Facile Fabrication of Core–Shell Structure Fe₃O₄@C Nanodots for Enhanced Lithium–Sulfur Batteries

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Abstract

Lithium sulfur battery (LSB) is widely considered as a next-generation battery system due to its high theoretical energy density of 2567 Wh kg^{−1}. However, several inherent issues obstruct the business application of LSB. To address these issues, we assemble core–shell structure Fe₃O₄@C nanodots with 5 nm diameter as a valid sulfur host via a convenient organic pyrolysis treatment followed by calcination. The nanosized Fe₃O₄ particles could expose more chemisorption sites and inhibit the polysulfides shuttle. Moreover, the carbon layer could not only increase the conductivity but also ensure structural integrity during cyclic process. Furthermore, the mesoporous channels around Fe₃O₄@C could supply sufficient space to load sulfur and physically restrict the shuttle of polysulfides. Thus, the resultant S/Fe₃O₄@C cathode shows a highly initial capacity of 1089 mAh g^{−1} at 0.2 C, even retains 655 mAh g^{−1} over 200 cycles at 1 C.

Keywords Fe₃O₄ · Nanodots · Cathode · Lithium–sulfur batteries

1 Introduction

Currently, with the constantly updated electric vehicles and portable electronics, the energy storage devices with high energy and power density, low cost, long cycling life and safety are urgently demanded [1, 2]. Lithium ion battery (LIB) is known as one of the promising future in energy storage fields [3]. But due to low specific capacity and almost arrival of theoretical energy limits, LIB nearly cannot

satisfies the more and more electric storage demands [4]. In that case, lithium sulfur battery (LSB) is widely considered as a next-generation energy storage device [5], because of its high theoretical energy density (2567 Wh kg^{−1}), high theoretical specific capacity (1675 mAh g^{−1}), low cost and environmental friendliness [6, 7].

However, the commercial application of LSB is obstructed by several challenges: the solubility of polysulfide intermediates (Li₂S_x, 4 < x < 8) in the liquid electrolyte and passing through separator repeatedly, called shuttle effect [8]; the huge volume change of sulfur during charge/discharge bring about mechanical degradation and poor cycling life [9]; natural low electronic conductivity of sulfur (5 × 10^{−30} S cm^{−1} at 25 °C) [10]. To overcome these difficulties, a series of techniques and strategies have been intensively investigated, such as application of new electrolytes or electrolytes additives, formation of polysulfide trapping interlayers, impregnation of sulfur into conductive host [11–13].

As we know, various carbon materials, including graphene, mesoporous carbon and carbon fabrics have been utilized as the sulfur host in the cathode [14–17]. While Van der Waals forces of these non-polar carbon materials have a weak effect in adsorbing polysulfides, the capacities still decrease rapidly with long-term cycles. To solve this problem, a series of polar metal oxides with strong chemical

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adsorption toward polysulfides have been considered as additives in the cathode for LSB, such as NiCo₂O_{4-x}, TiO₂ and Fe₃O₄ [18–21].

Based on the theory of Lewis acid–base, transition metal oxides could also play the role of efficient immobilization of polysulfides [22]. Generally, transition metal oxides could further enhance the chemical adsorption of polysulfides compared with carbon based materials, which means more effective suppression of the shuttle effect [23]. Benefits from strong chemical adsorption of polysulfides, low cost, natural abundance and environmental friendliness, Fe₃O₄ have a promising prospect to be used in the cathode of Li–S battery.

However, lacking electrical conductivity and poor specific surface area limit the electrochemical performance of transition metal oxides with traditional structure [24]. Nanoparticles with precisely engineered shape, size, and surface chemistry show several advantages over their bulk counterparts, including higher specific surface area, more active site, and higher utilization efficiency of active materials. Furthermore, nanostructure coated with proper carbon has been widely used to improve electronic transport of transition metal oxides. Therefore, nanoparticles of transition metal oxides with carbon coat could be expected to provide enough electrical conductivity, effective physical and chemical adsorption and abundant specific surface area for sulfur hosts enhance the electrochemical performance of LSB.

Herein, we design and prepare a core–shell structure Fe₃O₄@C as sulfur host. Basic building unit of Fe₃O₄@C is a carbonized Fe₃O₄ nanoparticle about 5 nm diameter. The Fe₃O₄ nanodots could expose more chemisorption sites and inhibit polysulfides shuttle. The surface carbon coating layer supported by Fe₃O₄ cores could provide efficient conductivity and structural stability. In addition, the mesoporous channels around Fe₃O₄@C are expected to alleviate mechanical degradation by volume change, supply space to load sulfur and physically restrict polysulfides losing. Thus, the S/Fe₃O₄@C cathode presents the expected electrochemical performance with a high initial capacity of 1089 mAh g⁻¹ at 0.2 C and 816 mAh g⁻¹ at 1 C. This nanostructure provides a promising choice to improve specific capacity and cycling stability and suppress shuttle effect for LSB.

2 Experimental

2.1 Synthesis of OA-Capped Fe₃O₄

Monodisperse OA-capped Fe₃O₄ was synthesized by the method with slight modifications [25]. Iron oleate was synthesized by the reaction between sodium oleate and iron chloride. Iron oleate (18.0 g) and OA (4.3 g) were dissolved in 80 g ODE in a 500 ml three-neck flask at room temperature. Subsequently, the reaction mixture was heated at 320

°C for 1 h under N₂ atmosphere. Then, the reaction was quenched by removing the heating mantle. After cooling down to room temperature, acetone and hexane were added to separate and purify Fe₃O₄ nanodots. The precipitated Fe₃O₄ NPs were redispersed in hexane to form a stable colloidal solution with a concentration of ~20 mg mL⁻¹.

2.2 Synthesis of Fe₃O₄@C

The randomly-packed, carbon-coated Fe₃O₄ nanodots were obtained by a heat treatment procedure with carbonized OA-capped Fe₃O₄ precursor. In typical procedure, 20 ml hexane solution containing OA-capped Fe₃O₄ nanodots was added to a quartz boat and then was dried at 70 °C for 1 h in a dryness box. The carbon-coated Fe₃O₄ nanodots were obtained after carbonization at 500 °C for 2 h under Ar atmosphere.

2.3 Synthesis of S/Fe₃O₄@C and S/C

The S/Fe₃O₄@C host material was obtained by a facile melt-diffusion method. The as-prepared Fe₃O₄@C was milled with pure sulfur in a mass ratio of 1:2. Then, the mixture was treated at 155 °C for 12 h in a Teflon-lined stainless steel autoclave. The S/C was fabricated with the same way, and the source of the carbon was the commercial carbon black.

2.4 Characterization

The crystal structure of the samples was investigated by X-ray diffraction (XRD, Smartlab). The structure and morphology research was performed by scanning electron microscopy (SEM, JSM-7800) and transmission electron microscopy (TEM, JEM-2100). The element mapping was characterized by energy-dispersive spectroscopy (EDS). The sulfur and carbon contents of the samples were studied on a thermogravimetric analyzer system (TGA, LABSYS EVO) with a heating rate of 5 °C min⁻¹ from room temperature to 800 °C in air and Ar atmosphere, individually. The chemical bonds and functional groups were explored by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Escalab Xi+). Specific surface area measurement was obtained with an automated gas sorption analyzer (BET, AUTOSORB-IQ-XR-C).

2.5 Electrochemical Measurements

The electrodes were prepared by a slurry-coating procedure. The cathode material was obtained by mixing S/Fe₃O₄@C or S/C composites, Super P, and polyvinylidene fluoride with a mass ratio of 7:2:1 in *N*-Methyl pyrrolidone to form a homogeneous slurry. The slurry was uniformly painted on a piece of aluminum foil current collector. Then, the electrode was dried at 90 °C under vacuum overnight. The sulfur

loading was $\sim 1 \text{ mg cm}^{-2}$. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide with 2% LiNO_3 addition in a 1:1 v/v solution of 1,3-dioxolane (DOL) and dimethoxymethane (DME). The lithium metal was used as an anode and microporous polypropylene membrane was used as a separator. The coin-type (CR2025) cells were fabricated in a glovebox with Ar atmosphere. Cyclic voltammetry (CV) was evaluated at a voltage range of 1.7–2.8 V with a scan rate of 0.1 mV/s using a biologic VMP3 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was measured in a frequency range of 100 mHz–1 MHz by the same biologic VMP3 electrochemical workstation. The electrochemical charging/discharging measurements were performed at a voltage range of 1.7–2.8 V on Neware battery

test system. In addition, we calculate the specific capacity based on active sulfur.

3 Results and Discussion

The synthesis procedure of the core-shell structure $\text{Fe}_3\text{O}_4@\text{C}$ material is shown in Fig. 1. Firstly, the brown oily type iron oleate is prepared by a simple organic pyrolysis reaction. Secondly, the monodisperse oleate(OA)-capped Fe_3O_4 nanodots are manufactured by a high-temperature pyrolysis treatment with the obtained oily type iron oleate as precursor. Then, the porous, carbon-coated Fe_3O_4 nanodots ($\text{Fe}_3\text{O}_4@\text{C}$) are obtained by a directly heat treatment with Fe_3O_4 NPs as precursor. Ultimately, $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ is gained with a simple melt-diffusion technique.

Figure 2a displays a low-magnification SEM image of $\text{Fe}_3\text{O}_4@\text{C}$. The porous and loose $\text{Fe}_3\text{O}_4@\text{C}$ is clearly observed. The $\text{Fe}_3\text{O}_4@\text{C}$ with large rugged area is fabricated by treating at 500 °C for 2 h under Ar atmosphere with monodisperse OA-capped Fe_3O_4 NPs precursor. Figure S1 evidently illustrates that $\text{Fe}_3\text{O}_4@\text{C}$ is assembled with uniform nanoscale particles with a high-magnification SEM image.

Figures 2b and S2 show the typical TEM image of $\text{Fe}_3\text{O}_4@\text{C}$. We could observe that the Fe_3O_4 nanodots under calcination have good dispersibility and their porous and loose surface is more likely to adsorb sulfur and polysulfides. Compared to OA-stabilized Fe_3O_4 nanodots (Figure S3), the calcined Fe_3O_4 particles have a certain degree of aggregation

Fig. 1 Schematic illustration of the structure of $\text{Fe}_3\text{O}_4@\text{C}$ host and $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ composite cathode

Fig. 2 **a** SEM image of $\text{Fe}_3\text{O}_4@\text{C}$, **b** TEM image of $\text{Fe}_3\text{O}_4@\text{C}$, **c** SEM image of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and corresponding Fe, O, C, S element mappings

on the carbon surface. From Figure S3 we could observe that the monodisperse OA-stabilized Fe₃O₄ nanodots are about 5 nm diameter, which is consistent with the size of the Fe₃O₄ nanodots after calcination. Therefore, the carbon layer that derives from oleate after 500 °C treatment could be beneficial to maintain Fe₃O₄ nanodots size and morphology. In Figure S4, the selected area diffraction pattern (SADP) further indicates the crystal nature of Fe₃O₄@C. The diffraction rings were ascribed to the (220), (311), (400), and (511) planes of the Fe₃O₄ phase.

As shown in Fig. 2c, after loading sulfur, except for the surface becoming smooth, the morphology of Fe₃O₄@C does not change much. The element analyses demonstrate the uniform distribution of Fe, O, C and S, which indicates that S is well loaded on the Fe₃O₄@C.

Figure 3a shows the XRD spectra of S/Fe₃O₄@C, sulfur and Fe₃O₄@C. The significant diffraction peaks of Fe₃O₄@C are consistent well with Fe₃O₄ (JPDFS: 19-0629), indicating that there are not diffraction peaks of other impurities. The peaks of Fe₃O₄@C are preserved in S/Fe₃O₄@C after sulfur-loading treatment, which signifies that sulfur-loading treatment does not affect the composition of Fe₃O₄@C. Based on Scherrer formula, we calculated the crystallite dimension of Fe₃O₄@C to be 4.2 nm, which could provide more adsorption sites for polysulfides [26]. The Brunauer–Emmett–Teller (BET) analysis was carried out for studying the specific surface area and pore size distribution of Fe₃O₄@C in Fig. 3b, c. From the type IV isotherm and type H3 loop appearing we could observe that the pores are mesoporous, arising from the aggregates of nanodots Fe₃O₄@C [27]. We calculated

that the specific surface area of the Fe₃O₄@C nanodots was 216.2 m² g^{−1}. The pore size distribution is shown in Fig. 3c. Among a series of peaks, two peaks can be seen at 18.4 nm, 56.4 nm with relatively obvious adsorption phenomena. The mesoporous structures not only increase the specific surface area of the sample, but also enable the contact between the nanodots and sulfur. Thus, more active sites are exposed to adsorb the polysulfides, which is effective to inhibit the shuttle effect. Thermogravimetric analysis (TGA) was carried out at air atmosphere to investigate the carbon content in Fig. 3d. The carbon content in Fe₃O₄@C nanodots is 29% with a mass loss from ~270 to 400 °C. From Fig. 3e, we could calculate that the sulfur content of the S/Fe₃O₄@C host material is 66%, which results from porous and loose surface of Fe₃O₄@C. The Raman spectroscopy was used to monitor the degree of graphitization of the carbon layer in Fig. 3f. The *I_D*/*I_G* ratio represents that there are many storage sites resulting from defects and disorders for lithium ions.

XPS was applied to investigate the chemical bond states of Fe₃O₄@C in Fig. 4. Two peaks at 724.8 eV, 711.4 eV in core-level spectrum of Fe 2*p* agree with Fe²⁺, and other two peaks at 720.1 eV, 714.7 eV agree with Fe³⁺ in Fig. 4b [18, 28]. The O 1*s* spectrum can be fit to three peaks at 532.7, 531.4 and 530.5 eV in Fig. 4c. The most intense peak at 530.5 eV results from lattice oxygen in Fe₃O₄, the peak at 531.4 eV is attributed to the two monodentate bonds of O–C and O=C, and the peak at 532.7 eV is attributed to the bidentate species of O–C=O [29]. In Fig. 4d, we observe the peaks of C=O and C–O, which indicate there are many defects and disorders in carbon layer.

Fig. 3 **a** XRD patterns of S/Fe₃O₄@C, sulfur and Fe₃O₄@C, **b** N₂ adsorption/desorption isotherms, **c** pore size distribution pattern of Fe₃O₄@C, **d** TGA curve of Fe₃O₄@C in air, **e** TGA curve of S/Fe₃O₄@C in Ar atmosphere, **f** Raman spectrum of Fe₃O₄@C

Fig. 4 XPS spectra of $\text{Fe}_3\text{O}_4@\text{C}$ composite: **a** survey, **b** Fe 2p, **c** O 1s, **d** C 1s

The electrochemical behavior of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode is investigated by coin cells. In Fig. 5a, the CV test was carried out in a potential window of 1.7–2.8 V at a scan rate of 0.1 mV s^{-1} . There are two cathodic peaks and one anodic peak. During the discharge, two reduction peaks at 2.28 V and 2.02 V are related to the two discharge platforms (Fig. 5b). The first platform is the conversion of S_8 to long-chain polysulfides (Li_2S_8 , Li_2S_6), and the second platform is corresponding to the conversion of Li_2S_4 to solid $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ [30, 31]. In addition, the oxidation peak at 2.39 V responds to a series of reversible transformation from $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ to sulfur. All CV curves exhibit good overlapping of the redox peaks, indicating the outstanding reversibility of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode. The galvanostatic charge/discharge curves of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode at 0.2 C (1 C = 1675 mAh g^{-1}) are shown in Fig. 5b. We observe that the voltage plateaus are highly-overlapped even over 100 cycles. And the polarization phenomenon does not change significantly after 100 cycles, which further proves the reversibility and structural stability of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode.

The rate performance of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C cathodes from 0.1 C to 2 C is evaluated in Fig. 5c, d. The reversible capacities of 1188, 960, 845, 763 and 674 mAh g^{-1} are achieved respectively at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C with

$\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode. Then, the specific capacity of the same cell returns to 924 mAh g^{-1} at 0.2 C, showing effectively capacity reserved ability. As a comparison, the capacities of 550, 557, 238, 190 and 145 mAh g^{-1} are shown at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C with S/C cathode, respectively. The charge/discharge curves at different rates could also prove that the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode has the better electrochemical performance in Fig. 5d.

The electrochemical performance of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode is evidenced by electrochemical impedance spectroscopy (EIS) in Figure S5. Compared to S/C cathode, the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode has a smaller semicircle and higher slope, demonstrating the smaller charge transfer resistance (R_{ct}) and faster ion diffusion rate [32]. The charge transfer resistances of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C are 38.07 and 65.69Ω , respectively, which means improved electrochemical performance of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$.

The long-term cyclic performance of the cells with $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C cathodes was tested at 0.2 C and 1 C with the same sulfur loading of 1 mg cm^{-2} and a potential range of 1.7–2.8 V in Fig. 6. As shown in Fig. 6a, the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode delivers a high initial specific capacity of 1089 mAh g^{-1} at 0.2 C and the specific capacity still maintains 762 mAh g^{-1} after 200 cycles. In contrast, the S/C cathode

Fig. 5 **a** CV curves of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ cathode at 0.1 mV s^{-1} in the potential window from 1.7 to 2.8 V, **b** galvanostatic charge–discharge curves of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ electrode at different cycles, **c** rate capability of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C cathodes from 0.1 C to 2 C, **d** galvanostatic charge–discharge curves of the $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ electrode under varied currents from 0.1 C to 2 C

Fig. 6 **a** Cycle performance of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C cathodes at 0.2 C, **b** cycle performance of $\text{S}/\text{Fe}_3\text{O}_4@\text{C}$ and S/C cathodes at 1 C

delivers an initial specific capacity of 650 mAh g^{-1} and fades to low capacity of 416 mAh g^{-1} after 200 cycles. We think the capacity fluctuation may be caused by two factors. Firstly, the capacity can be largely influenced by room temperature. The capacities may become higher when the temperature becomes higher. The temperature affecting cyclic performance has been reported [33]. Secondly, there are side effects during charge/discharge process, such as decomposition of electrolyte. The good electrochemical performance of $\text{S/Fe}_3\text{O}_4\text{/C}$ cathodes is mainly due to two aspects. On the one hand, the carbon layer could physically block polysulfide shuttle. On the other hand, the polar Fe_3O_4 nanodots could adsorb the polar polysulfides to inhibit polysulfides shuttle. Even at a high current density of 1 C, the $\text{S/Fe}_3\text{O}_4\text{/C}$ cathode delivers an initial specific capacity of 816 mAh g^{-1} and still maintains 655 mAh g^{-1} after 200 cycles, which shows that the $\text{S/Fe}_3\text{O}_4\text{/C}$ cathode has good long cycle performance and structural stability (Fig. 6b). In Figure S6, the separator of the cycled cell with $\text{S/Fe}_3\text{O}_4\text{/C}$ does not turn yellow, while the separator of the cycled cell with S/C and S/C cathodes appears clear yellow, indicating that the shuttle of polysulfides is effectively alleviated by core-shell structure $\text{Fe}_3\text{O}_4\text{/C}$ nanodots.

4 Conclusion

In summary, the core-shell structured $\text{Fe}_3\text{O}_4\text{/C}$ nanodots as sulfur host is successfully synthesized by a classic pyrolysis reaction followed by calcination. The $\text{Fe}_3\text{O}_4\text{/C}$ nanodots are assembled by monodisperse oleate-capped Fe_3O_4 nanodots about 5 nm diameter after calcination. The resultant $\text{Fe}_3\text{O}_4\text{/C}$ with mesoporous and high specific surface area not only has high-load sulfur, but also could fix polysulfides by chemical and physical adsorption. In the same time, the multiple mesoporous channels could alleviate volume change between S_8 and $\text{Li}_2\text{S/Li}_2\text{S}_2$ during charge/discharge to extend cell life. In addition, the carbon layer could ensure fast electronic transmission during charge and discharge to facilitate redox reactions. Therefore, the $\text{S/Fe}_3\text{O}_4\text{/C}$ cathodes show the specific capacity of 1089 mAh g^{-1} at 0.2 C and 816 mAh g^{-1} at 1 C, respectively. The nanodot restriction polysulfide shuttle by chemical and physical adsorption is a promising choice for Li-S batteries.

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References

- [1] C.Y. Wang, G. Zhang, S. Ge, T. Xu, Y. Ji, X. Yang, Y. Leng, *Nature* **7587**, 515 (2016)
- [2] L.M. Pazos-Outón, M. Szumilo, R. Lamboll, J. Richter, M. Crespo-Quesada, M. Abdi-Jalebi, H. Beeson, M. Vrućinić, M. Alsari, H. Snaith, *Science* **6280**, 1430 (2016)
- [3] A. Manthiram, S.H. Chung, C. Zu, *Adv. Mater.* **12**, 1980 (2015)
- [4] H.D. Yoo, E. Markevich, G. Salitra, D. Sharon, D. Aurbach, *Mater. Today* **3**, 110 (2014)
- [5] L. Ma, H.L. Zhuang, S. Wei, K. Hendrickson, M. Kim, G. Cohn, R. Hennig, L. Archer, *ACS Nano* **1**, 1050 (2016)
- [6] C.B. Bucur, M. Jones, M. Kopylov, J. Spear, J. Muldoon, *Energy Environ. Sci.* **4**, 905 (2017)
- [7] M.R. Kaiser, S. Chou, H.K. Liu, S. Dou, C. Wang, J. Wang, *Adv. Mater.* **48**, 1700449 (2017)
- [8] C. Barchasz, F. Molton, C. Duboc, J. Leprêtre, S. Patoux, F. Alloin, *Anal. Chem.* **9**, 3973 (2012)
- [9] G. He, S. Evers, X. Liang, M. Cuisinier, A. Garsuch, L. Nazar, *ACS Nano* **12**, 10920 (2013)
- [10] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L. Archer, *Angew. Chem. Int. Ed.* **26**, 5904 (2011)
- [11] M.R. Kaiser, Z. Ma, X. Wang, F. Han, T. Gao, X. Fan, J. Wang, H. Liu, S. Dou, C. Wang, *ACS Nano* **9**, 9048 (2017)
- [12] T. Tao, S. Lu, Y. Fan, W. Lei, S. Huang, Y. Chen, *Adv. Mater.* **48**, 1700542 (2017)
- [13] S.A. Abbas, J. Ding, S.H. Wu, J. Fang, K. Boopathi, A. Mohapatra, L. Lee, P. Wang, C. Chang, C. Chu, *ACS Nano* **12**, 12436 (2017)
- [14] S. Lorgier, R.E. Usiskin, J. Maier, *Adv. Funct. Mater.* **6**, 1807688 (2019)
- [15] D. Ghosh, M. Gad, I. Lau, M. Pope, *Adv. Energy Mater.* **27**, 1801979 (2018)
- [16] J. Chang, J. Shang, Y. Sun, L. Ono, D. Wang, Z. Ma, Q. Huang, D. Chen, G. Liu, Y. Cui, *Nat. Commun.* **1**, 1 (2018)
- [17] S. Li, J. Jiang, Z. Dong, J. Wu, Z. Cheng, H. Zhu, Z. Fan, Y. Wang, D. Leng, *Microporous Mesoporous Mater.* **293**, 109822 (2020)
- [18] L. Fan, H. Wu, X. Wu, M. Wang, J. Cheng, N. Zhang, Y. Feng, K. Sun, *Electrochim. Acta* **295**, 444–451 (2019)
- [19] F. Luna-Lama, C. Hernández-Rentero, J. Morales, A. Caballero, *Electrochim. Acta* **292**, 522 (2018)
- [20] D. Luo, G. Li, Y.P. Deng, Z. Zhang, J. Li, R. Liang, M. Li, Y. Jiang, W. Zhang, Y. Liu, *Adv. Energy Mater.* **18**, 1900228 (2019)
- [21] K. Lu, Y. Liu, J. Chen, Z. Zhang, Y. Cheng, *ACS Nano* **12**, 14540 (2019)
- [22] Y. Zhong, K. Yang, W. Liu, P. He, V. Batista, H. Wang, *J. Phys. Chem. C* **121**, 14222 (2017)
- [23] J. He, L. Luo, Y. Chen, A. Manthiram, *Adv. Mater.* **34**, 1702707 (2017)
- [24] Y. Choi, B. Jung, D. Lee, J. Jeong, K. Kim, H. Ahn, K. Cho, H. Gu, *Phys. Scr.* **T129**, 62 (2007)
- [25] J. Park, K. An, Y. Hwang, J. Park, H. Noh, J. Kim, J. Park, N. Hwang, T. Hyeon, *Nat. Mater.* **12**, 891 (2004)
- [26] O.M. Lemine, *Superlattices Microstruct.* **6**, 576 (2009)
- [27] K.S. Sing, *Pure Appl. Chem.* **4**, 603 (1985)
- [28] H. Li, J. Wang, Y. Zhang, Y. Wang, A. Mentbayeva, Z. Bakenov, *J. Power Sources* **437**, 226901 (2019)
- [29] D. Wilson, M.A. Langell, *Appl. Surf. Sci.* **303**, 6 (2014)
- [30] Y.V. Mikhaylik, J.R. Akridge, *J. Electrochem. Soc.* **11**, A1969 (2004)
- [31] D. Moy, A. Manivannan, S. Narayanan, *J. Electrochem. Soc.* **1**, A1 (2015)
- [32] Y. Liu, X. Qin, S. Zhang, G. Liang, F. Kang, G. Chen, B. Li, *A.C.S. Appl. Mater. Interfaces* **31**, 26264 (2018)
- [33] S.Z. Xiong, K. Xie, X.B. Hong, *J. Natl. Univ. Def. Technol.* **2**, 150 (2012)