Synthesis of Metal Oxides@C (Metal = Ni, Fe) Based Prussian Blue Analogs as a High-performance Anode Material for Lithium-ion Battery

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Abstract

Ni₃[Fe(CN)₆]₂ nano-cubic precursors were prepared by chemical coprecipitation at room temperature with nickel acetate and potassium ferricyanide as raw materials. The corresponding NiFe₂O₄-NiO@C composites with excellent crystallization were prepared by two-stage oxidation at low temperature. The microstructure and electrochemical behavior of the materials showed that the Prussian blue analog was transformed into metal oxide while the carbon coating was maintained in the two-stage oxidation at low temperature. The existence of the carbon coating reduces the charge transfer impedance to 31.5 Ω. At the current density of 500 mA/g, the reversible capacity of 632.7 mAh/g is maintained after 500 cycles. At the same time, carbon cladding can also enhance the role of pseudocapacitance in the material. At the scanning rate of 0.1 mV/s, the pseudocapacitance account for 54.4% of the total discharge capacity, which is significantly higher than that of uncoated materials.

Keywords Lithium-ion battery · Anode materials · Metal oxide · Prussian blue

1 Introduction

Owing to eco-friendly, high energy density and long cycling stability without memory effect, lithium-ion batteries (LIB) have been extensively used as rechargeable energy storage systems for portable electronic devices and electric vehicles. However, with the improvement of performance requirements for electronic products, LIB has been unable to satisfy the requirements of higher capacity and energy density due to the low theoretical capacity (about 372 mAh/g) of graphite as a positive electrode material [1–3]. Compared with graphite, metal oxide, metal sulfide, metal nitride and

other materials have extremely high specific capacity for LIB anode material [4–7]. Based on conversion reaction mechanism of metal oxides has several times theoretical specific capacity more than that of graphite [8–11]. For example, the theoretical specific capacity of NiO is 731 mAh/g, and the theoretical specific capacities of FeO, Fe₂O₃ and Fe₃O₄ are 744, 1007 and 992 mAh/g, respectively [12–15]. These materials have attracted more attention, which makes that one of the important ways to improve the specific capacity of lithium-ion batteries. In addition, iron oxides and manganese oxides also have the advantages of abundant raw materials, low cost, environmental friendliness, and easy recycling and reuse [16].

However, when the transition metal oxide is used as the anode material of lithium-ion battery, the micro-nano structure of metal oxide would change and damage due to the severe volume effect during charge and discharge [17]. Some active materials lose their lithium storage function, and then the specific capacity of the lithium battery decays sharply. This is a major obstacle to the promotion and application of transition metal oxide anode materials. Therefore, alleviating the volume effect of transition metal oxide anode materials during charge and discharge is a pivotal way to further promote the development of lithium-ion batteries [18, 19]. Based on the

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above reasons, in recent years, researchers mainly put forward the design and construction of special structures to achieve this goal. Among them, the widely used ways are to construct hollow structures [20], core-shell structures [21], nanotubes [22], nanoribbons [23] and so on, and the construction of core-shell structures is one of the most effective methods to maintain the structural stability of materials [24]. In addition, due to the poor conductivity of metal oxides, it limits the electrochemical performance as cathode materials of lithium-ion batteries greatly. The researchers combine metal oxides with conductive materials [19, 25]. In commonly, carbon materials used as composite materials because of the superior electrical conductivity. The composite of transition metal oxides and carbon materials can effectively improve the electrical conductivity of the materials [26–28], and further obtain transition metal oxides/carbon composites with predominant electrochemical properties [29, 30]. Previous studies on the charge storage mechanism in batteries have found that there is an electrochemical behavior of pseudocapacitance during charge and discharge. Pseudocapacitance refers to a supercapacitor in which highly reversible chemical absorption and REDOX reactions occur on the electrode surface, near the surface or in the bulk phase in two or quasi-two dimensions, and the relevant capacitance is generated [31, 32]. In this pseudocapacitive charge storage behavior, the charge is stored on the surface of the material due to the faradaic reactions. Therefore, the study of pseudocapacitance behavior in electrode materials is of great significance for the design and optimization of high-performance electrode materials.

2 Experimental

2.1 Preparation of $\text{NiFe}_2\text{O}_4\text{-NiO@C}$

In this work, authors used the prepared nanocube as the matrix material, dopamine hydrochloride was polymerized on the surface of the material under the action of tris(hydroxymethyl)aminomethane, and formed a polydopamine (PDA) coating, as shown in Fig. 1. After calcination, the polydopamine layer decomposes into a carbon layer, and the corresponding Prussian blue analogs were transformed into transition metal oxides [33]. We found that the transition metal oxide materials with advantageous crystallization can be obtained by this synthesis method under lower temperature, and the existence of carbon coating greatly increases the proportion of pseudocapacitance contribution in the discharge capacity of the materials. The rate capability and cycle stability of the materials have also been greatly improved.

Prussian blue analog $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ nanocube was prepared by chemical coprecipitation at room temperature. Firstly, 1.2 mmol nickel acetate and 1.6 mmol trisodium citrate were dissolved into 40 ml deionized water. Secondly, 0.8 mmol of potassium ferricyanide was dissolved into 40 ml deionized water, and then slowly dropped into the aforementioned mixed solution of nickel acetate and trisodium citrate at a drop acceleration of 2 ml/min. The solution was thoroughly mixed by continuous stirring during the process. After the dripping was completed, aging for 24 h at room temperature. Then, it was centrifuged with deionized water and anhydrous ethanol for several times and dried in a vacuum oven at 60 °C for 10 h. Finally, the orange $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ precursor powder was obtained.

Fig. 1 Preparation process diagram of $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ composite material with core shell structure

0.5 g as-prepared $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ was added into 100 ml deionized water and completely dispersed. 0.121 g of tris(hydroxymethyl)aminomethane was dissolved in the above dispersion, and then 0.1 g of dopamine hydrochloride was added, and stirred for 6 h under 600 r/min at room temperature. The black red powder $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ @PDA material was obtained through centrifugation and washing with deionized water and anhydrous ethanol for several times, drying in the oven at 60 °C for 10 h.

The prepared $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ @PDA material was roasted in a tube furnace for 4 h at 2 °C/min heating rate to 400 °C in a high-purity nitrogen atmosphere. After natural cooling, it was re-roasted in a muffle furnace at 2 °C/min heating rate to 350 °C in air nitrogen atmosphere for 4 h. Finally, the carbon-coated metal oxide materials NiFe_2O_4 -NiO@C was obtained, labeled as NFO@C.

Comparatively, $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ was roasted directly in muff furnace at 600 °C under air atmosphere for 4 h to obtain NiFe_2O_4 -NiO, labeled as NFO.

2.2 Electrochemical Measurements

The prepared NiFe_2O_4 -NiO@C and NiFe_2O_4 -NiO materials were assembled to CR2032 coin cell. The CR2032 coin cell assembled from working electrode, PP membrane and lithium tablet. The active materials (70 wt%), super-P (20 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) were ground evenly. The PVDF dissolved in NMP with a mass concentration of 2% was added. After evenly mixed, the mixture was coated on copper foil to prepare the working electrode. The working electrode was placed in an oven at 60 °C for 10 h for preliminary drying. After drying for 24 h in a vacuum oven at 60 °C, the working electrode was assembled into the coin battery. The dried copper sheet was cut by sheet-punching machine and weighed, and the mass of the active material on the working electrode plate was 1.0–1.5 mg/cm². The 1.0 M LiPF_6 was dissolved in ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate (volume ratio of 1:1:1) as the electrolyte. Complete the assembly of the coin battery in the nitrogen environment. Cyclic voltammetry (CV) curves at different scanning rates were measured at an electrochemical workstation (CHI760B electrochemical, China) with potential ranges from 0.01 to 3.00 V (vs Li/Li). Cyclic charge and discharge tests and rate capability tests were conducted on the Neware BTS tester. The rate capability experiment was conducted with a step current of 100–5000 mA/g (based on the actual mass of the transition metal oxide prepared in the corresponding battery), while the current density of 100 or 500 mA/g was used for the cycle performance experiment. Electrochemical impedance spectroscopy (EIS) was conducted with amplitude of 5 mV, and the frequency ranging at 0.01–100 kHz. The measured data were fitted and analyzed using Zview software.

2.3 Characterization

The crystal structure of the prepared samples was analyzed by X-ray powder diffractometer (XRD, XD-3, Beijing Purkinje General, China) with Cu K α radiation at 36 kV and 20 mA. Field-emission scanning electron microscopy (FE-SEM, JSM-5600, JEOL, Japan) was used to observe the microstructure of the samples.

3 Results and Discussion

Figure 2 shows the XRD diffraction spectrum of the NiFe_2O_4 -NiO@C sample. The diffraction peaks at $2\theta = 37.2^\circ$, 43.3° , 62.9° and 75.4° are matched with (111), (200), (220) and (311) faces of the standard card PDF#47-1049 NiO, respectively. The diffraction peaks at $2\theta = 30.3^\circ$, 35.7° and 57.4° are matched with (220), (311) and (511) faces of standard card PDF#54-0964 NiFe_2O_4 , respectively. Although the roasting temperature was 350 °C in the air atmosphere, transition metal oxide crystals were formed in the NiFe_2O_4 -NiO@C material. The relatively sharp diffraction peaks demonstrate an excellent crystalline state in the material. These testify that $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ @PDA can obtain the corresponding NiFe_2O_4 -NiO material well by calcining in nitrogen at 400 °C and in air at 350 °C successively. However, no diffraction peak of C is found in the XRD pattern, which can be interpreted as the obtained carbon coating is amorphous carbon. The existence of carbon coating layer does not affect the crystal structure of NiFe_2O_4 and NiO. In addition, some studies have shown that the presence of carbon coating shorts the path of ion transfer, and its own porous and fluffy structure can provide a larger specific surface area and additional active sites, so that the material shows excellent performance [21, 26].

Fig. 2 XRD patterns of NiFe_2O_4 -NiO@C sample

To further characterize the as-prepared materials, the morphology of the materials was investigated by SEM. The pure $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ presents as uniform nanocube particles as shown in Fig. 3a, with a particle size of about 110 nm. The product calcined at 600 °C still maintains the uniform nano-cubic morphology, but its size shrinks slightly shown in Fig. 3b. After coating PDA, the general morphology of the material does not change, and still maintains the nano-cubic structure shown in Fig. 3c. The particle size of $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2\text{@PDA}$ is between 185 and 230 nm. After two-stage calcination at 400 °C in nitrogen and 350 °C in air, the material was transformed into $\text{NiFe}_2\text{O}_4\text{-NiO@C}$. There is a depression in the center of the six faces, which is due to the shrinkage of the original nanoparticles after roasting as shown in Fig. 3d. The polydopamine coating is relatively thick, part of the surface carbon layer is burned. The size of the $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ nanocube seen from the figure is about 200 nm.

The as-prepared $\text{NiFe}_2\text{O}_4\text{-NiO}$ and $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ were assembled into a button battery with lithium metal sheet to test their electrochemical properties. Figure 4a, b indicates the cyclic voltammetry curve of the two materials at a scanning rate of 0.1 mV/s, and the scanning potential interval is 0.01–3.00 V. These cyclic voltammetry curves can be used to analyze the impact of carbon coating on the electrochemical behavior of NiFe_2O_4 and NiO in materials, and further explain the electrochemical performance of transition metal oxide/carbon composite cells. For $\text{NiFe}_2\text{O}_4\text{-NiO}$ material, a reduction peak only appeared at 0.42 V during the first round of scanning, in which NiO [formula (2)] and NiFe_2O_4 [formula (1)] had a reduction reaction [34, 35], and a solid electrolyte interface (SEI) membrane was formed. This potential is mainly determined by the generation

potential of SEI membrane. In the following oxidation process, two peaks appeared at the positions of 1.65 and 2.26 V, respectively, caused by the oxidation of Fe [formula (5)] and Ni [formula (4)] [36]. In the second and subsequent reduction process, NFO has a reduction peak at 0.85 V, and the electrochemical reaction occurring in this process is the reduction of Fe_2O_3 [formula (3)] and NiO . Correspondingly, the $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ material also had corresponding electrochemical reactions at various similar potential positions. However, the positions of these peak potentials were all shifted to a certain extent, especially in the discharge process of the first turn, the peak position was shifted downward to 0.31 V, and the peak strength was greatly enhanced. This can be explained as an excellent amorphous carbon coating enhances the growth of SEI membranes during the first discharge, and drag the reduction potential of NiFe_2O_4 and NiO downward [37].

Meanwhile, in Fig. 4b, the oxidation potential increased to 1.74 and 2.40 V, respectively, corresponding to the oxidation of Fe and Ni. Similar to the reduction potential of the first turn, the peak is also shifted downward to 0.70 V in the second turn and the posterior reduction process. The movement of reduction potential to a smaller direction is mainly due to the embedding of lithium ions in the carbon material and the formation of more SEI films, which makes it more difficult for lithium ions generated by Li_2O inside the material in the process of electrode oxidation to leave, thus pushing up the oxidation potential.

To confirm the rate capabilities of $\text{NiFe}_2\text{O}_4\text{-NiO}$ and $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ anode materials, cyclic charge and discharge under various current densities in the range of 100–5000 mA/g were conducted. Figure 4c indicates the rate capability curves of the prepared materials, and $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ exhibits better rate capability. The reversible capacities of $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ at current densities of 100, 200, 500, 1000, 2000 and 5000 mAh/g are 923.9, 852.2, 704.8, 554.5, 396.1 and 193.2 mAh/g, respectively.

Fig. 3 SEM images: **a** $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ precursor, **b** $\text{NiFe}_2\text{O}_4\text{-NiO}$ calcined at 600 °C in air; **c** $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2\text{@PDA}$ precursor; **d** $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ obtained through two-stage low-temperature roasting

Fig. 4 Cyclic voltammogram curves of **a** NiFe₂O₄-NiO and **b** NiFe₂O₄-NiO@C at a scan rate of 0.1 mV/s; **c** rate cycle test at various current densities; **d** Nyquist plots and the equivalent circuit used to fit impedance statistics; **e** charge/discharge voltage profiles of NiFe₂O₄-NiO@C at 500 mA/g and **f** cyclability at 500 mA/g

The discharge capacity still maintains 953.5 mAh/g when the current density returns to 100 mA/g. The coulombic efficiency of NiFe₂O₄-NiO@C is higher than that of NiFe₂O₄-NiO.

In order to further testify the impact of carbon composite on the conductivity of NiFe₂O₄-NiO@C, the AC impedance spectra of the two materials were conducted. The results show AC impedance spectra of both materials consist of a distinct high-frequency semicircle that corresponds to the process of charge transfer, and a straight line at low frequencies that correspond to the diffusion process of lithium ions near the nanoparticles shown in Fig. 4d. Lower charge

transfer resistance can improve the diffusion rate and charge transfer rate of lithium ion, thus improving the rate property [17, 18]. Table 1 demonstrates the corresponding fitting data. Among them, R_s represents the ohmic resistance, CPE and W represent the constant phase angle element and Warburg impedance, respectively, and they are all process parameters fitted by the software Zview. Compared with NiFe₂O₄-NiO, the charge transfer impedance (R_{ct}) in the electrochemical reaction process of NiFe₂O₄-NiO@C significantly decreases from 365.6 to 32.1 Ω due to the existence of carbon coating layer. This indicates that in NiFe₂O₄-NiO@C material, the carbon coating and transition metal oxide composite

Table 1 EIS spectrum fitting data of NiFe₂O₄-NiO@C and NiFe₂O₄-NiO

Samples	R_s (Ω)	CPE-T	CPE-P	R_{ct} (Ω)	$W-R$	$W-T$	$W-P$
NFO	20.3	3.2×10^{-5}	0.57	365.6	2.4×10^3	2.8×10^2	0.48
NFO@C	19.2	5.6×10^{-7}	0.55	32.1	4.2×10^6	7.1×10^5	0.78

material can well integrate the good electrical conductivity advantage of carbon into the transition metal oxide, which greatly reduces the charge transfer impedance of the composite material, and thus greatly improves the rate capability of the composite material.

Figure 4f shows the cycle stabilities of NiFe₂O₄-NiO@C and NiFe₂O₄-NiO materials under the long cycle charge-discharge test at 500 mA/g current. Figure 4e shows the corresponding charge-discharge curve. In the test process, the material was activated by 5 cycles of charge and discharge at 100 mA/g, and then the current density was adjusted to 500 mA/g. Obviously, the NiFe₂O₄-NiO@C material maintained a higher discharge capacity after 500 cycles, and the final reversible capacity was 632.7 mAh/g, while the NiFe₂O₄-NiO was only 58.8 mAh/g. During the cycle, the initial discharge capacity of NiFe₂O₄-NiO@C material decreases rapidly due to the change of current density. The subsequent continuous decline is due to the change in the volume of transition metal oxide. Compared with NiFe₂O₄-NiO, the volume change has been weakened on NiFe₂O₄-NiO@C during charging and discharging, because the carbon coating greatly mitigates the pulverization caused by volume change, and stabilize lithiation/delithiation space. When the cycle reaches around the 100th cycle, its discharge capacity decays to the lowest point and then gradually increases, reaching about 620 mAh/g at the 232nd cycle, and then maintaining around this capacity until the end of the test. This capacity change is mainly attributed to the structural changes of internal transition metal oxide materials due to volume changes in the early charging and discharging process, as well as the formation of a large number of SEI films. These SEI membranes are essentially passivated layers formed between the electrolyte and the carbon material as a result of electrochemical reaction. The quality of these membranes is closely related to the performance and safety of the battery. The presence of SEI films on composite materials prevents solution co-insertion to a certain extent, and these films adhere to the particles of negative materials, which can expand with the material expansion and effectively alleviate the volume effect in the cycling process [26]. Similar to most transition metal oxide materials, reversible SEI films containing a large number of metallic particles are formed on the surface of the materials. The rapid charging and discharging process contributed by the reversible SEI films is the main reason for pushing up the reversible capacity after 100 cycles. Carbon cladding, on the other hand, provides a stable site for these changes,

resulting in a continuously stable capacity and, ultimately, great cyclic stability of NiFe₂O₄-NiO@C.

In order to further analyze the electrode dynamics information during the charging and discharging process, several different scanning speeds of 0.1–2.0 mV/s were selected to test the CV curve of NiFe₂O₄-NiO and NiFe₂O₄-NiO@C. The test results of NiFe₂O₄-NiO are shown in Fig. 5a. A reduction peak and two oxidation peaks in the figure increase regularly with the change of scanning rate. Based on the tested CV curve data, formulas (7) and (8) are used to obtain the b value and further fit the contribution ratio of pseudocapacitance in the charging and discharging process [38, 39].

$$\log i = b \log v + \log a. \quad (7)$$

$$i(V) = k_1 v + k_2 v^{1/2}. \quad (8)$$

By calculating the b values of the three REDOX peaks, it is found that the three b values are all between 0.5 and 1, which means that the discharge capacity is jointly contributed by capacitor and electrochemical reaction during the charging and discharging process [31]. The b values corresponding to Peak1, Peak2 and Peak3 are 0.62, 0.53 and 0.51, respectively. By solving the k_1 and k_2 in the formula, the performance of the pseudocapacitance at the scanning rate of 0.1 mV/s is obtained. As shown in Fig. 5c, the shadow part is a fitted CV curve made at the scanning rate of 0.1 mV/s, which accounts for 19.4% of the real measured CV curve area, which means that the pseudocapacitance contribution accounts for 19.8% at this scanning rate [32]. Figure 5d shows the corresponding pseudocapacitance contribution ratio obtained by fitting at different scanning rates. As the scan rate increases, the reversible capacity of the conversion reaction mechanism in NiFe₂O₄-NiO materials decreases gradually, so the reversible capacity decreases greatly after increasing the charge-discharge current.

Correspondingly, Fig. 6a shows the CV curve of NiFe₂O₄-NiO@C at disparate scanning rates, and Fig. 6b shows the fitting of b values of Peak1, Peak2 and Peak3, which are, respectively, 0.82, 0.76 and 0.74. By solving the k_1 and k_2 in the formula, the performance of pseudocapacitance at the scanning rate of 0.1 mV/s is investigated. As shown in Fig. 6c, the shaded part is the pseudocapacitance contribution of fitting, accounting for 54.4% of the real measured CV curve area. Figure 6d shows the pseudocapacitance contribution ratio of NiFe₂O₄-NiO@C fitted at disparate scanning rates, which is much better than that

Fig. 5 Kinetics information of working electrode, contribution analysis of pseudocapacitance calculation of $\text{NiFe}_2\text{O}_4\text{-NiO}$: **a** cyclic voltammogram curves at various scan rates; **b** b value calculation; **c** the fitted CV curves at 0.1 mV/s; **d** the fitted pseudocapacitance contribution rate at various scan rates

of $\text{NiFe}_2\text{O}_4\text{-NiO}$. This explains its excellent performance at high current density. The capacity contributed by the pseudocapacitance comes from a rapid charge–discharge process, and at higher charge–discharge currents the pseudocapacitance is less affected than the conversion reaction mechanism. Therefore, the $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ material with more contribution of pseudocapacitance has excellent cyclic stability. The test results effectively show that the composite with carbon materials increases the proportion of capacitive reaction mechanism of $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ in electrochemical reaction. The electrochemical stability of the material at high current density and the reason of capacity attenuation are also explained from another point of view.

4 Conclusion

Uniform $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2\text{@PDA}$ nanocube was prepared by self-polymerization of dopamine on the surface of Prussian blue analog in alkaline aqueous solution. The transition metal oxide carbon composite with good crystallization was prepared by two-stage oxidation at low temperature. The micromorphology and electrochemical performance analysis of the prepared materials showed that the charge transfer impedance of the $\text{NiFe}_2\text{O}_4\text{-NiO@C}$ composite material decreased from 365.6 to 31.5 Ω of the carbon-free cladding material. At the current density of 500 mA/g, the reversible capacity of the composite material after 500 cycles is maintained at 632.7 mAh/g, while $\text{NiFe}_2\text{O}_4\text{-NiO}$ only 58.8 mAh/g is left. Moreover, carbon cladding can also enhance the role of pseudocapacitance in these materials. At the scanning rate of 0.1 mV/s, the composite's pseudocapacitance ratio is 54.4%, which is significantly higher than that of the corresponding uncoated materials.

Fig. 6 Kinetics information of working electrode, contribution analysis of pseudocapacitance calculation of NiFe₂O₄–NiO@C: **a** cyclic voltammogram curves at different scan rates; **b** b value calculation; **c** the fitted CV curves at 0.1 mV/s; **d** the fitted pseudocapacitance contribution rate at various scan rates

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References

- [1] B. Ding, Z. Cai, Z. Ahsan, Y. Ma, S. Zhang, G. Song, C. Yuan, W. Yang, C. Wen, A review of metal silicides for lithium-ion battery anode application. *Acta Metall. Sin.-Engl. Lett.* (2020). <https://doi.org/10.1007/s40195-020-01095-z>
- [2] Z. Xue, L. Li, L. Cao, W. Zheng, W. Yang, X. Yu, J. Alloys Compd. **825**, 153966 (2020)
- [3] M. Jiang, M. Jiang, H. Gao, J. Chen, W. Liu, Y. Ma, W. Luo, J. Yang, Comparison of additives in anode: the case of graphene, MXene, CNTs integration with silicon inside carbon nanofibers. *Acta Metall. Sin.-Engl. Lett.* (2020). <https://doi.org/10.1007/s40195-020-01153-6>
- [4] A. Eftekhari, *Energy Storage Mater.* **7**, 157 (2017)
- [5] Y. Chen, Z. Bi, X. Li, X. Xu, S. Zhang, X. Hu, *Electrochim. Acta* **224**, 534 (2017)
- [6] H. Xu, X.D. Zhu, K.N. Sun, Y.T. Liu, X.M. Xie, *Adv. Mater. Interfaces* **2**, 15000239 (2015)
- [7] X. Chen, Y. Huang, K. Zhang, X. Feng, M. Wang, *Electrochim. Acta* **259**, 131 (2018)
- [8] J. Wu, W. Tu, Y. Zhang, B. Guo, S. Li, Y. Zhang, Y. Wang, M. Pan, *Powder Technol.* **311**, 200 (2017)
- [9] X. Shen, Z. Tian, R. Fan, L. Shao, D. Zhang, G. Cao, L. Kou, Y. Bai, *J. Energy Chem.* **27**, 1067 (2018)
- [10] Z. Liu, Q. Yu, Y. Zhao, R. He, M. Xu, S. Feng, S. Li, L. Zhou, L. Mai, *Chem. Soc. Rev.* **48**, 285 (2019)
- [11] Y. Ding, D. Mu, B. Wu, R. Wang, Z. Zhao, F. Wu, *Appl. Energy* **195**, 586 (2017)
- [12] S. Yu, V.M.H. Ng, F. Wang, Z. Xiao, C. Li, L.B. Kong, W. Que, K. Zhou, *J. Mater. Chem. A* **6**, 9332 (2018)
- [13] S.L. Zhang, B.Y. Guan, H.B. Wu, X.W. Lou, *Nano-Micro Lett.* **10**, 44 (2018)
- [14] J.R. He, L. Luo, Y.F. Chen, A. Manthiram, *Adv. Mater.* **29**, 5 (2017)
- [15] L. Zhang, H.B. Wu, X.W. Lou, *Adv. Energy Mater.* **4**, 1300958 (2014)
- [16] K. Zhang, S.J. Liang, X.X. Yin, P. Gao, R. Ding, E.H. Liu, *J. Electroanal. Chem.* **851**, 4 (2019)
- [17] S. Mohapatra, S.V. Nair, A.K. Rai, *Acta Metall. Sin.-Engl. Lett.* **31**, 164 (2018)
- [18] X. Yang, Y.Y. Wang, B.H. Hou, H.J. Liang, X.X. Zhao, H.S. Fan, G. Wang, X.L. Wu, Nano-SnO₂ decorated carbon cloth as flexible, self-supporting and additive-free anode for sodium/lithium-ion

- batteries. *Acta Metall. Sin. (Engl. Lett.)* (2020). <https://doi.org/10.1007/s40195-020-01001-7>
- [19] K. Cao, T. Jin, L. Yang, L. Jiao, *Mater. Chem. Front.* **1**, 2213 (2017)
- [20] J. Tian, Q. Shao, X. Dong, J. Zheng, D. Pan, X. Zhang, H. Cao, L. Hao, J. Liu, X. Mai, Z. Guo, *Electrochim. Acta* **261**, 236 (2018)
- [21] X.R. He, Y.J. Zhang, L.F. Yang, J.L. Zhao, H.T. Li, Y.B. Gao, B. Wang, X.D. Guo, Facile fabrication of core-shell structure Fe_3O_4 @C nanodots for enhanced lithium-sulfur batteries. *Acta Metall. Sin.-Engl. Lett.* (2020). <https://doi.org/10.1007/s40195-020-01104-1>
- [22] Z. Wang, Z. Zhang, J. Xia, W. Wang, S. Sun, L. Liu, H. Yang, *J. Alloy. Compd.* **769**, 969 (2018)
- [23] W. Shi, Y. Zhang, J. Key, P.K. Shen, *J. Power Sour.* **379**, 362 (2018)
- [24] W. Lu, X. Guo, Y. Luo, Q. Li, R. Zhu, H. Pang, *Chem. Eng. J.* **355**, 208 (2019)
- [25] T. Dong, G. Wang, P. Yang, *Diam. Relat. Mat.* **73**, 210 (2017)
- [26] S.Z. Liang, X.Y. Wang, Y.G. Xia, S.L. Xia, E. Metwalli, B. Qiu, Q. Ji, S.S. Yin, S. Xie, K. Fang, L.Y. Zheng, M.M. Wang, X.X. Zuo, R.J. Li, Z.P. Liu, J. Zhu, P. Muller-Buschbaum, Y.J. Cheng, *Acta Metall. Sin.-Engl. Lett.* **31**, 910 (2018)
- [27] S. Mu, Q. Liu, P. Kidkhunthod, X. Zhou, W. Wang, Y. Tang, Molecular grafting towards high-fraction active nanodots implanted in N-doped carbon for sodium dual-ion batteries. *Natl. Sci. Rev.* (2020). <https://doi.org/10.1093/nsr/nwaa178>
- [28] F. Dou, L. Shi, G. Chen, D. Zhang, *Electrochem. Energy Rev.* **2**, 149 (2019)
- [29] D. Du, W. Yue, X. Fan, K. Tang, X. Yang, *Electrochim. Acta* **194**, 17 (2016)
- [30] J. Shao, J. Feng, M. Zhu, H. Zhou, A. Yuan, *J. Mater. Sci.-Mater. Electron.* **30**, 982 (2019)
- [31] R. Yang, F. Zhang, X. Lei, Y. Zheng, G. Zhao, Y. Tang, C.S. Lee, *A.C.S. Appl. Mater. Interfaces* **12**, 47539 (2020)
- [32] N. Li, F. Zhang, Y. Tang, *J. Mater. Chem. A* **6**, 17889 (2018)
- [33] J. Nai, X.W. Lou, *Adv. Mater.* **31**, 1706825 (2019)
- [34] P. Preetham, S. Mohapatra, S.V. Nair, D. Santhanagopalan, A.K. Rai, *RSC Adv.* **6**, 38064 (2016)
- [35] L. Ma, X.Y. Pei, D.C. Mo, Y. Heng, S.S. Lyu, Y.X. Fu, *J. Mater. Sci.-Mater. Electron.* **30**, 5874 (2019)
- [36] H. Xu, X. Wang, H. Liu, J. Wang, X. Dong, G. Liu, W. Yu, Y. Yang, H. Zhang, *J. Mater. Sci.* **53**, 15631 (2018)
- [37] Y. Zhang, W. Cao, Y. Cai, J. Shu, M. Cao, *Inorg. Chem. Front.* **6**, 961 (2019)
- [38] L.P. Wang, Y. Leconte, Z. Feng, C. Wei, Y. Zhao, Q. Ma, W. Xu, S. Bourrioux, P. Azais, M. Srinivasan, Z.J. Xu, *Adv. Mater.* **29**, 1603286 (2017)
- [39] P. Lu, Y. Sun, H. Xiang, X. Liang, Y. Yu, *Adv. Energy Mater.* **8**, 1702434 (2018)