Ni-CeO$_2$ Heterostructures in Li-S Batteries: A Balancing Act between Adsorption and Catalytic Conversion of Polysulfide

Yang Kong, Xin Ao,* Xiao Huang, Jinglong Bai, Shangquan Zhao, Jinyong Zhang,* and Bingbing Tian*

Lithium–sulfur (Li–S) batteries have attracted considerable attention over the last two decades because of a high energy density and low cost. However, the wide application of Li–S batteries has been severely impeded due to the poor electrical conductivity of S, shuttling effect of soluble lithium polysulfides (LiPSs), and sluggish redox kinetics of S species, especially under high S loading. To address all these issues, a Ni–CeO$_2$ heterostructure-doped carbon nanofiber (Ni-CeO$_2$-CNF) is developed as an S host that combines the strong adsorption with the high catalytic activity and the good electrical conductivity, where the LiPSs anchored on the heterostructure surface can directly gain electrons from the current collector and realize a fast conversion between S$_8$ and Li$_2$S. Therefore, Li–S batteries with S@Ni-CeO$_2$-CNF cathodes exhibit superior long-term cycling stability, with a capacity decay of 0.046% per cycle over 1000 cycles, even at 2 C. Noteworthy, under a sulfur loading up to 6 mg cm$^{-2}$, a high reversible areal capacity of 5.3 mAh cm$^{-2}$ can be achieved after 50 cycles at 0.1 C. The heterostructure-modified S cathode effectively reconciles the thermodynamic and kinetic characteristics of LiPSs for adsorption and conversion, furthering the development of high-performance Li–S batteries.

1. Introduction

Lithium–sulfur (Li–S) batteries are considered ideal candidates for next-generation energy storage devices due to a high theoretical specific capacity (1675 mAh g$^{-1}$) and energy density (2600 Wh kg$^{-1}$).

To date, strenuous efforts have been made to address the abovementioned issues.

To enhance chemical adsorption with LiPSs, polar materials (including various metal particles, oxides, sulfides, nitrides, and carbides) have been mixed/doped with carbon materials as sulfur hosts for Li–S batteries. Experimental and theoretical studies have shown that polar oxides can effectively immobilize LiPSs by strong chemisorption. Many polar oxides, such as SiO$_2$, SnO$_2$, MnO$_2$, CeO$_2$, TiO$_2$, MgO, and VO$_2$, have been introduced into cathodes to effectively adsorb LiPSs by chemical interactions. However, most of the metal oxides have poor electrical conductivities and cannot directly gain electrons from a current collector, such that the LiPSs anchored on the carbon surface cannot fully participate in electrochemical reactions. Thus, metal oxides are generally composed/doped with carbon materials as S carriers for cathodes in...
Li–S batteries. LiPSs can thus diffuse to the conductive carbon surface to complete the reaction. Unfortunately, carbon materials exhibit weak catalytic activity in accelerating the redox kinetics of S and Li₂S. The strong adsorption and weak conversion of LiPSs results in insufficient utilization of S and poor cycling performance. Transition metals, such as Fe, Co, and Ni, can provide the high electrical conductivity and good catalytic conversion in Li–S batteries, but the nonpolar metal particles cannot effectively anchor LiPSs and suppress the shuttle effect during cycling.

In this work, we innovatively present a Ni-CeO₂ heterostructure-doped carbon nanofiber (Ni-CeO₂-CNF) as an S host material for Li–S batteries (Figure 1a). Experimental measurements and theoretical calculations show that the...
Ni–CeO₂ heterostructure combines the strong adsorption with excellent catalytic activity and good electric conductivity, where the LiPSs anchored on the heterostructure can directly gain electrons from the current collector and realize a fast conversion between S₂ and Li₂S (Figure 1b). In the absence of catalysts, the S cathode with CeO₂-doped carbon nanofibers (S@CeO₂-CNF) has strong adsorption for LiPSs but achieves slow conversion of LiPSs (Figure 1c). By sharp contrast, carbon nanofibers (CNFs) without CeO₂ and Ni catalysts form a long-range conductive network but have weak adsorption and achieve slow conversion of LiPSs, leading to poor cycling performance (Figure 1d). As a result, in the presence of Ni-CeO₂-CNF, the sulfur cathode exhibits both excellent long-term cycling stability (a low decay rate of 0.046% per cycle during 1000 cycles at 2 C) and a high-rate capability (533.8 mAh g⁻¹ even at a 3 C rate). Meanwhile, under a sulfur loading up to 6 mg cm⁻², a high reversible areal capacity of 5.3 mAh cm⁻² can be reached after 50 cycles at 0.1 C. Thus, strong adsorption and fast redox kinetics of LiPSs are regulated in S cathodes, promoting the practical application of Li–S batteries.

2. Results and Discussions

SEM images of CNFs, CeO₂-CNFs, and Ni-CeO₂-CNFs obtained after high-temperature annealing (900 °C) present a crosslinked nanofiber morphology, where each fiber appears virtually uniform with a diameter of ≈200 nm (Figure 2a). A TEM image of CNFs (Figure 2b) shows no nanoparticles on the surface. By contrast, abundant nanoparticles uniformly decorate the CeO₂-CNF and Ni-CeO₂-CNF surfaces (Figure 2c). Clear lattice fringes of CeO₂ can be observed in a high-resolution transmission electron microscopy (HR-TEM) image of CeO₂-CNF (Figure 2d). In particular, an HR-TEM image (Figure 2f) of Ni-CeO₂-CNF exhibits clear lattice fringes of Ni(111) and CeO₂(111), demonstrating the in situ formation of Ni-CeO₂ heterostructures.[15] The Ni-CeO₂ heterostructures with homogeneous distributions of Ni, Ce and O elements are further confirmed by EDS elemental mappings (Figure 2g).

X-ray diffraction (XRD) patterns (Figure S4, Supporting Information) of CNF, CeO₂-CNF, and Ni-CeO₂-CNF exhibit relatively intense peaks at 23.5° (JCPDS 26–1076) and 44.5° (JCPDS 50–1086), which are in good agreement with those of graphitized carbon materials.[36] To further evaluate the graphic degree of the samples, Raman spectra were analyzed (Figure S5, Supporting Information). There are two typical characteristic peaks at 1350 cm⁻¹ (D band) and 1580 cm⁻¹ (G band) of disordered carbon and ordered graphitic carbon, respectively.[37] The intensity ratio of the D-to-G band (I_D/I_G), representing the carbon graphitization degree of CNFs, CeO₂-CNFs, and Ni-CeO₂-CNFs, are all close to 1, indicating similar graphitization of the three materials. The specific surface area and pore structure of CNF (Figure S6, Supporting Information), CeO₂-CNF (Figure S6, Supporting Information) and Ni-CeO₂-CNF (Figure 3a) were characterized using nitrogen adsorption-desorption isotherms.[26,37] The specific surface areas of CNF, CeO₂-CNF, and Ni-CeO₂-CNF are 66.7, 232.4, and 159.0 m² g⁻¹, respectively. The pore volume of CNF, CeO₂-CNF, and Ni-CeO₂-CNF are 0.05, 0.14, and 0.13 cm³ g⁻¹, respectively. The BJH pore size distribution curves demonstrate the presence of mesopores in the material structures (2–10 nm). Meanwhile, CNF and CeO₂-CNF present a small number of micropores, as confirmed by the BJH pore size distribution curves. TGA measurements were used to determine the sulfur contents of the S@CeO₂-CNF and S@Ni-CeO₂-CNF composites. The weight content of S in the S@CeO₂-CNF and S@Ni-CeO₂-CNF were determined to be 64 wt% from the change in the respective curve (Figure S7, Supporting Information, Figure 3b). The chemical bonding states of Ni-CeO₂-CNF were studied by X-ray photoelectron spectroscopy (XPS). The C 1s spectrum of Ni-CeO₂-CNF can be fit with four peaks (Figure 3c) corresponding to C–C (284.8 eV), C–O (285.7 eV), C–N (286.5 eV) and C–O (288.5 eV).[8] The C–N peak was produced by the decomposition of PAN and PVP. Figure 3d shows the XPS spectra of O 1 s, in which the peaks at 531.3, 532.5, and 533.8 eV are attributed to lattice oxygen (O²⁻), adsorbed oxygen species (O2⁻), and hydroxyl species (OH⁻), respectively.[38] The XPS spectra (Figure 3e) exhibits Ce 3d oxidation states at 885.6 and 903.5 eV that are assigned to Ce 3d₅/₂ and Ce 3d₃/₂, respectively. The i, ii, and II peaks are assigned to Ce²⁺. The i, iii, iv, I, III, and IV peaks are related to Ce⁴⁺.[39] The high-resolution XPS spectra (Figure 3f) of Ni 2p in Ni-CeO₂-CNF can be fitted to the zero-valence state (854.5 and 870.1 eV) and ionic state (856.5 and 872.5 eV) with satellites from the Ni–O species (861.1 eV), verifying the existence of metallic Ni, CeO₂-CNF can be fit with four peaks (Figure 3c) corresponding to C–C (284.8 eV), C–C (285.7 eV), C–N (286.5 eV) and C–O (288.5 eV).[8] The C–N peak was produced by the decomposition of PAN and PVP. Figure 3d shows the XPS spectra of O 1 s, in which the peaks at 531.3, 532.5, and 533.8 eV are attributed to lattice oxygen (O²⁻), adsorbed oxygen species (O2⁻), and hydroxyl species (OH⁻), respectively.[38] The XPS spectra (Figure 3e) exhibits Ce 3d oxidation states at 885.6 and 903.5 eV that are assigned to Ce 3d₅/₂ and Ce 3d₃/₂, respectively. The i, ii, and II peaks are assigned to Ce²⁺. The i, iii, iv, I, III, and IV peaks are related to Ce⁴⁺.[39] The high-resolution XPS spectra (Figure 3f) of Ni 2p in Ni-CeO₂-CNF can be fitted to the zero-valence state (854.5 and 870.1 eV) and ionic state (856.5 and 872.5 eV) with satellites from the Ni–O species (861.1 eV), verifying the existence of metallic Ni. The C 1s, Ce 3d and Ni 2p (Figure S8, Supporting Information) of S@Ni-CeO₂-CNF were further analyzed. The results show that Ni-CeO₂-CNF loaded with S is stable.

To corroborate the chemical interaction between the host matrix and LiPSs, a polysulfide adsorption visualization test was conducted on CNF, CeO₂-CNF, and Ni-CeO₂-CNF. The addition of CeO₂-CNF and Ni-CeO₂-CNF to a Li₄S₈ solution causes the solution color to change from dark yellow to colorless (transparent, inset of Figure 4a). Soluble Li₄S₈ is almost completely adsorbed by CeO₂-CNF and Ni-CeO₂-CNF, as confirmed by UV–vis results, in which the characteristic peaks of Li₄S₈ (280 nm) and Li₂S₄ (410 nm) are absent (Figure 4a).[40] By contrast, the solution containing CNFs and the blank Li₂S₈ solution remain yellow, and distinct characteristic peaks of Li₂S₈ and Li₄S₈ appear in the UV–vis spectra (Figure 4a). All the above mentioned results indicate that the CeO₂-CNF and Ni-CeO₂-CNF composite powders have a strong adsorption ability for soluble LiPSs. To determine the catalytic activity of Ni-CeO₂-CNF toward the reduction and oxidation of LiPSs, cyclic voltammetry (CV) measurements were performed on symmetrical cells with CNF, CeO₂-CNF, and Ni-CeO₂-CNF as the working and counter electrodes. In Figure 4b, the CV curves of Ni-CeO₂-CNF show four pronounced redox peaks and significantly higher current-density peaks than those of CNF and CeO₂-CNF, implying superior electrocatalytic activity for S reaction kinetics.[41] To analyze the superiority of Ni-CeO₂-CNF toward Li₂S nucleation, potentiostatic discharge curves (Figure 4c) of CNF, CeO₂-CNF, and Ni-CeO₂-CNF cells were tested at 2.05 V with an Li₄S₈ solution as the electrolyte. The Ni-CeO₂-CNF electrode exhibits the earliest and highest current responses (0.252 mA at 2170 s for Ni-CeO₂-CNF, 0.127 mA at 8185 s for CeO₂-CNF, and 0.068 mA at 20360 s for CNF). The Ni-CeO₂-CNF electrode also exhibits a higher Li₂S precipitation capacity (227.1 mAh g⁻¹) than the CeO₂-CNF (93.6 mAh g⁻¹) and CNF electrodes (75.0 mAh g⁻¹). This result indicates a lower barrier to Li₂S formation on the Ni-CeO₂ heterostructures compared to CeO₂-CNF and CNF.[42] The diffusivity of Li ions was determined from the CV measurements...
curves of S@CNF (Figure S9), S@CeO2-CNF (Figure S10, Supporting Information) and S@Ni-CeO2-CNF (Figure 4d) cathodes assembled in Li–S batteries. The linear relationship between the peak current density (I_{\text{peak}}) and the square root scanning rate (\sqrt{v}) is expressed by the Randles–Sevcik equation: 
\[ I_{\text{p}} = (2.65 \times 10^5)n^{1.5}S^{0.5}D^{0.5}C^{0.5}\sqrt{v}, \]
where \(n\) denotes the number of transfer charges, \(S\) denotes the surface area of the active electrode, \(D\) denotes the diffusion coefficient of Li ions, and \(C\) denotes the concentration of Li ions.\(^{[43]}\) The peak currents at the square root of different scan rates are shown in Figure 4e. The slopes of the S@CNF, S@CeO2-CNF, and S@Ni-CeO2-CNF curves are 2.18, 3.11, and 5.83, respectively, at peak 1; 1.10, 1.40, and 2.28, respectively, at peak 2; and 0.98, 2.27, and 2.98, respectively, at peak 3. The significantly larger slope corresponding to the S@Ni-
CeO$_2$-CNF compared to those of the other cathodes demonstrates a higher diffusion rate of Li ions and faster kinetics of LiPSs conversion during the redox process. To further investigate the internal resistances of cells with S@CNF, S@CeO$_2$-CNF, and S@Ni-CeO$_2$-CNF cathodes during the discharge/charge process, galvanostatic intermittent titration (GITT) profiles were measured at 0.1 C. The internal resistances to nucleation and activation of Li$_2$S are indicated by the dip depth in the discharging and charging profiles (shown by the arrows in Figure 4f–h). Polarization during the discharge–charge process can be quantified by the relative size of $\Delta R_{\text{internal}}$ in GITT tests according to the following relation:

$$\Delta R_{\text{internal}} (\Omega) = \left| \frac{\Delta V_{\text{QOCV–CCV}}}{I_{\text{applied}}} \right|$$

where $\Delta V_{\text{QOCV–CCV}}$ is the voltage difference between the points of quasi open-circuit voltage (QOCV) and closed-circuit voltage (CCV), and $I_{\text{applied}}$ is the applied current, as shown in Figure 4f–h inset. The S@Ni-CeO$_2$-CNF battery exhibits smaller $\Delta R_{\text{internal}}$ values than the other batteries (Figure 4i) between the Li$_2$S nucleation and activation points, indicating that the S@Ni-CeO$_2$-CNF electrodes have the lowest internal resistance. All the results of the abovementioned experiments indicate that the Ni-CeO$_2$ heterostructures have a strong adsorption ability for soluble LiPSs and effectively accelerate the electrochemical reaction kinetics during the redox process.

The CV profiles of the cells with S@Ni-CeO$_2$-CNF between 1.7 and 2.7 V at a scan rate of 0.05 mV s$^{-1}$ are clearly shown in Figure 5a. The two cathodic peaks at 2.328 and 2.071 V correspond to the reduction of S$_8$ to high-order LiPSs and further reduction of LiPSs to short-chain solid Li$_2$S/Li$_2$S. The two anodic peaks are attributed to the reverse process of transforming solid Li$_2$S/Li$_2$S to LiPSs (2.316 V) and further to S$_8$ (2.369 V).[44] Compared to S@CNF and S@CeO$_2$-CNF (Figure 5a), S@Ni-CeO$_2$-CNF has a cathodic peak at a higher potential (2.071 V) and anodic peaks at lower potentials (2.316 V), indicating enhanced reaction kinetics. Good overlap of the initial three CV cycles also suggests good
The galvanostatic discharge/charge profiles of batteries with different materials at 0.1 C are compared in Figure 5b. The initial discharge capacity is 1327.6 mAh g\(^{-1}\) for S@Ni-CeO\(_2\)-CNF, 1286.2 mAh g\(^{-1}\) for S@CeO\(_2\)-CNF, and 1190.2 mA h g\(^{-1}\) for S@CNF. The discharge/charge plateaus are significantly longer for S@Ni-CeO\(_2\)-CNF than the other materials, resulting in a higher capacity. Notably, the cell with the S@Ni-CeO\(_2\)-CNF cathode shows a stable and flat discharge plateau with the lowest polarization potential of 0.116 V. The electrochemical impedance spectroscopy (EIS) curves of the different batteries after ten cycles are shown in Figure 5c. The semicircle in the high-frequency region reflects the charge-transfer resistance at the carbon interface, and the semicircle in the medium-frequency region indicates the formation of a solid Li\(_2\)S@Li\(_2\)S\(_2\) film on the carbon interface.
The cell with S@Ni-CeO2-CNF produces the smallest semicircle in the Nyquist plot, indicating high ion transport and more ideal conductivity, which can also decrease the charge-transfer resistance.

The cells with S@Ni-CeO2-CNF also display the highest rate performance for rates ranging from 0.2 to 3 C (Figure 5d). The discharge capacity of S@Ni-CeO2-CNF reaches 1197.9 (0.2 C), 938.6 (0.5 C), 779.1 (1 C), 653.2 (2 C), and 572.8 mAh g\(^{-1}\) (3 C). An average specific capacity of 553.8 mAh g\(^{-1}\) can be achieved even at a high rate of 3 C. As the current rate is returned from 3 to 0.5 C, S@Ni-CeO2-CNF retains a high average specific capacity of 813.6 mAh g\(^{-1}\). This result indicates that the Li–S batteries with S@Ni-CeO2-CNF have a good rate capability and cycle stability. In Figure S12, Supporting Information, the capacity of the S@Ni-CeO2-CNF cathode is initially 1208.7 mAh g\(^{-1}\) and maintained at 919.5 mAh g\(^{-1}\) after 100 cycles at 0.2 C. The capacity of the S@Ni-CeO2-CNF cathode is initially 933.4 mAh g\(^{-1}\) and maintained at 783.6 mAh g\(^{-1}\) after 300 cycles at 0.5 C (Figure 5e). By contrast, the capacities of the S@CNF and S@CeO2-CNF cathodes decay faster (329.0 and 520.8 mAh g\(^{-1}\), respectively) after 300 cycles. Moreover, the S@Ni-CeO2-CNF cathode exhibits superior cycling performance with a small capacity decay of 0.046% per cycle during 1000 cycles at 2 C (Figure 5f). To further explore the electrochemical performance of S@Ni-CeO2-CNF cathodes, a series of tests were carried out under high S loadings of 3.0, 4.0, and 6.0 mg cm\(^{-2}\). A high areal capacity of 5.3 mAh cm\(^{-2}\) (0.1 C) after 50 cycles can be obtained under a sulfur loading of 6 mg cm\(^{-2}\) (Figure 5g). When S loadings are 3.0 and 4.0 mg cm\(^{-2}\),
the initial specific capacities at 0.1 C after the activation process are 1116.4 and 1091.8 mAh g$^{-1}$, respectively, and the remaining capacities after 80 cycles are 774.1 and 683.8 mAh g$^{-1}$ (Figure S13, Supporting Information). Therefore, these results illustrate the good electrochemical performances of the S@Ni-CeO$_2$-CNF cathode even under a high S loading.

Figure 6a,b show the binding energies of Ni, CeO$_2$, and Ni-CeO$_2$ heterostructures with S$_8$, Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_2$, and Li$_2$S. The Ni-CeO$_2$ heterostructure exhibits the stronger adsorption ability for soluble LiPSs than Ni and CeO$_2$. Therefore, the Ni-CeO$_2$ heterostructure can efficiently mitigate the shuttling of LiPSs.[32,46] To explain the improved conversion of LiPSs by the S@Ni-CeO$_2$-CNF cathode, we performed DFT calculations for the Gibbs free energies of different possible reactions of LiPSs on the Ni-CeO$_2$ heterostructure and compared the results to those for similar reactions on Ni and CeO$_2$. During the discharge process, S$_8$ undergoes double reduction with two Li$^+$ ions to form Li$_2$S$_8$. Subsequently, Li$_2$S$_8$ undergoes further reduction and disproportionation with the stepwise formation of Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_2$, and Li$_2$S, and the end product Li$_2$S.147 The Gibbs free energies of the abovementioned reactions on the Ni, CeO$_2$ and Ni-CeO$_2$ heterostructure models are shown in Figure 6c, and the optimized structures of the intermediates on the Ni-CeO$_2$ heterostructure models are shown in the inset of Figure 6c. After the spontaneous conversion of S$_8$ to Li$_2$S$_8$, the subsequent four steps for the formation of Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_2$, and Li$_2$S on all models are either spontaneous (negative Gibbs free energy) or endothermic (positive Gibbs free energy). During the entire discharge process, the rate-limiting step has the largest positive Gibbs free energy among all the steps, which is 1.21 eV for Ni, 0.67 eV for CeO$_2$, and 0.38 eV for the Ni-CeO$_2$ heterostructure. The lowest Gibbs free energy of the rate-limiting step for the Ni-CeO$_2$ heterostructure indicates that the reduction of S is thermodynamically more favorable on the Ni-CeO$_2$ heterostructure than on the Ni and CeO$_2$ substrates. We calculated the density of states (DOS) of the Ni, CeO$_2$ and Ni-CeO$_2$ heterostructures (Figure 6d). The Ni-CeO$_2$ heterostructure is considerably more metallic with a higher DOS at the Fermi level compared to CeO$_2$. The high electrical conductivity of the Ni-CeO$_2$ heterostructure will help the LiPSs on the heterostructure surface directly gain electrons from the current collector, and enhance the rapid electrochemical reactions of S and LiPSs. The results of the abovementioned calculations effectively explain the comprehensively excellent performance of Ni-CeO$_2$-CNF for sulfur hosts.

3. Conclusion

In summary, we developed a novel sulfur host material, Ni-CeO$_2$ heterostructure-doped carbon nanofibers, that combines strong adsorption with high catalytic activity and good electrical conductivity, striking a balance between adsorption and catalytic conversion of LiPSs. The cross-linked carbon nanofiber can also enhance electrical conductivity of the cathode and act as a second barrier to block the LiPSs shuttling. Therefore, in the presence of Ni-CeO$_2$-CNF, the S cathode exhibits both excellent long-term cycling stability (a low decay rate of 0.046% per cycle during 1000 cycles at 2 C) and a high-rate capability (553.8 mAh g$^{-1}$ at a 3 C rate). Moreover, a high reversible areal capacity of 5.3 mAh cm$^{-2}$ can be obtained even after 50 cycles at 0.1 C when the S loading is up to 6 mg cm$^{-2}$. The present study provides an effective strategy for accommodating the thermodynamic and kinetic characteristics of LiPS adsorption and conversion. The material prepared in
this study has considerable application potential for use in high-performance Li-S batteries. Considering the high reversible areal capacity under high S loading, such the Li-S batteries show great application potentials in drones, electric vehicles, portable electronics, and medical devices.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge the financial support from the Guangdong Natural Science Funds (2019A1515010675), the Science and Technology Project of Shenzhen (Grant Nos. JCYJ20190808142206019 and JCYJ20190808142209376). J.Z. acknowledges the financial support from the Guangdong Science and Technology and Open Sharing Fund for the Large-scale Instruments and Equipments of CMUT (DYGX-2021-018).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
adsorption of polysulfide, catalytic conversion, Li–S batteries, Ni-CeO2 heterostructures

Received: December 1, 2021
Revised: December 30, 2021
Published online: April 12, 2022

[1] a) H.-J. Peng, J.-Q. Huang, X.-B. Cheng, Q. Zhang, Adv. Energy Mater. 2017, 7, 1700260; b) Y. Yang, G. Zheng, Y. Cui, Chem. Soc. Rev. 2013, 42, 3018; c) A. Manthiram, S. H. Chung, C. Zu, Adv. Mater. 2015, 27, 1980.
[2] A. Manthiram, Y. Fu, S. H. Chung, C. Zu, Y. S. Su, Chem. Rev. 2014, 114, 11751.
[3] a) Z. Wang, J. Shen, J. Liu, X. Xu, Z. Liu, R. Hu, L. Yang, Y. Feng, J. Liu, Z. Shi, L. Ouyang, Y. Yu, M. Zhu, Adv. Mater. 2019, 31, 1902228; b) C. Li, Z. Xi, D. Guo, X. Chen, L. Yin, Small 2018, 14, 1701986.
[4] R. Fang, S. Zhao, Z. Sun, D. W. Wang, H. M. Cheng, F. Li, Adv. Mater. 2017, 29, 1606823.
[5] G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, Adv. Mater. 2018, 30, 1705590.
[6] a) R. Cao, W. Xu, D. Lv, J. Xiao, J.-G. Zhang, Adv. Energy Mater. 2015, 5, 1402273; b) M. A. Pope, I. A. Aksay, Adv. Energy Mater. 2015, 5, 1500124.
[7] Z. Xing, G. Li, S. Sy, Z. Chen, Nano Energy 2018, 54, 1.
[8] Y. Dai, W. Zheng, X. Li, A. Liu, W. Zhang, X. Jiang, X. Wu, J. Tao, G. He, ACS Appl. Mater. Interfaces 2021, 13, 2521.
[9] L. Zhang, F. Wan, X. Wang, H. Cao, X. Dai, Z. Niu, Y. Wang, J. Chen, ACS Appl. Mater. Interfaces 2018, 10, 5594.
[10] H.-J. Peng, W.-T. Xu, L. Zhu, D.-W. Wang, J.-Q. Huang, X.-B. Cheng, Z. Yuan, F. Wei, Q. Zhang, Adv. Funct. Mater. 2016, 26, 6351.
[11] J. Yan, K. Dong, Y. Zhang, X. Wang, A. A. Aboalhassan, J. Yu, B. Ding, Nat. Commun. 2019, 10, 5584.
[12] C. Chen, Q. Jiang, H. Xu, Y. Zhang, B. Zhang, Z. Zhang, Z. Lin, S. Zhang, Nano Energy 2020, 76, 105033.
[13] a) G.-C. Li, G.-R. Li, S.-H. Ye, X.-P. Gao, Adv. Energy Mater. 2012, 2, 1238; b) J. Zhang, W. Ma, Z. Feng, F. Wu, D. Wei, B. Xi, S. Xiong, J. Energy Chem. 2019, 39, 54; c) F. Wu, J. Chen, R. Chen, S. Wu, L. Li, S. Chen, T. Zhao, J. Phys. Chem. C 2011, 115, 6057.
[14] S. Wang, S. Feng, J. Liang, Q. Su, F. Zhao, H. Song, M. Zheng, Q. Sun, Z. Song, X. Jia, J. Yang, Y. Li, J. Liao, R. Li, X. Sun, Adv. Energy Mater. 2021, 11, 2003314.
[15] F. Wu, S. Zhao, L. Chen, Y. Lu, Y. Su, Y. Jia, L. Bao, J. Wang, S. Chen, R. Chen, Energy Storage Mater. 2018, 14, 383.
[16] Z. Yu, B. Wang, X. Liao, K. Zhao, Z. Yang, F. Xia, C. Sun, Z. Wang, C. Fan, J. Zhang, Y. Wang, Adv. Energy Mater. 2020, 10, 2000907.
[17] a) Y. Wei, Y. Wang, X. Zhang, B. Wang, Q. Wang, N. Wu, Y. Zhang, H. Wu, ACS Appl. Mater. Interfaces 2020, 12, 32058; b) H. Li, D. Liu, X. Zhu, D. Qu, Z. Xie, J. Li, H. Tang, D. Zheng, D. Qu, Nano Energy 2020, 73, 104763; c) T. Wang, D. Su, Y. Chen, K. Yan, L. Yu, L. Liu, Y. Zhong, P. H. L. Notten, C. Wang, G. Wang, Chem. Eng. J. 2020, 401, 126079.
[18] A. Jin, Y. Kim, B. E. A. H. Kim, Chem. Eng. J. 2020, 401, 125042.
[19] Z. Wei Seh, W. Li, J. J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P. C. Hsu, Y. Cui, Nat. Commun. 2013, 4, 1331.
[20] L. B. Ma, R. P. Chen, G. Y. Zhu, Y. Hu, Y. R. Wang, T. Chen, J. Liu, Z. Jin, ACS Nano 2017, 11, 7274.
[21] Z. Xiao, Z. Yang, L. Zhang, H. Pan, R. Wang, ACS Nano 2017, 11, 8488.
[22] D. R. Deng, F. Xue, Y. J. Jia, J. C. Ye, C. D. Bai, M. S. Zheng, Q. F. Dong, ACS Nano 2017, 11, 6031.
[23] W. Cai, G. Li, K. Zhang, G. Xiao, C. Wang, K. Ye, Z. Chen, Y. Zhu, Y. Qian, Adv. Funct. Mater. 2018, 28, 1704865.
[24] X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, W. S. Seh, Q. Cai, W. Li, G. Zhou, C. Zu, Y. Cui, Nat. Commun. 2016, 7, 11203.
[25] a) Z. Li, J. Zhang, X. W. Lou, Angew. Chem., Int. Ed. 2015, 54, 12886; b) H. Chen, W.-D. Dong, F.-J. Xia, Y.-J. Zhang, M. Yan, J.-P. Song, W. Zou, Y. Liu, Z.-Y. Hu, J. Liu, Y. Li, H.-E. Wang, L.-H. Chen, B.-L. Su, Chem. Eng. J. 2020, 381, 122746.
[26] J. Zhang, Q. Rao, B. Jin, J. Lu, Q.-g. He, Y. Hou, Z. Li, X. Zhan, F. Chen, Q. Zhang, Chem. Eng. J. 2020, 388, 124120.
[27] D. Xiao, C. Lu, C. Chen, S. Yuan, Energy Storage Mater. 2018, 10, 216.
[28] T. Zhou, W. Lv, J. Li, G. Zhou, Y. Zhao, S. Fan, B. Liu, B. Li, F. Kang, Z.-H. Yang, Energy Environ. Sci. 2017, 10, 1694.
[29] M. Wang, Y. Song, Z. Sun, Y. Shao, C. Wei, Z. Xia, Z. Tian, Z. Liu, J. Sun, ACS Nano 2019, 13, 13235.
[30] Y. Song, W. Zhao, L. Kong, L. Zhang, X. Zhu, Y. Shao, F. Ding, Q. Zhang, J. Sun, Z. Liu, Energy Environ. Sci. 2018, 11, 2620.
[31] Z. Wu, S. Chen, L. Wang, Q. Deng, Z. Zeng, J. Wang, S. Deng, Energy Storage Mater. 2021, 38, 381.
[32] H. Zhao, B. Tian, C. Su, Y. Li, ACS Appl. Mater. Interfaces 2021, 13, 7171.
[33] X. Song, D. Tian, Y. Qiu, X. Sun, B. Jiang, C. Zhao, Y. Zhang, L. Fan, N. Zhang, Energy Storage Mater. 2021, 47, 248.
[34] S. Zhang, X. Ao, J. Huang, B. Wei, Y. Zhai, D. Zhai, W. Deng, C. Su, D. Wang, Y. Li, Nano Lett. 2021, 21, 9691.
[35] M. Yang, X. Wang, J. Wu, Y. Tian, X. Huang, P. Liu, X. Li, X. Li, H. Li, J. Mater. Chem. A 2021, 9, 18477.
[36] H. Wang, B. Zhang, X. Zeng, L. Yan, J. Zheng, M. Ling, Y. Hou, Y. Lu, C. Liang, *J. Power Sources* **2020**, *473*, 228588.

[37] D. Gueon, J. Yoon, J. T. Hwang, J. H. Moon, *Chem. Eng. J.* **2020**, *390*, 124548.

[38] Z. Kong, Y. Li, Y. Wang, Y. Zhang, K. Shen, X. Chu, H. Wang, J. Wang, L. Zhan, *Chem. Eng. J.* **2020**, *392*, 123697.

[39] X. Ao, X. T. Wang, J. W. Tan, S. L. Zhang, C. L. Su, L. Dong, M. X. Tang, Z. C. Wang, B. B. Tian, H. H. Wang, *Nano Energy* **2021**, *79*, 105475.

[40] D. Luo, G. Li, Y. P. Deng, Z. Zhang, J. Li, R. Liang, M. Li, Y. Jiang, W. Zhang, Y. Liu, W. Lei, A. Yu, Z. Chen, *Adv. Energy Mater.* **2019**, *9*, 1900228.

[41] H. Lin, L. Yang, X. Jiang, G. Li, T. Zhang, Q. Yao, G. W. Zheng, J. Y. Lee, *Energy Environ. Sci.* **2017**, *10*, 1476.

[42] a) Y. Zhang, J. Liu, J. Wang, Y. Zhao, D. Luo, A. Yu, X. Wang, Z. Chen, *Angew. Chem., Int. Ed.* **2021**, *60*, 26622; b) D. Yang, Z. Liang, C. Zhang, J. J. Biendicho, M. Botifoll, M. C. Spadaro, Q. Chen, M. Li, A. Ramon, A. O. Moghaddam, J. Llorca, J. Wang, J. R. Morante, J. Arbiol, S. L. Chou, A. Cabot, *Adv. Energy Mater.* **2021**, *11*, 2101250.

[43] T. Zhang, F. Hu, W. Shao, S. Liu, H. Peng, Z. Song, C. Song, N. Li, X. Jian, *ACS Nano* **2021**, *15*, 15027.

[44] S. Zhang, D. Xu, C. Su, W. Tang, H. Ju, J. Zhang, B. Tian, *Chem. Commun.* **2020**, *56*, 810.

[45] J. Yan, X. Liu, B. Li, *Adv. Sci.* **2016**, *3*, 1600101.

[46] Y. S. He, M. J. Li, Y. G. Zhang, Z. Z. Shan, Y. Zhao, J. D. Li, G. H. Liu, C. Y. Liang, Z. Bakenov, Q. Li, *Adv. Funct. Mater.* **2020**, *30*, 2070123.

[47] a) R. S. Assary, L. A. Curtiss, J. S. Moore, *J. Phys. Chem. C* **2014**, *118*, 11545; b) Z. Du, X. Chen, W. Hu, C. Chuang, S. Xie, A. Hu, W. Yan, X. Kong, X. Wu, H. Ji, L. J. Wan, *J. Am. Chem. Soc.* **2019**, *141*, 3977.