_3\text{O}_4/\text{N-C}$ in **Figure 2d-d1** further demonstrate the universality and versatility of this strategy to create diverse nanostructured materials.

The high distribution of Co_3O_4 nanocrystals with an average diameter of 10 nm in N-doped carbon spheres was confirmed by the transmission electron microscopy (TEM) in **Figure 3a-b**. The lattice fringes with interplanar spacing of 0.47 nm in HRTEM are consistence with the

planar distance between (111) planes of cubic Co_3O_4 phase (**Figure 3c**). Note that the N-doped carbon has an oriented multilayer graphitic sheets stacked in parallel with a d-spacing of 0.35 nm, which is a little bit higher than 0.335 nm of graphitic layer in (002) crystal planes. The reason may be ascribed to the doping of nitrogen in the structure or the effect of thermal conditions.³⁹ Besides, the characteristics of meso-porosity resulting from the evaporation of zinc and the shell of N-doped carbon around each Co_3O_4 nanocrystal is about 2-5 nm in thickness (**Figure 3c**). The uniform distribution of Co_3O_4 and the N-doped carbon were further demonstrated by the energy dispersive spectroscopy (EDS) elemental mappings of the sample in **Figure 3d-h**.

Structural evolution and Confirmation

The crystalline structural variation from $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precursor over Co/N-C intermediate to the $\text{Co}_3\text{O}_4/\text{N-C}$ product was confirmed by the X-ray diffraction patterns (XRD) (**Figure 4a**). While the carbonization of organic compositions with the retention of nitrogen atom in structure, volatilization of zinc and oxidation of Co to oxide status were proved by the energy-dispersive X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum in Figure S2a reveals the existence of C, N, O and Co elements in composite. Note that the N *1s* spectrum in **Figure 4b** indicates that four types of nitrogen species exist in the structure, including the pyridinic N (398.2 eV), pyrrolic N (399.3 eV), graphitic N (400.3 eV) and pyridine-N-oxide groups (404.8 eV). Besides, the presence of nitrogen was further confirmed by the slightly asymmetric tail at higher binding energy in C *1s* core-leveled XPS spectra, which is a common characteristic of nitrogen-doped carbon materials.²⁵ Apart from the further analysis of carbon and oxygen element in **Figure S2b-c**, the two spin-orbit doublets located at the high energy band of 794.1 eV (Co $2p_{1/2}$) and the low energy band of 779.0 eV (Co $2p_{3/2}$) with the energy difference of 15.1 eV in Co2*p* XPS spectrum (**Figure 4c**, **Figure S2b**) fully certify the status of Co_3O_4 phase,

which is also proved by the two shake-up satellites (named as “Sat.”) at 786.8 and 803.4 eV corresponding to the typical characteristics of Co_3O_4 .

The disappearance of elemental zinc in Zn 2p XPS spectrum indicates that the zinc was completely removed during the thermal treatment (**Figure 4d**), fully demonstrating the reasonability of our design. The Raman spectroscopy in Figure S2d also confirms the characteristics of $\text{Co}_3\text{O}_4/\text{N-C}$ composite, where the vibrational peaks around 1340 and 1578 cm^{-1} match well with the typical D-band and G-band of graphitization carbon while the peaks at 188, 465, 509, 605 and 670 cm^{-1} assigned to the F_{2g} , E_g , F_{2g}^1 , F_{2g}^2 , and A_{1g} modes confirm the presence of crystalline Co_3O_4 .⁴⁰ Benefiting from the uniqueness of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ framework, an extremely high surface area of 312 $\text{m}^2 \text{g}^{-1}$ and pore volume of 0.74 $\text{cm}^3 \text{g}^{-1}$ was obtained for the $\text{Co}_3\text{O}_4/\text{N-C}$, which demonstrates a typical type IV isotherm in physical N_2 adsorption/desorption measurement and has 30.9 wt% carbon in the structure (**Figure 4e-f**).

Superior Lithium Storage Capability Beyond Theoretical

The predominant properties of porous $\text{Co}_3\text{O}_4/\text{N-C}$ spheres with extremely high lithium storage capacities and stability were verified in lithium (ion) batteries. The stability was observed in cyclic voltammetry (CV) first, in which the CV can be stabilized and overlap fast after the 1st cycle. The main cathodic peak at 0.9 V was ascribed to the reduction of Co_3O_4 to metallic Co and the degradation of electrolyte to form solid electrolyte interphase (SEI). Afterwards, the cathodic peak was split into two broad peaks around 1.1 V, demonstrating the multistep reactions of Co_3O_4 and lithium to Co gradually (*i.e.*, total reaction, $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}$). Subsequently, the anodic peak at 2.1 V was ascribed to the oxidation reaction of Co to Co_3O_4 (**Figure 5a**). The stability and high lithium storage capability were demonstrated in galvanostatic charge-discharge curves (**Figure 5b**). The discharge voltage plateau around at 1.1 V is

consistence with the CV results, where the average capacity of 1293 mAh g^{-1} can be obtained at the current density of 100 mA g^{-1} in initial 100 cycles. Note that the capacity can increase from 1175 mAh g^{-1} at the 2nd cycle to 1255 mAh g^{-1} at the 100 cycles (**Figure 5c**), demonstrating the gradient activation of active materials.⁴¹ By contrast, the pure Co_3O_4 particles without the nitrogen-rich carbon coating in **Figure 2d** demonstrates fast capacity fading and delivers a much lower capacity of 454 mAh g^{-1} after 100 cycles (**Figure 5c**). The low capacity of pure Co_3O_4 particles electrode results from the low utilization of metal oxide while the fast capacity decay was ascribed to the pulverization of Co_3O_4 particles in the repeated (de)lithiation processes.³¹⁻³³ The advantages of porous $\text{Co}_3\text{O}_4/\text{N-C}$ spheres were further shown in rate capability test (**Figure 5d, Figure S3a**). Average capacities of 1285, 1257, 1137, 993 and 835 mAh g^{-1} can be delivered at the current densities of 100, 200, 500, 1000 and 2000 mA g^{-1} respectively, where the capacity can even recover to 1258 mAh g^{-1} at 100 mA g^{-1} (**Figure S3b**). The improved rate capacity is more obvious at the high current density comparing to those of pure Co_3O_4 particles, fully displaying the great features of porous $\text{Co}_3\text{O}_4/\text{N-C}$ spheres. Note that, the long cycle life over 500 cycles at 1000 mA g^{-1} with the high capacity of 798 mAh g^{-1} further shows the prominent properties (**Figure 5e**).

Electrochemical Analysis

To understand the reason of superior performances, the kinetics analysis was studied first based on the cyclic voltammetry. We find that the anodic and cathodic peaks in CV shift gradually to the higher and the lower voltages respectively as varying the scan rate from 0.1 to 1.0 mV s^{-1} due to the electrode polarization (**Figure 6a-b**). A linear correlation between the peak current (i_p) and the square root of the scan rate ($v^{1/2}$) can be fitted (**Figure 6c**), based on which the Li^+ diffusion coefficient (D) can be extracted by the *Randles-Sevcik* equation.^{42, 43}

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

where the n is the number of electron in reaction (*i.e.*, $n = 8$), A is the electrode area (*i.e.*, $A = 1.13 \text{ cm}^2$), and C is the variation of lithium-ion concentration in electrolyte (*i.e.*, $C = 0.001 \text{ M}$). The calculated diffusion coefficient within $\text{Co}_3\text{O}_4/\text{N-C}$ is about $8.46 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is much higher than $9.32 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ of pure Co_3O_4 and $5.82 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ of $\text{Co}_3\text{O}_4@\text{GNs}$ reported before.⁴⁴ The results can explain the reason of the higher rate capability of $\text{Co}_3\text{O}_4/\text{N-C}$ over that of pure Co_3O_4 . Note that the lithium diffusion constant of Co_3O_4 is always lower than most Fe_2O_3 ,^{45, 46} MnO_2 ⁴⁷ and TiO_2 ⁴⁸ based composite (**Figure S4**), thus it is imperative to enhance the value through morphology and structural design. The improved lithium diffusion constant should be mainly ascribed to the rich pores in N-doped carbon and ultrafine Co_3O_4 nanocrystals, which can facilitate the penetration of electrolyte for the Li^+ migration and also shorten the Li^+ diffusion path within the particles respectively. This point was proved by the electrochemical impedance spectroscopy (EIS) in **Figure S5**. The $\text{Co}_3\text{O}_4/\text{N-C}$ exhibits distinctly lower resistance (*i.e.*, charge transfer resistance) at the high frequency region and shaper inclined line (*i.e.*, solid-state diffusion of Li^+ within electrodes) at the low frequency than those of pure Co_3O_4 , implying the capability of N-doped carbon to improve the electrical conductivity and promote the lithium diffusion constant.

To interpret the higher capacity of $\text{Co}_3\text{O}_4/\text{N-C}$ than the theoretical 730 mAh g^{-1} (see details in experiment), the electrochemical transport analysis further identifies the pseudocapacitive charge storage in the $\text{Co}_3\text{O}_4/\text{N-C}$. There is a power law relationship between the peak current (i) and the scan rate (v) in a sweep voltammetry measurement:^{49, 50}

$$i = av^b$$

where both a and b are constants. The value of b for the $\text{Co}_3\text{O}_4/\text{N-C}$ at the current peak (i) and (ii) obtained from the slope of the $\log i_p$ versus $\log v$ plot are 0.77 and 0.74 respectively (**Figure 6d**), indicating a combination of diffusion controlled process and surface capacitive processes (*i.e.*, $b=0.5$, diffusion-controlled Li^+ insertion process; $b=1$, surface-controlled charge storage behavior; $0.5 < b < 1$, a mixed mechanisms). Thus, the ratio of capacitive contribution was obtained through a quantitative calculation separating the current response i at a given fixed potential V into surface capacitive effects (proportional to the scan rate v , k_1v)⁵¹ and diffusion-controlled Li^+ -insertion reactions ($k_2v^{1/2}$), according to the formula:⁵²

$$i(V) = k_1v + k_2v^{1/2}$$

We find that the capacitive charge contributes 60.3% for the total capacity of $\text{Co}_3\text{O}_4/\text{N-C}$ at a sweep rate of 0.5 mV s^{-1} ; meanwhile the contribution of capacitive charge increases as increasing the sweep rates in **Figure 6e-f**. All these values are responsible for the capacities of $\text{Co}_3\text{O}_4/\text{N-C}$ higher than the theoretical one. By contrast, we also analyze the capacitive behavior of the pure Co_3O_4 , where the b -value for the current peak (iii) and (iv) of pure Co_3O_4 are 0.88 and 0.83, respectively (**Figure 6d**). We find that the pure Co_3O_4 shows a relatively high capacitive contribution of 78.7% at 0.5 mV s^{-1} and it increases as increasing the sweep rates (**Figure S6**), demonstrating the lower lithium diffusion process in Co_3O_4 which is consistence with the kinetic analysis. This result also confirms the high utilizations of Co_3O_4 in $\text{Co}_3\text{O}_4/\text{N-C}$, thereby giving rise to the higher capacity. Note that the protective effect of N-doped carbon to accommodate volumetric variation and also avoid the direct contact of oxide and electrolyte (*i.e.*, reduce the side reaction for the formation of new SEI upon cycling) are all responsible for the great stability.

Electrochemical Features in High Voltage Battery

To pursue the higher energy density, the lithium storage capabilities of $\text{Co}_3\text{O}_4/\text{N-C}$ was further studied in lithium ion battery, in which the cathode of lithium layer oxide (*e.g.*, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) was particularly charged to the high voltage of 4.5 V for much higher capacity of $\sim 200 \text{ mAh g}^{-1}$ (*vs.* $\sim 160 \text{ mAh g}^{-1}$ at 4.2 V)^{53, 54} (**Figure 7a**). This is the first time to explore the metal oxide-based anode in high voltage batteries (*e.g.*, 4.5 V) and investigate the features of cathode in this kind of battery configuration. One merit of the stabilized $\text{Co}_3\text{O}_4/\text{N-C}$ is the high capacity around 1107 mAh g^{-1} (**Figure 7b**), which can reduce three times mass amount of anode in battery for the same energy capacity comparing to that of graphite (*i.e.*, 372 mAh g^{-1}), thereby paving the way to the higher energy density. The designed battery has a total capacity about 1.95 mAh (*vs.* the mass of cathode), in which the capacity ratio of anode and cathode is controlled around at 1.1/1 (**Figure 7b**). The stability of battery was demonstrated by the cyclic voltammetry (CV) curves (**Figure 7c**), in which we find that the battery can be stabilized fast since the first cycle. The good cycle performance and fine (dis-)charge profiles are also confirmed at the 0.25C (where define $1\text{C} = 800 \text{ mA g}^{-1}$) in **Figure 7c-d**, where the capacity can be maintained at 1.50 and 1.27 mAh with the capacity retention of 81 % and 69% after 100 and 200 cycles respectively, fully demonstrating that the stability of metal oxide based anode and cathode at high voltage conditions. Besides, the battery has great rate capabilities, where the capacity can be preserved 100%, 100%, 96%, 88%, 80% and 74% (*vs.* 1.92 mAh) under the rate of 0.05C, 0.1C, 0.25C, 0.5C, 1C to 2C, respectively (**Figure 7e**). This should be ascribed to the faster lithium diffusion constant within the $\text{Co}_3\text{O}_4/\text{N-C}$ and considerable capacitive contribution of $\text{Co}_3\text{O}_4/\text{N-C}$ for the storage of lithium ions at high rate. Thus, our preliminary results show that the metal oxide-based anode (*e.g.*, $\text{Co}_3\text{O}_4/\text{N-C}$) has great potential applications in high voltage battery for greater energy density.

Conclusions

An intriguing kind of porous $\text{Co}_3\text{O}_4/\text{N-C}$ spheres with a high dispersion and uniform size distribution was introduced, in which the Co_3O_4 nanocrystals were finely encapsulated within the N-doped carbon spheres. The uniqueness of structure and predominant properties of porous $\text{Co}_3\text{O}_4/\text{N-C}$ with extremely high lithium storage capacities and stability were verified in lithium batteries. The reason of better rate capability and higher capacity beyond theoretical values were studied by the kinetic analysis and electrochemical transport process. We identify that porous N-doped carbon and ultrafine Co_3O_4 are the necessities for the faster lithium diffusion constant and greater performances, where the pseudocapacitive can contribute additionally for the greater capacity. Besides, the lithium storage capacity and stability of $\text{Co}_3\text{O}_4/\text{N-C}$ spheres were further confirmed in lithium ion battery versus lithium layered oxide at high voltage conditions. We believe that the approach using metal-organic frameworks for new nanostructured materials with more fantastic properties can be further explored while the investigated electrochemical behaviors of $\text{Co}_3\text{O}_4/\text{N-C}$ in lithium (ion) battery is meaningful for the researches.

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Notes and references

1. J. M. Tarascon, M. Armand, *Nature* 2001, **414**, 359-367.
2. B. Scrosati, J. Hassoun and Y. K. Sun, *Energy Environ. Sci.* 2011, **4**, 3287-3295.
3. J. B. Goodenough, K. S. Park, *J. Am. Chem. Soc.* 2013, **135**, 1167-1176.
4. J. W. Choi, D. Aurbach, *Nat. Rev. Mater.*, 2016, **1**.
5. J. Ming, M. Li, P. Kumar and L. J. Li, *ACS Nano* 2016, **10**, 6037-6044.
6. A. Manthiram, *ACS Cent Sci.* 2017, **3**, 1063-1069.
7. Y. K. Sun, Z. H. Chen, H. J. Noh, D. J. Lee, H. G. Jung, Y. Ren, S. Wang, C. S. Yoon, S. T. Myung and K. Amine, *Nat. Mater.* 2012, **11**, 942-947.
8. S. T. Myung, F. Maglia, K.-J. Park, C. S. Yoon, P. Lamp, S.-J. Kim and Y.-K. Sun, *ACS Energy Lett.* 2016, **2**, 196-223.
9. Y. Wu, L. Xie, X. He, L. Zhuo, L. Wang and J. Ming, *Electrochim Acta* 2018, **265**, 115-120.
10. S. Yin, D. Zhao, Q. Ji, Y. Xia, S. Xia, X. Wang, M. Wang, J. Ban, Y. Zhang, E. Metwalli, X. Wang, Y. Xiao, X. Zuo, S. Xie, K. Fang, S. Liang, L. Zheng, B. Qiu, Z. Yang, Y. Lin, L. Chen, C. Wang, Z. Liu, J. Zhu, P. Muller-Buschbaum and Y. J. Cheng, *ACS Nano* 2018, **12**, 861-875.
11. P. Nie, X. Liu, R. Fu, Y. Wu, J. Jiang, H. Dou and X. Zhang, *ACS Energy Lett.* 2017, **2**, 1279-1287.
12. J. Yu, Y. Wang, L. Mou, D. Fang, S. Chen and S. Zhang, *ACS Nano* 2018, **12**, 2035-2047.

13. J. Sun, C. Lv, F. Lv, S. Chen, D. Li, Z. Guo, W. Han, D. Yang and S. Guo, *ACS Nano* 2017, **11**, 6186-6193.
14. L. Zhou, Y. Cheng, Q. Sun, L. Sun, C. L. Wang, X. Wang, D. Yin, L. Wang and J. Ming, *Chem. Commun.* 2018, **54**, 4049-4052.
15. D. C. Lee, D. Lei and G. Yushin, *ACS Energy Lett.* 2018, 794-801.
16. S. Abouali, M. Akbari Garakani, B. Zhang, H. Luo, Z.-L. Xu, J.-Q. Huang, J. Huang and J. K. Kim, *J. Mater. Chem. A* 2014, **2**, 16939-16944.
17. H. Ming, J. Qiu, S. Zhang, M. Li, X. Zhu, L. Wang and J. Ming, *ChemElectroChem* 2017, **4**, 1165-1171.
18. M. V. Reddy, G. V. S. Rao and B. V. R. Chowdari, *Chem. Rev.* 2013, **113**, 5364-5457.
19. L. Wang, S. Yue, Q. Zhang, Y. Zhang, Y. R. Li, C. S. Lewis, K. J. Takeuchi, A. C. Marschilok, E. S. Takeuchi and S. S. Wong, *ACS Energy Lett.* 2017, **2**, 1465-1478.
20. L. Peng, Z. Fang, J. Li, L. Wang, A. M. Bruck, Y. Zhu, Y. Zhang, K. J. Takeuchi, A. C. Marschilok, E. A. Stach, E. S. Takeuchi and G. Yu, *ACS Nano* 2018, **12**, 820-828.
21. H. Ming, H. Zhou, X. Zhu, S. Zhang, P. Zhao, M. Li, L. Wang and J. Ming, *Energy Technol.* 2018, **6**, 1-8.
22. H. Zhong, C. H. Wang, Z. B. Xu, F. Ding and X. J. Liu, *Sci. Rep.* 2016, **6**.
23. F. Cao, M. Zhao, Y. Yu, B. Chen, Y. Huang, J. Yang, X. Cao, Q. Lu, X. Zhang, Z. Zhang, C. Tan and H. Zhang, *J. Am. Chem. Soc.* 2016, **138**, 6924-6927.
24. G. Huang, Q. Li, D. Yin and L. Wang, *Adv. Funct. Mater.* 2017, **27**, 1604941.

25. D. Yuan, G. Huang, D. Yin, X. Wang, C. Wang and L. Wang, *ACS Appl. Mater. Interfaces*. 2017, **9**, 18178-18186.
26. M. Li, Y. Wan, J. K. Huang, A. H. Assen, C. E. Hsiung, H. Jiang, Y. Han, M. Eddaoudi, Z. Lai, J. Ming and L. J. Li, *ACS Energy Lett.* 2017, **2**, 2362-2367.
27. C. Guan, W. Zhao, Y. Hu, Z. Lai, X. Li, S. Sun, H. Zhang, A. K. Cheetham and J. Wang, *Nanoscale Horiz.* 2017, **2**, 99-105.
28. C. Guan, W. Zhao, Y. Hu, Q. Ke, X. Li, H. Zhang and J. Wang, *Adv. Energy Mater.*, 2016, **6**, 1601034.
29. C. Guan, A. Sumboja, H. Wu, W. Ren, X. Liu, H. Zhang, Z. Liu, C. Cheng, S. J. Pennycook and J. Wang, *Adv. Mater.* 2017, **29**, 1704117.
30. C. Guan, X. Liu, A. M. Elshahawy, H. Zhang, H. Wu, S. J. Pennycook and John Wang, *Nanoscale Horiz.* 2017, **2**, 342-348.
31. L. Ma, R. Chen, Y. Hu, G. Zhu, T. Chen, H. Lu, J. Liang, Z. Tie, Z. Jin and J. Liu, *Nanoscale* 2016, **8**, 17911-17918.
32. X. Wang, X. L. Wu, Y. G. Guo, Y. Zhong, X. Cao, Y. Ma and J. Yao, *Adv. Funct. Mater.* 2010, **20**, 1680-1686.
33. W. Hao, S. Chen, Y. Cai, L. Zhang, Z. Li and S. Zhang, *J. Mater. Chem. A*. 2014, **2**, 13801-13804.
34. N. Venugopal, D.-J. Lee, Y. J. Lee and Y. K. Sun, *J. Mater. Chem. A* 2013, **1**, 13164.
35. L. Wang, Y. Zheng, X. Wang, S. Chen, F. Xu, L. Zuo, J. Wu, L. Sun, Z. Li, H. Hou and Y. Song, *ACS Appl. Mater. Interfaces* 2014, **6**, 7117-25.

36. Y. Xu, X. Wang, C. An, Y. Wang, L. Jiao and H. Yuan, *J. Power. Sources* 2014, **272**, 328-334.
37. K. Wenelska, C. Neef, L. Schlestein, R. Klingeler, R. J. Kalenczuk and E. Mijowska, *Chem. Phys. Lett.* 2015, **635**, 185-189.
38. L. Zhan, Y. Wang, W. Qiao, L. Ling and S. Yang, *Electrochim Acta* 2012, **78**, 440-445.
39. H. Zhang, H. Ming, W. Zhang, G. Cao and Y. Yang, *ACS Appl. Mater. Interfaces* 2017, **9**, 23766-23774.
40. B. Rivas-Murias, V. Salgueiriño, *J. Raman Spectrosc.* 2017, **48**, 837-841.
41. X. Ding, X. Huang, J. Jin, H. Ming, L. Wang and J. Ming, *Electrochim Acta* 2018, **260**, 882-889.
42. J. Ming, M. Li, P. Kumar, A.-Y. Lu, W. Wahyudi and L. J. Li, *ACS Energy Lett.* 2016, **1**, 529-534.
43. M. Li, W. Wahyudi, P. Kumar, F. Wu, X. Yang, H. Li, L. J. Li and J. Ming, *ACS Appl. Mater. Interfaces* 2017, **9**, 8047-8054.
44. C. T. Hsieh, J. S. Lin, Y. F. Chen and H. Teng, *J. Mater. Chem. C* 2012, **116**, 15251-15258.
45. M. Chen, E. Zhao, Q. Yan, Z. Hu, X. Xiao and D. Chen, *Sci. Rep.* 2016, **6**, 29381.
46. W. Guo, W. Sun, L. P. Lv, S. Kong and Y. Wang, *ACS Nano* 2017, **11**, 4198-4205.
47. M. S. Wu, P. C. J. Chiang, *Electrochem. Commun.* 2006, **8**, 383-388.
48. K. Li, B. Li, J. Wu, F. Kang, J. K. Kim and T. Y. Zhang, *ACS Appl. Mater. Interfaces* 2017, **9**, 35917-35926.

49. M. Chen, D. Chao, J. Liu, J. Yan, B. Zhang, Y. Huang, J. Lin and Z. X. Shen, *Adv. Funct. Mater.* 2017, **27**, 1606232.
50. J. Min, K. Wang, J. Liu, Y. Yao, W. Wang, L. Yang, R. Zhang and M. Lei, *J. Power Sources.* 2017, **363**, 392-403.
51. J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C* 2007, **111**, 14925-14931.
52. Y. Chu, L. Guo, B. Xi, Z. Feng, F. Wu, Y. Lin, J. Liu, D. Sun, J. Feng, Y. Qian and S. Xiong, *Adv. Mater.* 2018, **30**.
53. Akira Yano, Atsushi Ueda, Masahiro Shikano, Hikari Sakaebe and Zempachi Ogumi, *J. Electrochem Soc.* 2016, **163**, A75-A82.
54. Akira Yano, Shigeo Aoyama, Masahiro Shikano, Hikari Sakaebe, Kuniaki Tatsumi and Zempachi Ogumi, *J. Electrochem Soc.* 2016, **162**, A3137-A3144.

Figure 1 Schematic illustration of synthetic process

Figure 2 Morphology and structural variation. SEM images, size distribution and structural variation of (a, a1) $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precursor, (b, b1) Co/N-C intermediate, (c, c1) $\text{Co}_3\text{O}_4/\text{N-C}$ and (d, d1) derivate of Co_3O_4 nano-spheres. Inset of (a1-d1) are the schematic uniqueness of structure according to the real model.

Figure 3 Structural characterizations. (a, b) TEM and (c) HRTEM images of Co₃O₄/N-C at different magnifications. (d) STEM image of Co₃O₄/N-C, and (e-h) elemental mapping images of C, Co, N and O within the Co₃O₄/N-C nano-spheres.

Figure 4 Structural evolution and elemental confirmation. (a) Variation of XRD patterns from the precursor to final products. High resolution XPS spectra of (b) N 1s, (c) Co 2p, (d) Zn 2p for the $\text{Co}_3\text{O}_4/\text{N-C}$. (e) N_2 adsorption/desorption isotherms and (f) TGA curve of the $\text{Co}_3\text{O}_4/\text{N-C}$. Inset of (c) is the pore size distribution profile.

Figure 5 Electrochemical performance. (a) Cyclic voltammetry and (b) voltage vs. capacity profiles of the $\text{Co}_3\text{O}_4/\text{N-C}$ at the current density of 100 mA g^{-1} . Comparative (c) cycle performance and (d) rate capabilities of the pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{N-C}$. (e) Cycle performance of $\text{Co}_3\text{O}_4/\text{N-C}$ at the current density of 1000 mA g^{-1} .

Figure 6 Electrochemical Analysis. (a) Comparative cyclic voltammetry curves of (a) $\text{Co}_3\text{O}_4/\text{N-C}$ and (b) pure Co_3O_4 under different scan rate from 0.1 mV s^{-1} to 1 mV s^{-1} . (c) Fitted line of the normalized current of peak A vs. square root of the scan rate. (d) Linear relationship between $\log i$ (logarithm currents) and $\log \nu$ (logarithm scan rate) at the peaks of (i) and (ii) for $\text{Co}_3\text{O}_4/\text{N-C}$, while the peaks of (iii) and (iv) are for pure Co_3O_4 respectively. (e) Cyclic voltammetry of $\text{Co}_3\text{O}_4/\text{N-C}$ with the capacitive contribution at the scan rate of 0.5 mV s^{-1} and (f) Normalized contribution ratio of capacitive capacities as increasing the scan rates.

Figure 7 Electrochemical features at high voltage conditions. (a) Schematic configuration of lithium ion full battery consisting of metal oxide based anode (e.g., $\text{Co}_3\text{O}_4/\text{N-C}$) and lithium layered oxide (e.g., $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$). (b) Typical voltage vs. capacity profiles of $\text{Co}_3\text{O}_4/\text{N-C}$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ charged to the high voltage of 4.6 V. (c) Cyclic voltammetry, (d) cycle performance, (e) typical voltage vs. capacity profiles in cycling at 0.25C and (f) rate capabilities of lithium ion battery at the high voltage of 4.5 V.