Long life rechargeable Li-O₂ batteries enabled by enhanced charge transfer in nanocable-like Fe@N-doped carbon nanotube catalyst

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ABSTRACT Rechargeable Li-O₂ batteries have attracted considerable interests because of their exceptional energy density. However, the short lifetime still remained as one of the bottle-neck obstacles for the practical application of rechargeable Li-O₂ batteries. The development of efficient cathode catalyst is highly desirable to reduce the energy barrier of Li-O₂ reaction and electrode failure. In this work, we report a facile strategy for the fabrication of a high-performance cathode catalyst for rechargeable Li-O₂ batteries by the encapsulation of high content of active Fe nanorods into N-doped carbon nanotubes with high stability (denoted as Fe@NCNTs). First-principles calculations reveal that the synergistic charge transfer and redistribution between the interface of Fe nanorods, the CNT walls and the active N dopants greatly facilitate the chemisorption and subsequent dissociation of O₂ molecules into the epoxy intermediates on the carbon surface, which benefits the uniform growth of nanosized discharge products on CNT surface and thus boosts the reversibility of Li-O₂ reactions. As a result, the cathode with Fe@NCNT catalyst exhibits long cycling stability with high capacities (1000 mA h g⁻¹ for 160 cycles and 600 mA h g⁻¹ for 270 cycles). Based on the total mass of Fe@NCNTs + Li₂O₂, high gravimetric energy densities of 2120–2600 W h kg⁻¹ can be achieved at the power densities of 50–795 W kg⁻¹.

Keywords: Li-O₂ battery, cathode catalyst, N-doped carbon nanotube, Fe nanorods, first-principles calculation

INTRODUCTION

Rechargeable Li-O₂ batteries have attracted considerable

interests as a high-energy power source for low-emission electric vehicles (EV) [1–7]. Compared with the state-of-the-art Li-ion batteries, Li-O₂ batteries possess dramatically higher energy density (~3500 W h kg⁻¹) originated from the reversible reaction of $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ ($E_0 = 2.96$ V vs. Li/Li⁺), where the cathode active material (O₂) is never exhausted in surrounding environment. However, the application of Li-O₂ batteries has still largely hindered by a series of problems such as poor rate capability, low round-trip efficiency, short lifespan and electrolyte instability [8–13]. Most of these problems primarily originate from the sluggish kinetics of the oxygen evolution reaction (OER) involved in Li-O₂ batteries, which leads to poor reversibility and high polarization [12,14–19]. The inevitable precipitation of insoluble and insulating discharge products (mainly the Li₂O₂) on the air electrode further gradually blocks the pathway for inward diffusion of oxygen and electrolyte. This so-called problem of “air electrode clogging” eventually starves the cells to failure in short time [20,21]. The development of efficient and durable cathode catalyst that can efficiently reduce the energy barrier for Li-O₂ reaction and electrode failure is highly desirable to overcome these critical obstacles for the practical application of Li-O₂ batteries.

So far, great efforts have been devoted to developing the cathode catalyst with high activity and stability for oxygen-involved reactions in Li-O₂ batteries [22–35]. Peng *et al.* [7] firstly reported the rechargeable Li-O₂ batteries by

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catalyzing the reversible formation/decomposition of the Li_2O_2 on porous Au catalyst, which makes Li- O_2 batteries promising for practical use. Wang *et al.* [36] developed a MnCo_2O_4 -graphitic carbon hybrid material as the non-precious metal catalyst, which delivers a lower overpotential (0.8 V) and a cut-off capacity of 1000 mA h g^{-1} for 40 cycles. On this base, Jian *et al.* [37] further reduced the overpotential for Li- O_2 reactions to 0.72 V by using carbon nanotubes (CNTs) supported RuO_2 shells as the cathode catalyst. Xu *et al.* [38] also demonstrated that the rate capability and lifespan of Li- O_2 batteries can be significantly improved by tailoring the deposition behavior and morphology of the discharge products on a Pd-loaded hollow carbon air cathode. Despite the exciting success, the use of precious noble metal catalysts significantly increases the processing cost of Li- O_2 cells, while most metal oxides suffer from intrinsically low electronic conductivity. Carbon materials have been recognized as promising low-cost cathode catalysts in rechargeable Li- O_2 batteries. However, they generally suffer from a large overpotential of 1.5 V and low round-trip efficiency (53%–64%). Heteroatom doping or hybridization with metal species represents an efficient way to enhance the activity of carbon-based catalysts towards oxygen reduction reaction (ORR)/OER reactions [39–42]. The presence of heteroatoms (e.g., N) and metal species not only reduces the local work function on carbon surface for better O_2 adsorption, but also changes the charge density on the carbon surface via electron transfer effect [16,43–51]. Nevertheless, the understanding on the origin of their activity and the chemical nature of the reaction pathways is still quite limited, which hinders the development of high-performance cathode catalysts.

In this work, we report a facile strategy for the fabrication of a high-performance cathode catalyst for rechargeable Li- O_2 batteries by the encapsulation of high content of active Fe nanorods into N-doped carbon nanotubes with high stability (denoted as Fe@NCNTs). Distinct from the common way for filling the CNTs such as chemical vapor deposition, arc discharge or capillary filling in solution, the Fe nanorods are filled into the N-doped CNTs in an efficient *in-situ* manner through one-pot pyrolysis of the dicyandiamide and FeCl_3 , which are low-cost basic chemicals of industry. In cable-like Fe@NCNTs, the active Fe nanorods are well protected by dense CNT sheath from oxidation and corrosion, which in turn steadily strengthen the adsorption of O_2 on N-doped carbon surface for homogenous nucleation and growth of discharge products. First-principles calculations reveal that the Fe@NCNT catalyst owes high

activity to the charge transfer and redistribution between Fe nanorods, the graphitic carbon of CNT walls and the active N dopants. Their synergistic effect greatly strengthens the chemisorption and subsequent dissociation of O_2 molecule into the epoxy intermediates on the carbon surface, which is favorable for homogenous coverage of nano-sized Li_2O_2 on CNTs. As a result, the air cathodes with Fe@NCNT catalyst exhibit a high capacity of 5280 mA h g^{-1} at a current density of 100 mA g^{-1} and greatly enhanced rate capability. By restricting the discharge capacity to 600 and 1000 mA h g^{-1} , the Fe@NCNT- O_2 /Li cells show excellent reversibility for 160 and 270 cycles with 100% capacity retention, respectively. High gravimetric energy densities of 2120 – 2600 W h kg^{-1} can be achieved at the power densities of 50 – 795 W kg^{-1} based on the total mass of Fe@NCNTs + Li_2O_2 .

EXPERIMENTAL SECTION

Materials preparation

In a typical run, the dicyandiamide (1.0 g) was thoroughly mixed with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 g) in ethanol solution (30 mL) under ultrasonic. Afterwards, the mixture solution was heated at 40°C until completely drying. The obtained tawny powder was subjected to annealing at 800°C for 3 h in N_2 flow at a ramp rate of $10^\circ\text{C min}^{-1}$, yielding black powder of the Fe@NCNTs.

Materials characterization

The morphology of the samples was characterized with field-emission scanning electron microscopy (FESEM, FEI NanoSEM 450) and transmission electron microscopy (TEM, FEI TF30). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 type X-ray spectrometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The surface characteristics of the samples were investigated using a Thermo ESCALAB 250 X-ray photoelectron spectrometer (XPS). The textural properties of the samples were measured by a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer at 77 K. The content of the elements in the sample was measured by energy-dispersive X-ray spectroscopy (EDS) and XPS. Thermogravimetric analysis (TGA) was carried out by using a NETZSCH scientific instrument in O_2 atmosphere heating from room temperature to 800°C at a ramp rate of $10^\circ\text{C min}^{-1}$. The discharged cathodes were examined using a Nicolet-20DXB Fourier transform infrared spectrometer (FTIR). Before test, the discharged electrode was sealed inside the glove box to

avoid exposure to air.

Electrochemical measurements

The battery tests were conducted using meshed CR2032 coin cells with a pure Li foil as the counter and reference electrode at room temperature. The working electrode consists of the Fe@NCNTs or CNTs, carbon black and polyvinylidene difluoride (PVDF) in a weight ratio of 5:4:1, which was coated on a carbon paper with a diameter of ca. 1.0 cm. The anode and cathode were separated by a glass fiber separator. The electrolyte used was 1 mol L⁻¹ LiTFSI in TEGDME. The mass loading of the electrode was around 0.8–1.0 mg cm⁻². The carbon black cathode was prepared by casting the slurry consisting of 90 wt.% carbon black and 10% PVDF in *N*-methyl-2-pyrrolidone onto a carbon paper. The galvanostatic discharge-charge measurement of cells was performed on a Land CT2001 A battery tester at different current densities. All the electrochemical tests were performed in 1 atm dry O₂ at 25°C in a home-made autoclave.

Computational method

First-principles calculations were performed by spin polarized density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [52]. We used the planewave basis set with energy cutoff of 450 eV, the projector augmented wave (PAW) potentials [53] and the generalized gradient approximation parameterized by Perdew, Burke and Ernzerhof (GGA-PBE) for the exchange-correlation functional [54]. A slab model consisting of monolayer graphitic carbon adsorbed on Fe (110) surface was constructed to model the surface of Fe@NCNTs. The curvature effect from CNTs and Fe nanorods was neglected considering their large radius of tens of nanometers. The (110) facet was cleaved from Fe crystal in the *bcc* phase, which was represented by a three-layer slab with vacuum region of 16 Å in the out-of-plane direction. The Fe (110) surface has a rhombohedral structure with lattice constant of 2.48 Å and included angle of 109.47° [55]. We used a supercell for Fe (110) with in-plane lattice vectors of $\mathbf{b}_1 = 5\mathbf{a}_1 + \mathbf{a}_2$ and $\mathbf{b}_2 = -2\mathbf{a}_1 + 4\mathbf{a}_2$ ($\mathbf{a}_1$, $\mathbf{a}_2$ are the primitive lattice vectors), such that $b_1 = 11.81$ Å, $b_2 = 12.48$ Å and the included angle equals to 120.05°. We then deformed $\mathbf{b}_1$ and $\mathbf{b}_2$ to fit 5×5 graphitic carbon unit cells, yielding lattice mismatch less than 4%. The Brillouin zone of each supercell was sampled by $3 \times 3 \times 1$ uniform k-point mesh. The model structures were optimized by only ionic and electronic degrees of freedom using thresholds for the total energy of 10^{-4} eV and force of 0.02 eV Å⁻¹. During

the structural relaxation, the bottom layer Fe atoms were fixed to mimic a semi-infinite metal solid. The semiempirical dispersion-corrected DFT-D3 scheme proposed by Grimme [56] was used to describe the van der Waals (vdW) interactions between the graphitic sheet and Fe surface. To simulate the adsorption and diffusion kinetics of O₂ on the Fe@NCNT surface, we employed the climbing-image nudged elastic band (CI-NEB) method [57]. Five intermediate images were used to describe the reaction path, and each image was optimized until the maximum projected force was below 0.02 eV Å⁻¹.

RESULTS AND DISCUSSION

Typical FESEM images of Fe@NCNT sample are shown in Fig. 1a, b, revealing the formation of sinuous CNTs with uniform diameter of around 50 nm and the length of hundreds of micrometers. As a result, they need only a few contact points to ensure the continuous charge transport whereas the nanoparticle catalysts may easily become electrically isolated during deep cycling. The quality of the products is highly dependent on the pyrolysis temperature: insufficient conversion of Fe³⁺/dicyandiamide composite at lower temperature (e.g., 700°C) results in the mixture of the CNTs and large impurity particles while the products of the reaction at higher temperature (e.g., 900°C) suffer from poor size distribution (Fig. S1). Element mapping analysis reveals the presence of Fe element and homogenous distribution of the C and N elements in the sample (Fig. 1c). The TEM analysis reveals the formation of a cable-like structure composed of high content of Fe nanorods with dark contrast inside the CNTs with graphite-like orientated layered walls (Fig. 1d). Along the CNTs, the Fe nanorods with the length of several hundred nanometers distribute across the whole tube with high filling rate of over 90% based on TEM observation. High resolution TEM (HRTEM) examination confirms the confinement of single crystalline Fe nanorods inside the CNTs with a high degree of graphitization. Specifically, the (110) plane of the Fe nanorods ($d_{110}=0.203$ nm) is parallel to the (002) plane of CNT walls. Namely, the Fe nanorods grow along the *c*-axis within the confinement nanospace of CNTs.

The crystallographic structure and phase purity of the Fe@NCNT sample were determined by XRD, as shown in Fig. 2a. The sharp peaks at ca. 44.6°, 65.0° and 82.3° can be ascribed to the diffraction from (110), (200) and (211) planes of metallic Fe (JCPDS No. 06-696), while the broad peak centered at ca. 26° is due to the presence of the CNTs. The rest of weak peaks can be assigned to the inevitable formation of trace amount of Fe₃C phase at high temperature.

Figure 1 (a, b) FESEM images of the Fe@NCNT sample; (c) elemental mapping showing the uniform distribution of C, Fe and N element; (d, e) TEM images of Fe@NCNTs; (f) HRTEM image revealing the single crystalline nature of Fe nanorods within CNT shells with a high degree of graphitization.

The presence of Fe_3C phase implies that the formation of Fe@NCNTs may follow a “dissolution-precipitation” mechanism where metal carbide phase serves as the nucleation site for the growth of metal-filled CNTs [58]. XPS survey scan confirms the presence of Fe, C, N and O elements in Fe@NCNTs, as shown in Fig. 2b. The high-resolution N 1s spectrum visualizes the presence of three forms of N, namely, pyrrolic N (399.6 eV), pyridinic N (398.6 eV) and graphitic N (401.1 eV). The N content in the sample is around 4 at.%, where the pyridinic N and graphitic N accounts for 94 % of total N content (Fig. 2c). The N doping simultaneously creates extra surface defects on CNTs for the adsorption of moisture and atmospheric gases, leading to a high content of oxygen (12 at.%) in the sample. This feature is desirable for enhancing the O_2 adsorption capability of inert carbon surface. Very low Fe content detected (2 at.%) by XPS suggests that the Fe nanorods are well protected by the carbon sheath with less residue on CNT surface. N_2 adsorption-desorption isotherms of Fe@NCNT sample display a type-IV curve with an obvious hysteresis loop at relative pressure of 0.45–0.9 (Fig. 2d). The mesoporous structure of Fe@NCNT is mainly generated from the interspace between individual CNTs. It reveals that the sample contains abundant mesopores with high specific surface area of $72.7 \text{ m}^2 \text{ g}^{-1}$. The Fe content in the Fe@NCNT

sample is measured to be 63.27 wt.% by TGA, as shown in Fig. S2.

The electrochemical properties of Fe@NCNTs were investigated for the potential use as the cathode catalysts in Li- O_2 batteries. The galvanostatic discharge curve of Fe@NCNT electrodes at a current density of 100 mA g^{-1} is shown in Fig. 3a. It delivers a high capacity of 5280 mA h g^{-1} with a cut-off voltage window of 2.0–4.5 V, which is much higher than those of CNT (4160 mA h g^{-1}) and carbon black (3730 mA h g^{-1}) electrodes under identical conditions. The charge overpotential for Fe@NCNT electrode is reduced to 1.12 V as compared with those for the CNT (ca. 1.3 V) and carbon black (ca. 1.43 V) electrodes, indicating greatly enhanced activity towards OER in Li- O_2 batteries. With the current density further increases, the capacities and operating potential of the cell are gradually reduced due to the increasing electrode polarization. However, high capacities of $2600\text{--}4100 \text{ mA h g}^{-1}$ can still remain at high current densities of $500\text{--}1000 \text{ mA g}^{-1}$ (Fig. 3b). To further investigate the gravimetric energy and power characteristics, Ragone plots of the Fe@NCNT electrodes are drawn in Fig. 3c. Remarkably, they deliver high gravimetric energy of up to $6930\text{--}14,240 \text{ W h kg}^{-1}$ at the power rate of $273\text{--}2665 \text{ W kg}^{-1}$, corresponding to high gravimetric energy of $2150\text{--}2710 \text{ W h kg}^{-1}$ when the mass

Figure 2 (a) XRD pattern, (b) XPS full scan spectrum and (c) N 1s XPS spectrum of Fe@NCNT sample; (d) nitrogen-adsorption-desorption isotherm and pores size distribution of Fe@NCNT sample.

of the Li_2O_2 is included. This value is still 4-fold higher than that of the current Li intercalation electrodes (e.g., LiCoO_2 with an energy density of 600 W h kg^{-1}), and meets the energy demand of the batteries in automotive applications (1700 W h kg^{-1} , the usable energy content of gasoline) [1,59]. Since the stainless steel shell takes a very large weight fraction (85 %) in coin-type batteries, the batteries deliver the gravimetric energy densities of $0.68\text{--}1.4 \text{ W h kg}^{-1}$ with power densities of $0.027\text{--}0.255 \text{ W kg}^{-1}$. Technically, this performance can be significantly improved by optimizing the battery configuration, e.g., the soft-packing battery with multilayered electrodes and lighter plastic shells. Noting that the density of Li_2O_2 (2.3 g cm^{-3}) is only a half of the LiCoO_2 (5 g cm^{-3}) [22], the volumetric energy advantage of the Fe@NCNT electrodes may be lower than the enhancement in gravimetric energy, which is common for Li-O_2 electrodes.

By restricting the discharge capacity to 1000 mA h g^{-1} , the Li-O_2 battery with Fe@NCNT electrodes shows excel-

lent reversibility for 160 cycles with 100% capacity retention at a current density of 200 mA g^{-1} , whereas the cells with NCNT, CNTs or carbon black electrodes failed in less than 35 cycles (Fig. 3d, e and Fig. S3). Since pure NCNT is hardly obtained by acidic etching of Fe@NCNT, NCNTs were made by treating the CNTs in ammonia flow at 900°C for the comparison. When the discharge depth is limited to 600 mA h g^{-1} , the lifetime of the battery can be further prolonged to 270 cycles with stable capacity retention at 200 mA g^{-1} (Fig. 3d). Even this value is superior to that of the state-of-the-art Li-ion full cells ($100\text{--}150 \text{ mA h g}^{-1}$), of which the capacities are largely limited by lithium metal oxide cathodes (e.g., LiCoO_2 , LiFePO_4 , LiMnO_2 , etc.). In this case, the charge overpotential for the Fe@NCNT electrode (ca. 1.05 V) is also much lower than that of the NCNT (ca. 1.22 V), CNT (ca. 1.24 V) and carbon black (ca. 1.38 V) electrodes (Fig. 3f). The excellent cycling performance of the Fe@NCNT electrode indicates the stable electrochemical behavior with reduced polarization and high rever-

Figure 3 (a) The discharge-charge voltage curves of the Fe@NCNT, CNT and carbon black electrodes at a current density of 100 mA g⁻¹; (b) the discharge-charge voltage curves of the Fe@NCNT electrodes at varied current densities of 100, 500 and 1000 mA g⁻¹. (c) Gravimetric Ragone plot comparing energy and power characteristics of the Fe@NCNT electrodes with other energy storage technologies. (d) Cycling performance of the Fe@NCNT, NCNT, CNT and carbon black electrodes with a restricted capacity of 600 and 1000 mA h g⁻¹; (e) the discharge-charge voltage curves of the Fe@NCNT electrodes with a restricted capacity of 1000 mA h g⁻¹ for the 1st, 20th, 50th, 100th and 160th cycles; (f) the discharge-charge voltage curves of the Fe@NCNT, NCNT, CNT and carbon black electrodes with a restricted capacity of 1000 mA h g⁻¹ at 200 mA g⁻¹.

sibility originated from the coupling of Fe and NCNTs at molecular level. It should be noted that the cycling performance of current Li-O₂ batteries is largely harmed by the decomposition of the organic electrolyte during the electrochemical reaction [8,60]. With more stable electrolyte, the lifespan of the cells with Fe@NCNT electrode may be

significantly extended for practical application.

In order to uncover the reasons for the enhanced electrochemical properties of the Fe@NCNT electrodes, their morphology and structure after discharge and charge were examined by XRD and FESEM, as shown in Fig. 4. The diffraction peaks of hexagonal Li₂O₂ are detected by XRD

analysis of the Fe@NCNT electrodes after discharge to 2.0 V. After fully recharging, the characteristic Li_2O_2 peaks completely disappear, indicating the high reversibility of the oxygen evolution reaction over the Fe@NCNT catalyst. Some other weak bumps are also observed in XRD spectrum of the recharged cathode possibly due to the formation of a small amount of side reaction products such as Li_2CO_3 , HCO_2Li and other Li-based organic compounds during cycling, as suggested by FTIR analysis (Fig. S4) [8,9,44]. FESEM examination reveals the formation of toroidal-aggregates of Li_2O_2 on the surface of CNTs or carbon black electrode after discharge (Fig. S5). The majority of the CNTs have a smooth surface without the coverage of Li_2O_2 [20,22,61,62]. The low Li_2O_2 coverage region might induce localized distribution of Li_2O_2 on the cathode, and eventually aggravates the electrode polarization. As a result, a high charge potential is needed to decompose the large particles of insulating Li_2O_2 remote from the cathode surface. In sharp contrast, the surface of

Fe@NCNTs is homogeneously covered by a smooth layer of the nanosized discharge products without aggregation or appearance of free particles (Fig. 4c). The uniform distribution of nanosized Li_2O_2 intimately contacting with highly conductive CNTs facilitate the smooth decomposition across large interface area at lower charge potential and thus the Li_2O_2 could be sufficiently decomposed after charging (Fig. 4d) [2,30,61,63]. After 10th discharge, the structure of Fe@NCNT is well preserved (Fig. S6) without the variation in peak characteristics of Fe in XRD pattern, showing the high stability of Fe@NCNT against oxygen attacking.

Apparently, the encapsulation of Fe nanorods has great influence on both the morphology and distribution of the Li_2O_2 on the surface of CNT wrapped around them, which determines the specific growth and decomposition behavior of the discharge products during battery cycling. Since the Fe nanorods are sealed within CNTs without direct contact with O_2 , they should interact with the CNTs and affect

Figure 4 (a) XRD patterns of the fresh, discharged and recharged Fe@NCNT electrodes; (b, c, d) SEM images of the fresh, fully discharged and fully charged Fe@NCNT electrodes, respectively.

the properties of the CNT surface where O_2 is reduced. To understand the origin of the electroactivity of Fe@NCNT catalyst, the first-principles calculations were carried out based on the spin polarized DFT method. It is noteworthy that the conventional cluster models are not applied to describing the Fe@NCNT structure because the radius of realistic CNTs and Fe crystals attains tens of nanometers [64]. Instead, a slab model was used to represent the Fe@NCNT structure nearby the Fe-CNT interface area. The model consists of graphitic carbon monolayer doped with different types of N atoms (e.g., pyridinic N, graphitic N or pyrrolic N), which is adsorbed on the (110) facet of Fe crystal, as shown in Fig. 5a. The (110) plane of Fe is adopted in terms of the HRTEM result (Fig. 1f). A 3-layer slab is adopted for Fe (110) with a vacuum region of 16 Å. The in-plane dimensions of the supercell include 4.76×5.03 Fe unit cells, which are slightly deformed to match 5×5 graphitic carbon unit cells with a lattice mismatch of $< 4\%$. The size of this model is far small than that of the realistic Fe@NCNT structure, thereby the effect of surface curvature on material properties is minimized. The interlayer spacing between the Fe (110) surface and graphitic carbon layer doped with pyridinic N, graphitic

N or pyrrolic N is 2.12, 2.09 and 2.04 Å, respectively, due to the formation of appreciable Fe–C bonding. Mulliken charge analysis indicates an electron transfer of $0.13 e$ to each C atom from the underneath Fe crystal. The increase of electron density on carbon surface greatly reduces the enthalpy change to 0.24 eV and energy barrier to 0.56 eV for stronger chemisorption of O_2 molecules on the CNT surface (Fig. 6a). In contrast, the adsorption of O_2 on the pristine CNTs is endothermic and thermodynamic unfavorable with a huge energy barrier of 2.74 eV and enthalpy change of 1.65 eV (Fig. S7). On this basis, the incorporation of N heteroatoms into graphitic carbon layer induces the charge redistribution to the C atoms nearby, which further strengthens the interaction of Fe@NCNT with O_2 . Specifically, the adsorption of O_2 becomes exothermic with enthalpy change of -0.13 and -1.72 eV at the C sites close to pyridinic N and graphitic N atoms with free long-pair electrons, respectively (Fig. 6b, c). On these sites, the dissociation of chemically adsorbed O_2 into two epoxy intermediates is identified as the rate-limiting step with small energy barrier of 0.22 and 0.42 eV for chemisorption of O_2 on Fe@NCNTs. These oxygenated intermediates could act as the active sites to accelerate the nucleation and

Figure 5 (a) A slab model of Fe@NCNTs for DFT calculation; (b, c, d) the structural models of Fe@CNTs doped with pyridinic-N, graphitic-N and pyrrolic-N, respectively. The grey, blue, pink and purple spheres represent the C, N, the top-layer Fe and the bottom-layer Fe atoms in the models, respectively.

Figure 6 Energy diagrams of the reaction pathway for the adsorption of O_2 molecule on (a) Fe@CNTs, (b) Fe@pyridinic-N doped CNTs, (c) Fe@graphitic-N doped CNTs, (d) Fe@pyrrolic-N doped CNTs. The grey, blue, red, pink and purple spheres represent C, N, O, and the top layer Fe atoms in the models, respectively. The structures above red line are the transition states.

uniform growth of nanosized Li_2O_2 on the CNT surface, which in turn benefits the kinetics for the fast decomposition of discharge products upon charging. For pyrrolic N atoms, the lone-pair electrons belonging to them are included in the conjugation system, and thereby the C sites

close to them are less active. The adsorption of O_2 on them is endothermic with adsorption free energy of 0.50 eV and larger energy barrier of 0.48 eV, which however is still much active than that on the pristine CNTs due to the electron transfer from underlying Fe atoms (Fig. 6d). The pyridinic

N and graphitic N in our sample account for over 94% of total N content, which guarantees the high activity of the Fe@NCNT catalyst.

CONCLUSIONS

In conclusion, a one-pot solid-state pyrolysis strategy has been developed for facile synthesis of N-doped CNTs filled with high content of Fe nanorods. The incorporation of Fe nanorods inside the CNTs greatly enhances the reversibility and activity of CNTs towards Li-O₂ reaction by tailoring the morphology and distribution of the discharge products (Li₂O₂) on the electrode surface. First-principles calculations reveal that the high activity of Fe@NCNT catalyst is originated from the charge transfer and redistribution between Fe nanorods, the graphitic carbon on CNT walls and the active N dopants. Their synergistic effect greatly strengthens the chemisorption and subsequent dissociation of O₂ molecule into the epoxy intermediates on carbon surface. As a result, the Li-O₂ batteries with Fe@NCNT cathode deliver high gravimetric energy density, excellent cycle stability and low charge overpotential to meet the potential demand of high-energy applications.

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Author contributions Wang Z and Qiu J directed and designed the project. Yu M performed the experiments. Liu Y, Zhao Z and Zhou T contributed to the strategy optimization. Wang Z and Yu M analyzed the results and wrote the paper. Zhou S and Zhao J performed the DFT calculation. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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用于长寿命锂-空气二次电池的铁-碳纳米管纳米电缆结构电化学催化剂及其电荷迁移增强机制

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摘要 锂-空气二次电池是当前能量密度最高的二次电池体系之一, 高效阴极催化剂的创制构筑是构筑高性能锂-空气电池的关键技术之一. 本文基于简便易行的全固相热解反应, 设计构筑了一种具有纳米电缆结构的新型铁-碳纳米管电化学催化剂. 第一性原理计算表明碳纳米管与其内部包覆的铁纳米棒之间的电荷迁移与协同分布效应可有效促进氧气在碳纳米管表面的化学吸附与转化. 得益于此, 基于其的锂-空气电池在限制比容量为 600 mA h g^{-1} 时, 循环寿命可达270次, 基于此催化剂与固态放电产物 (Li_2O_2) 总质量的电极比能量可达 $2120\text{--}2600 \text{ W h kg}^{-1}$. 本研究为锂-空气二次电池用高性能阴极催化剂的开发提供了有效途径.