Research Article

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Electrospun nanofibers of Co_3O_4 nanocrystals encapsulated in cyclized-polyacrylonitrile for lithium storage

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Abstract: The coupling of metal oxide nanoparticles and electrochemically active polymers has been considered as an effective way to improve the lithium storage performance of individual electrode materials. This work reports an electrospinning process followed by thermal annealing to produce composite nanofibers of cyclized-polyacrylonitrile (cPAN) containing Co_3O_4 nanoparticles (cPAN/ Co_3O_4). The as-prepared cPAN/ Co_3O_4 nanofiber exhibits a porous nanostructure with an average diameter of 85 nm. When used for lithium-ion battery, the cPAN/ Co_3O_4 anode delivers a reversible specific capacity as high as $997.6 \text{ mA h g}^{-1}$ at 0.1 A g^{-1} , and still maintains $396.5 \text{ mA h g}^{-1}$ at 1.0 A g^{-1} . Meanwhile, the cPAN/ Co_3O_4 anode shows good cycling stability with a retention of 81% capacity after running 50 cycles at 0.1 A g^{-1} . The

electrochemical performance of cPAN/ Co_3O_4 significantly outperforms its individual counterparts of cPAN and Co_3O_4 .

Keywords: cyclized polyacrylonitrile, Co_3O_4 , electrospun nanofibers, composite anode, lithium-ion batteries

1 Introduction

With the increasing demand for energy conservation and emission reduction, rechargeable batteries such as lithium-ion batteries (LIBs) have been widely applied in power grid energy storage and new energy vehicles [1]. Graphite is one of the most commonly used anode materials for LIBs because of its low-cost and good theoretical capacity of 372 mA h g^{-1} [2,3]. However, due to the low ion diffusion efficiency in graphite electrodes, it is still a great challenge to improve the energy density and power density of commercial LIBs and it is necessary to develop new anode materials with high capacity, excellent rate performance, and long cycle stability [4,5].

Transition metal oxides (TMOs, such as Co_3O_4 , Mn_3O_4 , and Fe_2O_3) have been regarded as promising alternatives to graphite due to their relatively high theoretical capacity [6–8]. Nevertheless, TMOs still face the problems of low inherent conductivity and large volume change in the charging and discharging process, which inevitably leads to low rate performance and poor cycle stability, and seriously hinders their applications. An effective way to improve the ionic conductivity of TMOs is to construct nanostructures [9,10] because the reduced size significantly shortens the Li^+ diffusion path, making it easy to transfer to the surface of electrochemically active material, leading to high ionic conductivity and electrochemical utilization efficiency [11]; Another approach is to construct nanocomposites by combining TMOs with active carbon, multiwalled carbon nanotubes (CNTs), or graphene [12]. Carbon coating can not only significantly improve the electronic conductivity of electrode materials and hence the

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rate performance [13,14] but also restrain the electrode volume change during lithium insertion/deintercalation process, resulting in long cycling stability. Wan and co-workers [15] reported that carbon-coated Fe_3O_4 nanospindles showed high reversible capacities (745 mA h g^{-1} at C/5 and 600 mA h g^{-1} at C/2) and significantly enhanced cycling performance and rate capability as compared with bare hematite spindles. These improvements are mainly attributed to the continuous carbon coating, which maintains particle integrity and improves electrode conductivity, resulting in a uniform and stable solid electrolyte interface (SEI) film on the surface [16,17].

In recent years, coating conductive polymers (*e.g.*, polyaniline, polypyrrole, and polythiophene) onto TMO nanostructures have also been the focus of research [18]. Both conductive polymers and TMOs are electrochemically active, which makes polymer/TMO nanocomposites greatly attractive as electrode materials for lithium batteries [19]. Ponzio and co-workers [20] reported a reverse micelle method to prepare polyaniline-coated V_2O_5 nanofibers, and the composite electrode containing 30 mol% polyaniline delivered a steady capacity of about 300 mA h g^{-1} with no morphology change over 10 cycles, whereas the V_2O_5 nanofibers do not retain the morphology after cycling. However, conductive polymers typically have low actual capacities (mostly below 150 mA h g^{-1}) and poor cycling stability. In addition to the conductive polymers, nonconductive polymers with rich heteroatomic structures (redox-active centers of $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups) have large theoretical capacities, good wettability yet strong insolubility with electrolytes, fast redox kinetics, high-power capability, naturally abundant monomer sources [21], and thus, offer a promising direction for green, economical, high-performance, and sustainable batteries. However, there is still a lot of room to explore novel nanostructures for improving the porosity and active site utilization of redox-active polymers [22].

Electrospinning has been regarded as a simple and effective technology for the preparation of 1D nanomaterials, such as polymer nanofibers and metal oxide nanofibers with diameters ranging from tens of nanometers to several microns [23,24]. At the same time, electrospun nanofibers with different morphologic structures can also be prepared, such as cylindrical solid nanofibers, porous nanofibers, hollow nanofibers, core-shell nanofibers, and hierarchical nanofibers [25,26]. Compared with powder materials, 1D nanofiber with porous, hollow, and core-shell structures can improve the surface/volume ratio of the electrode to electrolyte interface and hence the electrochemical reaction efficiency. Meanwhile, it can also provide abundant void space to adapt to the huge volume

change during the charge/discharge cycle, thus effectively improving the cycling stability of electrode materials [27]. A breakthrough in the electrospinning method is co-electrospinning the mixture solution of polymer and inorganic salt. After that, the sintering of electrospun polymer-inorganic salt composite nanofibers can transform the polymer and inorganic salt into porous carbon and metal oxide nanocrystals, respectively. The two components as well as the unique 1D nanostructures could bring about synergetic effects to enhance their electrochemical performances. Polyacrylonitrile (PAN), a typical spinnable polymer, is one of the most commonly used materials for preparing nanofibers by electrostatic spinning [28]. Meanwhile, PAN nanofibers can also be carbonized at high temperature to prepare carbon nanofibers with high carbon yield and excellent mechanical properties [29]. Guo *et al.* [30] prepared ultra-uniform $\text{SnO}_x/\text{carbon}$ nanohybrids ($\text{U-SnO}_x/\text{C}$) by electrospinning a dimethylformamide (DMF) solution of SnO_2 nanoparticles and PAN followed by carbonization at 600°C in an argon atmosphere. The obtained 1D $\text{U-SnO}_x/\text{C}$ nanostructure has a strong interaction with SnO_x and the N-doped carbon matrix, which effectively inhibits SnO_x agglomeration and withstands large volume changes during lithium alloying/dealloying reactions, coupled with enhancing electron and ion transports due to shortened conducting and diffusion paths. As a result, $\text{U-SnO}_x/\text{C}$ shows an excellent rate capability and a high reversible capacity of 608 mA h g^{-1} after 200 cycles.

Notably, the thickness and percentage of carbon coating need to be controlled by regulating the conditions of the calcination process (such as temperature and atmosphere). However, when treated at a high temperature in an argon atmosphere, transition metal salts such as Co^{2+} and Ni^{2+} can be easily reduced into their metallic forms instead of metal oxides. In fact, annealing PAN at a relatively low temperature ($\sim 280^\circ\text{C}$) in an air atmosphere yields conjugated cyclized polyacrylonitrile (cPAN), which consists of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ groups, and also gives a high theoretical capacity ($2,102 \text{ mA h g}^{-1}$) when used directly as a LIB anode material [31]. In this work, we report an electrospinning approach to prepare polyacrylonitrile/cobalt acetate (PAN/Co(OAc)_2) composite nanofibers, followed by heating at 280°C in an air atmosphere. During this process, PAN was converted to porous cPAN coating on the surface of Co_3O_4 nanoparticles. The as-prepared $\text{cPAN/Co}_3\text{O}_4$ nanofiber was further used as an anode material with significantly improved lithium storage performance compared to neat cPAN and Co_3O_4 nanofibers. The $\text{cPAN/Co}_3\text{O}_4$ -based battery achieves a high reversible specific capacity up to $997.6 \text{ mA h g}^{-1}$ at a current density of 0.1 A g^{-1} , and still maintains $396.5 \text{ mA h g}^{-1}$

when the current density increases to 1.0 A g⁻¹. Meanwhile, the specific capacity retention rate is as high as 81% after 50 cycles at 0.1 A g⁻¹. The excellent electrochemical performance of cPAN/Co₃O₄ is attributed to its porous fiber structure and synergistic effect between the two components.

2 Experimental section

2.1 Materials

PAN, Co(OAc)₂, dimethyl formamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd; acetylene black and polyvinyl alcohol (PVA, $M_w = 100,000$) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd; and polyvinylidene fluoride (PVDF) ($\geq 99.0\%$) was purchased from Solvay USA Co., Ltd. All the chemicals were used as received without further treatment.

2.2 Fabrication of cPAN/Co₃O₄ nanofibers

The cPAN/Co₃O₄ oriented nanofiber was prepared by electrospinning the mixed solution of PAN and cobaltous acetate (Co(OAc)₂·4H₂O), followed by thermal treatment. In a typical process, 1.0 g of Co(OAc)₂·4H₂O was dissolved into 10 mL DMF by stirring for 1 h. After that, 0.5 g of PAN was slowly added into the above solution and stirred overnight at room temperature. The as-prepared homogeneous solution was then loaded into a plastic syringe (10 mL) with a 22 G needle, and subsequently placed into a commercial electrospinning setup; the flow rate was set to 0.08 mm min⁻¹. A high-voltage power of 10 kV was applied to the nozzle spinneret, and a grounded cylinder collector was placed 12 cm away and rotated at a high speed up to 2,800 rpm. The as-electrospun PAN/Co(OAc)₂ composite nanofibers were dried at 80°C in a vacuum to remove the residual solvent, and then heat-treated at 280°C for 3 h in an air atmosphere with a heating rate of 2.5°C min⁻¹.

For comparison, neat cPAN nanofibers were synthesized by a comparable electrospinning process without adding Co(OAc)₂. In addition, Co₃O₄ nanofibers were also prepared by using PVA as the polymer fiber substrate instead of PAN; then the as-electrospun PVA/Co(OAc)₂ composite nanofibers were calcined at 285°C for 3 h in air with a heating rate of 2.5°C min⁻¹, and the PVA component was decomposed completely during the thermal treatment.

2.3 Materials' characterization

The morphology of samples was recorded with a field-emission scanning electron microscope (FESEM) on a Hitachi SU 8010. The microstructure of the samples was observed on a TECN G220 S-TWIN system operating at an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) curves were collected on a Diamond TG/f DTG analyzer. X-ray diffraction (XRD) patterns were collected from a D/Max 2400 diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The specific surface areas and pore size distribution of samples were measured using the Brunauer–Emmett–Teller (BET) approach on the JW-BK132F equipment.

2.4 Electrochemical measurements

All the electrochemical studies were conducted in a two-electrode coin cell (CR 2032) configuration at room temperature (25°C). The composite anode was prepared by mixing the active material (cPAN/Co₃O₄ composite nanofibers), the conductive additive (acetylene black), and the binder (PVDF) in the mass ratio of 80:10:10. The mixture was coated on the etched copper foil, and then dried in a vacuum drying oven at 80°C overnight; metallic lithium serves as both counter and reference electrodes, and then lithium-ion half batteries were assembled in a glove box filled with argon.

3 Results and discussion

3.1 Material synthesis and structural characteristics

Figure 1a illustrates the synthesis routes to cPAN/Co₃O₄ nanofibers. Typically, PAN and Co(OAc)₂ were dispersed uniformly in DMF at ambient temperature and then transformed into a plastic syringe with a 22 Gauge needle (0.7 mm in outer diameter), which was regulated to reject the mixture solution with a flow rate of 0.08 mL min⁻¹, and applied a high-voltage power of 10 kV. A grounded cylinder collector was placed 12 cm away from the needle, rotating at a high speed up to 2,800 rpm. Owing to the ultra-high speed of the cylinder collector, the as-electrospun PAN/Co(OAc)₂ composite fibers become thin in diameter and regular in orientation. After that, the resultant

PAN/Co(OAc)₂ composite fibers were finally subjected to a heat treatment at 280°C in air for 4 hours. During this process, the PAN component was cyclized into conjugated poly(*N*-heteroacene) and partly oxidized to form carbonyl groups, resulting in porous cPAN nanoshells, as shown in Figure 1b. At the same time, Co(OAc)₂ was decomposed to form Co₃O₄ nanoparticles, encapsulated in the cPAN nanoshells.

The transformation of PAN/Co(OAc)₂ during heat treatment can be demonstrated by TGA curves, as shown in Figure 2a; the pure PAN fiber gives a large weight loss of 28% in the temperature range from 250 to 280°C, corresponding to the multiple reactions of cyclization, dehydrogenation, and oxidation. Then, the thermostable conjugated structure of cPAN was oxidized and decomposed completely above 700°C in an air atmosphere [32]. Co(OAc)₂ hydrate gradually decomposed to form Co₃O₄ above 240°C, and finally, maintained a mass retention rate of 37% above 350°C, while neat Co₃O₄ shows a negligible weight loss of 1.5% above 700°C. Based on the thermal properties of the PAN and Co(OAc)₂, the PAN/Co(OAc)₂ composite fiber was thermally treated at 280°C in this work; the as-produced cPAN/Co₃O₄ nanofiber presents a similar decomposition trend with that of cPAN, exhibiting good thermal stability below 400°C, and remaining 53% of the mass above 700°C due to the presence of Co₃O₄. The transformation of PAN, Co(OAc)₂, and their composite fiber were also characterized by XRD measurements, as shown in Figure 2b. The neat PAN fiber presents a distinct diffraction peak at $2\theta = 17^\circ$ with an average interlayer spacing (d) of 0.52 nm corresponding to (100) plane of hexagonal lattice [33,34]. After the thermal treatment at 280°C, the (001) diffraction peak disappears and a broad diffraction peak occurs at around $2\theta = 25.6^\circ$ in the curve of cPAN, demonstrating that the original structure of PAN was transformed into a new

crystal structure, which is consistent with that of the graphite structure for the (002) plane, indicating that a highly conjugate structure was formed in the cPAN fibers [33]. Both the neat Co₃O₄ and cPAN/Co₃O₄ composite fibers show typical diffraction peaks in accordance with the cubic spinel phase Co₃O₄ (JCPDS 42-1467), demonstrating that the cPAN/Co₃O₄ nanofiber was successfully produced as expected. FTIR analysis was further used to detect the chemical group changes of PAN to cPAN after the thermal treatment, as shown in Figure 2c. The original PAN shows sharp peaks of $\nu_{\text{C}\equiv\text{N}}$ and $\nu_{\text{C}-\text{H}}$ at 2,245 and 2,931 cm⁻¹, respectively. In comparison, the intensity of the above two peaks decreased significantly or even disappeared in the curves of cPAN and cPAN/Co₃O₄, indicating the occurrence of cyclization and dehydrogenation reactions in the thermal process. In addition, the peaks between 1,680 and 1,580 cm⁻¹ are related to the formation of conjugated carbonyl groups ($\nu_{\text{C}=\text{O}}$) and the cyclic structures ($\nu_{\text{C}=\text{C}} + \nu_{\text{C}=\text{N}}$), respectively [29]. The microscopic pore structure of cPAN/Co₃O₄ was further confirmed by N₂ adsorption-desorption isotherm, as shown in Figure 2d, which exhibits a typical type IV isotherm with a H3 type hysteresis loop at a high relative pressure range of 0.8–1.0, indicating the existence of abundant mesopores [35]. The Barrett-Joyner-Halenda (BJH) pore-size distribution curve is shown as an inset in Figure 2d, which presents two main peaks at around 2.4 and 4.8 nm, corresponding to the clearance of Co₃O₄ nanoparticles and the porous cPAN networks, respectively. It is clear that the main pore size distribution of the cPAN/Co₃O₄ composite is in the range of 2–50 nm, indicating its mesoporous feature. Consequently, the specific surface area of cPAN/Co₃O₄ reached 74.47 m² g⁻¹. The high specific surface area and unique porous structure could contribute to excellent electrochemical performances of the cPAN/Co₃O₄ composite.

Figure 1: (a) Schematic illustration of preparing cPAN/Co₃O₄ nanofiber. (b) The chemical structure transformation from PAN to cPAN during the thermal treatment.

Figure 2: (a) TGA curves, (b) XRD patterns, and (c) FT-IR spectra of PAN, Co(OAc)_2 , Co_3O_4 , cPAN, and cPAN/ Co_3O_4 . (d) N_2 adsorption-desorption isotherm and pore size distribution curve of cPAN/ Co_3O_4 .

The morphology of the samples was characterized using SEM. As shown in Figure 3a, the as-electrospun PAN/ Co(OAc)_2 nanofibers are clearly oriented with smooth surfaces with an average diameter of 316 nm. After the thermal treatment, the resulting cPAN/ Co_3O_4 nanofibers maintained the oriented state (Figure 3b). However, their surfaces become very wrinkled and the average diameter reduced to 85 nm (Figure 3c) due to the cyclization/oxidation of PAN and decomposition of Co(OAc)_2 during the annealing process. TEM images were also used to determine the microstructure of the cPAN/ Co_3O_4 nanofiber, as shown in Figure 3d and e; the nanofiber consists of dense dark spots representing Co_3O_4 nanoparticles, whereas the distributed light spots represent plenty of tunnels existing inside the nanofiber, which is beneficial for the infiltration and permeation of electrolytes, resulting in the improvement of utilization efficiency of active materials. The high-resolution TEM images of the cPAN/ Co_3O_4 nanofiber are shown in Figure 3f and g, which indicates that the Co_3O_4

nanoparticles are randomly coated by the amorphous cPAN shells and can inhibit the volume change of Co_3O_4 during the charge/discharge process and thus improve the cycling stability of the battery. Moreover, Co_3O_4 exhibited an obvious crystal lattice fringe with interplanar spaces of 0.47 and 0.28 nm, which are in good agreement with (111) and (220) crystal planes of Co_3O_4 [36]. The EDS mapping images (Figure 3h–k) of the cPAN/ Co_3O_4 nanofiber further demonstrated the successful coating of Co_3O_4 nanoparticles into the mesoporous cPAN nanofiber, where the C, O, N, and Co elements coexisted and were uniformly distributed in the nanofiber.

3.2 Lithium storage performance

The electrochemical properties and storage mechanism of cPAN, Co_3O_4 and cPAN/ Co_3O_4 nanofibers were investigated by using CV, GCD, and EIS techniques.

Figure 3: SEM images of oriented (a) PAN/Co(OAc)₂ and (b and c) cPAN/Co₃O₄ composite fibers. (d–g) TEM images of cPAN/Co₃O₄ at different magnifications and (h–k) the corresponding EDS mappings.

Figure 4a shows the CV curve of the cPAN nanofiber electrode with a scan rate of 0.5 mV s^{-1} in the voltage range of 0.001–3.00 V (vs Li/Li⁺) at room temperature. Typically, the CV curve of cPAN shows strong irreversible peaks at about 0.5 V during the first scan, corresponding to the decomposition of organic electrolytes and the formation of the SEI layer [31]. In the following several cycles, two wide redox peaks appeared in the voltage range of 0.001–0.4 and 0.6–1.3 V, corresponding to the insertion/extraction of lithium ion into/from the unsaturated C=C and C=N bonds in the heterocyclic ring of the cPAN chain, respectively, and the evolutions of the chemical structure are consistent with the redox mechanism reported earlier [37,38,31]. For the CV curves of pure Co₃O₄ in Figure 4b, there is a strong peak at about 0.75 V in the first cathodic scan of the discharge process, which corresponds to the electrochemical reduction process of Co₃O₄ to Co and the decomposition of the electrolyte solution; the former can be described as $\text{Co}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Co}_3\text{O}_4 \rightarrow 3\text{Co}^0 + 4\text{Li}_2\text{O}$, and the latter leads to the formation of the SEI [39]. In the following two cathodic

scans, the cathodic peak shifts into two peaks at 0.8 and 1.0 V with an apparent decrease in the area underneath the curve, contributing to the reduction of Co₃O₄ into Li₂O. During the anodic scan, a broad peak located at about 2.23 V is ascribed to the re-oxidization of metallic cobalt (Co⁰) and the decomposition of Li₂O according to the reversible conversion mechanism described as $3\text{Co}^0 + 4\text{Li}_2\text{O} \leftrightarrow \text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8e^-$. Notably, the anodic peak shifted to $\approx 2.31 \text{ V}$ and $\approx 2.37 \text{ V}$ at the second and third cycles, respectively, suggesting the formation of a thick SEI layer that may hinder ion transport [40]. The characteristic redox peaks of pure cPAN and Co₃O₄ can also be identified in the CV curve of the cPAN/Co₃O₄ anode, as shown in Figure 4c, which shows strong irreversible peaks at around 0.5, 0.8, and 1.0 V during the first cathodic scan, three wide redox peaks at around 0.97, 1.28, and 2.11 V in the first anodic scan, and then three peaks at around 0.87, and 0.57 V in the following cathodic scan, respectively. Furthermore, there is no significant difference between the main peaks of the second and third cycles, indicating improved reversibility

Figure 4: Cyclic voltammograms of (a) cPAN, (b) Co_3O_4 , and (c) cPAN/ Co_3O_4 nanofiber-based half-cells cycled between 0.001 and 3 V (vs Li^+/Li) at a scan rate of 0.5 mV s^{-1} . (d) CV curves at various scan rates from 0.2 to 1.0 mV s^{-1} , (e) the decoupling of capacitive contribution (shadow) at 0.2 mV s^{-1} , and (f) the normalized capacitive contribution at different scan rates for the cPAN/ Co_3O_4 anode.

of the cPAN/ Co_3O_4 anode in lithium storage [41]. The rate capability and redox kinetics of the cPAN/ Co_3O_4 anode were further examined by CV curves at various scan rates from 0.2 to 1.0 mV s^{-1} , as shown in Figure 4d; all the curves retain

similar small shifts, and the current increases accordingly with the increasing scan rate, implying high reversibility and negligible polarization. In fact, the response current (i) can be divide into the fast-kinetic capacitive current (k_1v) and

slow-kinetic diffusion-controlled current ($k_2v^{0.5}$) [42,43]. The decoupling of the CV curve shows that the capacitive contribution is 45.5% at 0.2 mV s^{-1} (Figure 4e); with the increase of the scanning rate, the capacitive contribution increases gradually and reaches 85.2% at 1.0 mV s^{-1}

(Figure 4f), indicating the fast ion transfer capability enabled by the unique porous structure of the cPAN/Co₃O₄ anode.

Figure 5a–c shows the GCD curves of cPAN, Co₃O₄, and cPAN/Co₃O₄ anodes at a current density of 0.1 A g^{-1} ; the first discharge/charge capacities are 1,012/667, 1,468/

Figure 5: Galvanostatic charge/discharge curves of (a) cPAN, (b) Co₃O₄, and (c) cPAN/Co₃O₄ nanofiber-based half-cells cycled between 0.001 and 3 V at 0.1 A g^{-1} ; (d) rate performances, (e) cyclic performances at 0.1 A g^{-1} after 50 cycles, and (f) cyclic performances at 1.0 A g^{-1} over 400 cycles for the cPAN, Co₃O₄, and cPAN/Co₃O₄.

944, and 1,634/1,052 mA h g⁻¹, with the coulombic efficiency (CE) of 65, 64, and 64%, respectively. Obviously, cPAN/Co₃O₄ has a higher capacity than that of pure cPAN and Co₃O₄; however, the low initial Coulombic efficiencies of the anodes were likely due to the possible irreversible processes such as lithium insertion/extraction into/from the active materials, electrolyte decomposition, and inevitable formation of SEI films. In contrast, the second and third cycles of these GCD curves almost coincide, indicating that the absorption and release of lithium in the following charging/discharging process is very stable and reversible [44]. Accordingly, cPAN, Co₃O₄, and cPAN/Co₃O₄ anodes exhibit the reversible capacity of 756.3, 897.2, and 997.6 mA h g⁻¹ at 0.1 A g⁻¹, respectively. cPAN/Co₃O₄ achieved the highest reversible capacity due to the unique porous structure and the synergistic effects between the two components. First, the highly conjugated poly(*N*-heteroacene)-like structure of cPAN significantly improves the electrochemical performance due to the elevated electronic conductivity. Second, the cPAN nanofibers are small in diameter and have a porous structure, which affords highly exposed multi-electron redox-active sites and enhanced capacity contributions. Third, the cPAN nanofiber substrate suppresses the size of Co₃O₄ nanoparticles, thus improving the electrochemical utilization and specific capacity.

The rate capabilities of cPAN, Co₃O₄, and cPAN/Co₃O₄ at various current densities of 0.1–1.0 A g⁻¹ are shown in Figure 5d. It is worth noting that cPAN/Co₃O₄ shows high reversible capacities of 764.4, 620.6, and 396.5 mA h g⁻¹ at current densities of 0.2, 0.4, and 1.0 A g⁻¹, respectively, with rate retention of 40%, and the capacity recovers to 746.5 mA h g⁻¹ when the current density returns to 0.1 A g⁻¹. The relatively poor rate capability of the cPAN/Co₃O₄ electrode can be attributed to the low annealing temperature of

280°C and the resulting low electron conductivity. In comparison, pure cPAN exhibits a reversible capacity of 156.4 mA h g⁻¹ (20.7%) at 1.0 A g⁻¹, while the value for Co₃O₄ is 40.5 mA h g⁻¹ (4.5%). The capacity and rate performance of cPAN/Co₃O₄ are apparently superior to the pure cPAN, Co₃O₄, and some Co₃O₄-based anodes, such as Co₃O₄ nanoparticles filled in an aligned mesoporous carbon nanotube (Co₃O₄@MCTs) electrode, which shows a reversible capacity of 179 mA h g⁻¹ at 1.0 A g⁻¹ [45]. The high capacity and good rate performance of the cPAN/Co₃O₄ anode are owing to its unique mesoporous morphology; the presence of the cPAN mesopores greatly enhances the storage of the interface and surface Li, providing less resistance of short path lengths for the electrode/electrolyte interface [46,47]. Meanwhile, cPAN/Co₃O₄ also delivers a reversible capacity of 767.8 mA h g⁻¹ at 0.1 A g⁻¹ after 50 cycles (Figure 5e), much higher than that of the pure cPAN (527.6 mA h g⁻¹) and Co₃O₄ (604 mA h g⁻¹), and also much superior to some reported results, such as the Co₃O₄@CNT electrode maintains 700 mA h g⁻¹ at 0.1 A g⁻¹ over 100 cycles [48], Co₃O₄ spheres remains 680 mA h g⁻¹ at 1/5 C after 50 cycles [49], the above-mentioned Co₃O₄@MCTs show 627 mA h g⁻¹ at 0.1 A g⁻¹ after the 50th discharge [45]. Furthermore, Figure 5f shows the cycling performances of cPAN, Co₃O₄, and cPAN/Co₃O₄ at a current density of 1.0 A g⁻¹, and the reversible capacity of Co₃O₄ decreases robustly during the first 100 cycles. It is due to the relatively low annealing temperature (280°C) and the resulting low crystallinity of Co₃O₄, which is more likely to cause volume changes during the charging/discharging process at a large current density, leading to rapid structural decomposition and capacity drop [41,50]. Nevertheless, when encapsulated in cPAN, the dissociation of the active material can be inhibited effectively, and thus the capacity retention of cPAN/Co₃O₄ was

Figure 6: (a) Nyquist plots and (b) the plots of Z' vs $\omega^{-0.5}$ for the cPAN, Co₃O₄, and cPAN/Co₃O₄.

improved. As a result, the reversible capacities of cPAN, Co_3O_4 , and cPAN/ Co_3O_4 remain at 56.4, 70.8, and 206.9 mA h g^{-1} after 400 cycles, with retentions of 40, 8, and 24%, respectively. The highly improved cycling stability of the cPAN/ Co_3O_4 anode is mainly due to its unique structure, and the cPAN layer on the surface of Co_3O_4 nanoparticles acts as a buffer matrix to prevent particle agglomeration, thus improving the utilization rate and the electrochemical activity of the active material; meanwhile, the cPAN layer also maintains the structural stability of Co_3O_4 nanoparticles during discharge/charging process and improves the cyclic stability [23].

The kinetics of lithium-ion transmission in two-electrode coin-cells was studied using electrochemical impedance spectroscopy (EIS) in the completely uncharged and undischarged states. The Nyquist plots of the three electrodes consist of three main regimes, as shown in Figure 6a; the intercept of the real axis at high frequency corresponds to the SEI layer resistance (R_f), a depressed semicircle in the high-frequency region corresponding to the charge transfer resistance (R_{ct}), while the quasi-line in the low-frequency region is associated with the impedance of Li^+ diffusion in the cPAN/ Co_3O_4 nanomaterials [51]. The impedance spectra were analyzed using the complex nonlinear least-squares fitting method, the cPAN electrode exhibits the smallest R_{ct} (150 Ω) due to the unique porous structure that promotes the electrolyte permeabilization and Li insertion/deintercalation. Notably, the cPAN/ Co_3O_4 shows smaller R_f (3.2 Ω) and R_{ct} (166 Ω) values than those of pure Co_3O_4 ($R_f = 3.8 \Omega$ and $R_{ct} = 192 \Omega$), which can be attributed to the porous cPAN network. Moreover, the slope of the quasi-line of cPAN/ Co_3O_4 in the low frequency range is larger than that of pure Co_3O_4 , indicating a faster ion diffusion dynamic due to the mesoporous nanostructure of cPAN/ Co_3O_4 , which provides a high surface area not only for lithium storage but also for the transport of lithium ion in electrolytes. Figure 6b shows the relationship curve between Z' and the negative square root of angular frequency ($\omega^{-1/2}$) in the low-frequency region; the diffusion coefficient of lithium ions (D_{Li^+}) can be calculated with the slope of the fitting line (Warburg coefficient) [52]. The D_{Li^+} values of cPAN, Co_3O_4 , and cPAN/ Co_3O_4 were 2.1×10^{-12} , 4.6×10^{-12} , and $2.6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively. Obviously, the Li^+ diffusion coefficient of cPAN/ Co_3O_4 is slightly larger than that of pure Co_3O_4 due to the multifunctionality of cPAN, which formed an interconnected three-dimensional porous network to give internal channels for the electrolyte. Meanwhile, it also significantly reduced the aggregation of Co_3O_4 nanoparticles during the thermal treatment, thus boosting the exposure of exterior surfaces and edges available.

4 Conclusion

In summary, the cPAN/ Co_3O_4 composite nanofiber was produced *via* an electrospinning method followed by heat treatment; the cPAN/ Co_3O_4 nanofiber is only 85 nm in diameter and has a porous structure, where cPAN shells were coated on the surface of Co_3O_4 nanoparticles. Owing to the unique nanostructure and synergistic effects inspiring electrochemical lithium storage performances, cPAN/ Co_3O_4 -based lithium ion battery achieved a high reversible specific capacity up to 997.6 mA h g^{-1} at a current density of 0.1 A g^{-1} and still maintained 396.5 mA h g^{-1} when the current density increased to 1.0 A g^{-1} . Meanwhile, the specific capacity retention rate was as high as 81% after 50 cycles at a current density of 0.1 A g^{-1} . This work may offer a new design idea and practical basis for the development of high-performance battery anode materials.

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