Novel Design and Facile Synthesis of Porous Carbon Nanocomposites for Lithium Sulfur Battery

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By

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Weizhai Bao

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DEDICATION

This thesis is dedicated to my family. Thank you for all of your love and support.

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RESEARCH PUBLICATIONS

1. **Bao, W.**; Liu, L., Wang, C., Choi, S., Wang, D. and Wang, G., 2018. Facile Synthesis of Crumpled Nitrogen- Doped MXene Nanosheets as a New Sulfur Host for Lithium–Sulfur Batteries. ***Advanced Energy Materials***. **Impact factor: 21.875.** (Selected as cover of the issue, and reported by WILEY Materials Views China in March 2018, one of the Top 10 most read articles of Advanced Energy Materials in March 2018)
2. **Bao, W.**;Su, D.;Zhang, W.;Guo, X.; Wang, G. 3D Metal Carbide@Mesoporous Carbon Hybrid Architecture as a New Polysulfide Reservoir for Lithium–Sulfur Batteries. ***Advanced Functional Materials*** 2016, *26*, 8746-8756. **Impact factor: 13.30.** (Reported by WILEY Materials Views China at June 12, 2017)
3. **Bao, W.**; X, Xie.; Xu, J.; Guo, X.; J, Song Su, D.; Wang, G. Confine sulfur in 3D flexible hybrid MXene/reduced graphene oxide nanosheets for lithium sulfur battery. ***Chemistry–A European Journal***, 2017, 23, 1-8. **Impact factor: 5.16.** (One of the most downloaded *Chemistry–A European Journal* articles in 2017)
4. **Bao, W.**; Tang, X., Guo, X., Choi, S., Wang, C., Gogotsi, Y. and Wang, G.,. Porous cryo-dried MXene for efficient capacitive deionization. ***Joule*** 2018, *2*(4), 778-78 (Cell Publishing Group journal, highlight and preview paper by editor)
5. **Bao, W.**;Mondal, A. K.;Xu, J.;Wang, C.;Su, D.; Wang, G. 3D hybrid–porous carbon derived from carbonization of metal organic frameworks for high performance supercapacitors. ***Journal of Power Sources*** 2016, *325*, 286-291. **Impact factor: 6.945.**
6. **Bao, W.**;Zhang, Z.;Zhou, C.;Lai, Y.; Li, J. Multi–walled carbon nanotubes @ mesoporous carbon hybrid nanocomposites from carbonized multi–walled carbon nanotubes@metal–organic framework for lithium sulfur battery. ***Journal of Power Sources*** 2014, *248*, 570-576. **Impact factor: 6.945.**
7. **Bao, W.**;Zhang, Z.;Chen, W.;Zhou, C.;Lai, Y.; Li, J. Facile synthesis of graphene oxide@mesoporous carbon hybrid nanocomposites for lithium sulfur battery. ***Electrochimica Acta*** 2014, *127*, 342-348. **Impact factor: 5.116.**
8. **Bao, W.**;Zhang, Z.;Qu, Y.;Zhou, C.;Wang, X.; Li, J. Confine sulfur in mesoporous metal–organic framework@reduced graphene oxide for lithium sulfur battery. ***Journal of Alloys and Compounds*** 2014, *582*, 334-340. **Impact factor: 3.779.**

9. **Bao, W.**;Zhang, Z.;Qu, Y.;Zhou, C.;Wang, X.; Li, J. Enhanced cyclability of sulfur cathodes in lithium–sulfur batteries with Na-alginate as a binder. ***Journal of Energy Chemistry***, *2013*, 22(5), pp.790-794. **Impact factor: 4.385.**
10. Zhang, Z.; **Bao, W.**; Chen, W.;Zhou, C.;Lai, Y.; Li. Water-soluble polyacrylic acid as a binder for sulfur cathode in lithium–sulfur battery. ***ECS Electrochemistry Letters***, 2012, 1(2), pp.A34-A37.
11. Xu, J.; Su, D.; Zhang, W.; **Bao, W.**; Wang, G. A nitrogen–sulfur co-doped porous graphene matrix as a sulfur immobilizer for high performance lithium–sulfur batteries. ***J. Mater. Chem. A,*** 2016, *4*, 17381-17393. **Impact factor: 9.931.**
12. Devaraj, S., Kretschmer, K., Sahu, T., **Bao, W**., Rojo, T., Wang, G. and Armand, M.B., 2018. Highly efficient, cost effective and safe sodiation agent for high performance sodium batteries. ***ChemSusChem.*** **Impact factor: 7.411**
13. Chen, W.;Zhang, Z.; **Bao, W.**; Lai, Y.;Li, J.;Gan, Y.; Wang, J. Hierarchical mesoporous γ–Fe_2O_3/carbon nanocomposites derived from metal organic frameworks as a cathode electrocatalyst for rechargeable Li–O_2 batteries. ***Electrochimica Acta*** 2014, *134*, 293-301. **Impact factor: 5.116.**
14. Song, J.;Su D, Xie X, Su, D.; Guo, X.; **Bao, W.**; Wang. Immobilizing Polysulfides with MXene-Functionalized Separators for Stable Lithium–Sulfur Batteries. ***ACS applied materials & interfaces***, 2016, 8(43): 29427-29433. **Impact factor: 8.097.**
15. Xu, J.;Su, D.; **Bao, W.**; Wang, G. Rose flower–like $NiCo_2O_4$ with hierarchically porous structures for highly reversible lithium storage. ***Journal of Alloys and Compounds***, 2016, 684: 691-698. **Impact factor: 3.779.**
16. Guo, X., Li, K., **Bao, W.**, Zhao, Y., Xu, J., Liu, H. and Wang, G., 2018. Highly Reversible Lithium Polysulfide Semiliquid Battery with Nitrogen- Rich Carbon Fiber Electrodes. Energy Technology, 6(2), pp.251-256. **Impact factor: 3.385.**

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ABSTRACT

Rechargeable energy storage devices are being seen as having a crucial role in thepowering of myriad portable electronic devices and hybrid electricalvehicles. The composition, morphology, structure and preparation method can affect the electrochemical performance. The properties of electrode materials are of extreme significance for the electrochemical performances of lithium-sulfur batteries.

Lithium-sulfur battery based on sulfur cathode has the advantages of high specific capacity, high energy density, low lost and natural abundance of sulfur. These advantages over conventional lithium-ion batteries have driven researchers to make a lot of efforts to understand the redox mechanisms and improve the electrode performance. In order to fully realize the potential of lithium-sulfur battery and to approach commercialization, there are still many problems to overcome. Among them are i) low conductivity nature of sulfur and the discharge product, ii) lithium polysulfide intermediates dissolution and shuttle phenomenon, iii) volumetric expansion upon discharge and iv) lithium metal dendrite formation on anode side. In this thesis, the work is mostly focused on the cathode materials in order to address the first two problems.

In the first part of the thesis, we report a rational design and synthesis of 3D hybrid–porous carbon with a hierarchical pore architecture for high performance supercapacitors. It contains nanopores (< 2 nm diameter) and mesopores (2 – 4 nm), derived from carbonization of unique porous metal organic frameworks (MOFs). Owning to the synergistic effect of micropores and mesopores, the hybrid-porous carbon has exceptionally high ion–accessible surface area and low ion diffusion resistance, which is desired for high performance Li-S battery. The

initial and 50th cycle discharge capacity 3D hybrid–C/S sulfur cathode are as high as 1343 mAh g^{-1} and 540 mAh g^{-1} at a high current rate of 0.5 C.

3D hybrid–C@graphene nanocomposites were prepared by a hydrothermal and chemical vapor deposition method. When applied as an cathode material in lithium-sulfur batteries. 3D hybrid–C@graphene/S nanocomposite exhibited a high lithium storage capacity of 907 mAh g^{-1}. The materials also demonstrated an excellent high rate capacity and a stable cycle performance. 3D porous MXene/S sulfur composite was successfully prepared that demonstrated high reversible capacity, high Coulombic efficiency and excellent cyclability. MXene@graphene/S hybrid sulfur composite were synthesized using a chemical hydrothermal method, exhibiting a high specific capacity of 1284 mAh·g^{-1} with a superior cycling stability and high rate capabilities.

The synthesis of 3D hybrid–C@MXene encapsulated sulfur composites were employed as cathode materials for Li-S batteries. The sulfur composite cathodes delivered a high specific capacity of 1378 mAh/g at 0.1 C current rate and exhibited a stable cycling performance. A rational synthesis of the novel porous N-$Ti_3C_2T_x$ nanosheets via the electrostatic self-assembly and effective nitrogen doping process, achieving the porous-modification and nitrogen group surface decoration for porous N-$Ti_3C_2T_x$ nanosheets, synchronously. The porous N-doped MXene nanosheets/sulfur composites electrodes with a high sulfur loading exhibits low polarization, stable cycling performance, and excellent rate capability, compared with mixed $Ti_3C_2T_x$/S electrodes showed electrochemical performance, including a high reversible capacity of 1144 mAh g^{-1} at 0.2 C rate, a high level of capacity retention of 950 mAh g^{-1} after 200 cycles and good cycling stability with a high sulfur loading of 5.1 mg cm^{-2} and high current rate of 2 C rate.