A Project Report On

Application of hollow silica particles as battery anodes in lithium ion batteries

Dissertation submitted to

GOA UNIVERSITY

In partial fulfillment of the award of the degree of

MASTER OF SCIENCE

SEMESTER IV

By

Nidhi H. Gaonkar

Roll No: 20P0490027

Under the guidance of

Prof. Anjani P. Nagvenkar

To the

SCHOOL OF CHEMICAL SCIENCES

GOA UNIVERSITY

ACKNOWLEDGEMENTS

I would like to express my heartful and sincere thanks to our Dean ***Prof. Vidhyadatta Verenkar*** for giving me a great opportunity to excel in my learning through this project.

I would also like to express my special thanks of gratitude to my guide teacher ***Prof. Anjani P. Nagvenkar,*** for her valuable and constant guidance and willingness to share her vast knowledge made us understand this project and its manifestation in great depths and helped us to complete the assigned tasks on time. I also sincerely thanks for the time spent proofreading and correcting my many mistakes.

CERTIFICATE

This is to certify that work incorporated in the project entitled "**Application of Hollow Silica Particles as Battery Anodes in Lithium Ion Batteries**" is the bonafied work done by Miss. Nidhi H. Gaonkar during the period of study under my guidance in partial fulfillment of requirement for the award of the Degree of Master of science in Chemistry at the School of chemical sciences, Goa University during the academic year 2021-2022.

Prof. Anjani P. Nagvenkar	**Prof. Vidhyadatta Verenkar**
Project guide	Dean
School of chemical sciences Goa University	School of chemical sciences Goa University

DECLARATION

*I declare that matter presented in this project entitled“**Application of hollow silica particles as battery anodes for lithium ion batteries**” is the original work done by me at School of chemical sciences, Goa University, Taleigao Plateau, Goa under the guidance of Prof. Anjani P. Nagvenkar. And to the best of my knowledge similar work has not been submitted elsewhere for the fulfillment of the requirement of course of study.*

Date: 11 May, 2022

Place: Goa University,
Taleigao – Goa

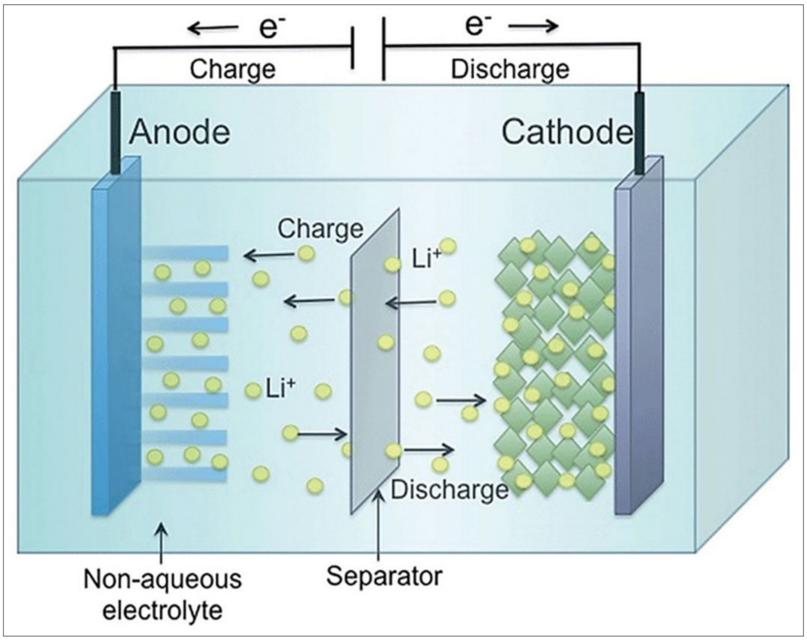
Candidate signature

NIDHI GAONKAR
(M.Sc. Part-II)

INDEX

APPLICATION OF HOLLOW SILICA PARTICLES AS BATTERY ANODES IN LITHIUM BATTERIES.

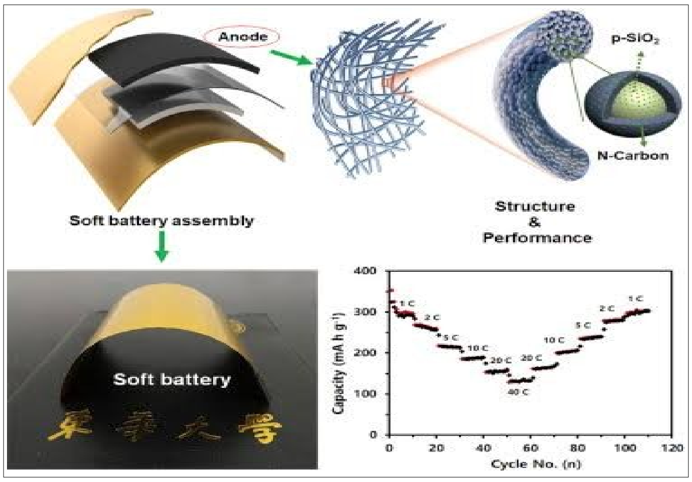
Introduction



Lithium ion battery

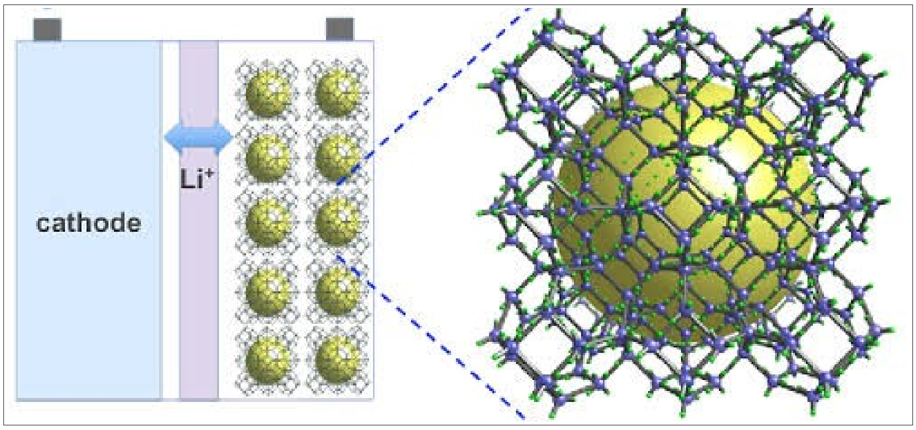
Lithium ion batteries (LIBs) have been widely used as the power source of portable devices such as laptop personal computers (PCs) and smartphones. The lowest electrode potential of Li/Li+ makes it possible to construct a high-voltage battery, which is the reason why LIBs are dominating the battery market. During a discharge cycle, lithium atoms in the anode are ionized and separated from their electrons. The lithium ions move from the anode and pass through the electrolyte until they reach the cathode, where they recombine with their electrons and electrically neutralize. The anode materials in lithium-ion cells act as the host where they reversibly allow lithium-ion intercalation / deintercallation during charge / discharge cycles. For the conventional LIBs, there are two major issues to overcome. One is the safety problem of the LIBs, which is frequently reported as the ignition of portable devices such as laptop PCs, smartphones, etc. These accidental fires of the LIBs originate from the flammable organic liquid used as the electrolyte. Because the anode potential of the LIBs is much lower than the reductive decomposition voltage of aqueous electrolytes, organic liquids are used as the electrolytes. The replacement of the organic liquid by a ceramic solid electrolyte is one of the solutions for the realization of safe LIBs. For this reason, all-solid-state batteries have attracted much attention as the next-generation LIBs. The other issue of the LIBs is the demand for a higher capacity because LIBs have started to be used for large-scale applications such as electric vehicles (EVs) and smart grids. In order to realize the cruising distance of EVs comparable to that of gasoline-fueled vehicles, the capacity of the LIBs should be four to five times higher than the current LIBs. It is easily predicted that LIB fires will be much more severe for the larger batteries compared to the batteries for portable use. Therefore, all-solid-state LIBs having an exceptionally high capacity and high safety are strongly required for the future.[1,2,3,4]

The vast majority of lithium-ion batteries use graphite powder as an anode material.Graphite materials are either synthetically-produced (artificial graphite) or mined from the ground (natural graphite), then heavily processed before being baked onto a copper foil to serve as anodes. But these graphite anodes has problems of relatively low theoretical capacity & low efficiency. Hence Group IV elements, such as silicon (Si), germanium (Ge), and tin (Sn) are used as battery anodes. Despite their high capacity, practical examples of applications are scarce since one of the issues of high-capacity anodes is their large volume expansion (~300%) during operation. The repetition of the large volume change results in the pulverization and disintegration of the active materials, leading to the low reversibility during cycling. Therefore in order to achieve stable charge–discharge cycling, the common strategies are to allow for accommodation of the volume expansions by the introduction of void spaces in the active materials.[5]



Schematic diagram of carbon coated silica anode

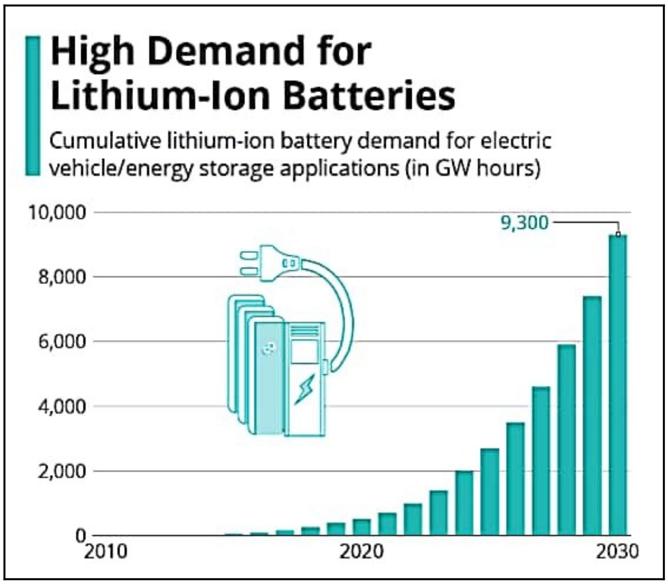
Hence recently hollow silica particles(HSPs) made of carbon coated silica nanoparticles have been demonstrated as battery anodes due to the high theoretical specific capacity & extremely low cost. These initial results were encouraging, but at present the use of HSPs in batteries is not attracting much interest due to the low ionic and electrical conductivity of HSPs.[6] Hence to overcome these HSPs were masked with MOFs (metal organic frameworks) which have stimulated huge research interest in the field of electrochemical energy storage and conversion.Their(MOFs) high porosity, versatile functionalities, diverse structures, and controllable chemical compositions offer immense possibilities in the search for adequate electrode materials for rechargeable batteries. Here Zr based porphinic MOFs were used which would generate highly stable & electrically conductive frameworks in which the mesopores remain accessible to other guests (Li^+).



Lithium ions encapsulated in metal organic frameworks

IMPORTANCE OF THE PROPOSED WORK

The demand for rechargeable lithium ion battery has remarkable growth in portable devices and automotive applications.Their triumph in the portable electronics market is due to the higher gravimetric and volumetric energy densities offered by them compared to other rechargeable systems. In such scenario, the development of high-performance lithium ion battery with high capacity retention, high coulombic efficiency, high energy density, and low cost becomes inevitable. To optimize the performance and to increase the electrical conductivity of batteries the idea of masking MOFs over hollow silica particles as battery anodes would make it a technology of choice for portable electronics, power tools, and hybrid/full electric vehicles.

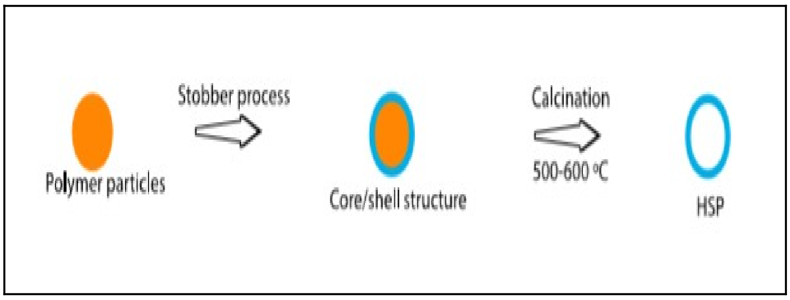


Schematic plot showing the demand for lithium ion batteries

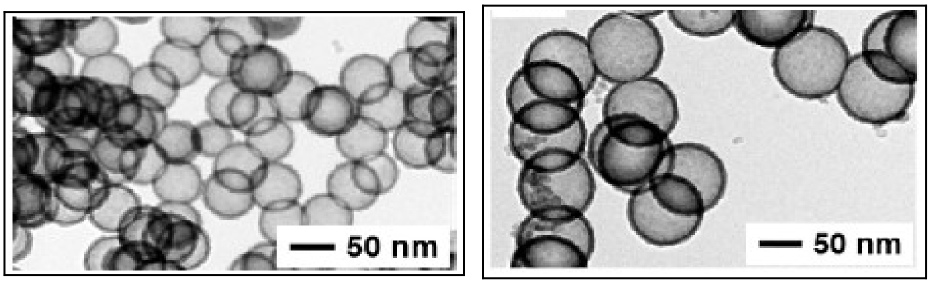
When compared with other electrode materials, silicon-based anode used in lithium batteries have high tolerance to electrode volume changes during cycling, and can avoid damage to the electrode structure to a greater extent; large specific surface area, which is conducive to the effective contact between the electrolyte and the electrode, shortens the charge and discharge time threshold; shortens the electron transport and ion diffusion distance, increases the battery capacity and rate. If electric vehicles (EVs) replace the majority of gasoline powered transportation, Li-ion batteries will significantly reduce greenhouse gas emissions. The high energy efficiency of these Li-ion batteries may also allow their use in various electric grid applications, including improving the quality of energy harvested from wind, solar, geo-thermal and other renewable sources, thus contributing to their more widespread use and building an energy-sustainable economy. Therefore Li-ion batteries are of intense interest from both industry and government funding agencies. [7,8,9,10]

METHODOLOGY

Hollow nanostructured materials have attracted considerable interest as lithium ion battery electrodes because of their good electrochemical properties. In this study, we developed a general procedure for the synthesis of hollow nanostructured metal silicates. The most common strategy for synthesis of HSPs involves the use of polymer or copolymer particles (e.g., polystyrene, polyresorcinol, polymethylmethacrylate (PMMA), poly(methylmethacrylate-co-2-diethylaminomethyl methacrylate)) as templates. This is followed by deposition of silica (using the Stöber method) using various silica precursors such as TEOS, TMOS, and sodium silicate.The Stöber method involves hydrolysis of silane molecules(e.g.,tetraethylorthosilicate(TEOS), sodiumsilicate, ortetramethylorthosilicate(TMOS) in an alcohol–water solution in the presence of a catalyst (e.g., ammonium hydroxide). The hydrolyzed molecules start polymerizing among themselves and make larger molecules(oligomers),which deposit on the template to make a silica shell. In the next step, polymer templates are removed by dissolving in organic solvents such as toluene or calcination at high temperature (≈550◦C). Because TMOS is highly reactive and prone to quick hydrolysis, it is less commonly used, whereas TEOS, being more stable to hydrolysis, is widely used. The polymer particle template-based approach is highly advantageous in providing HSPs in which the size is uniformly controlled, ranging from 50 nm to 1 μm.[11,12,13,14,15]

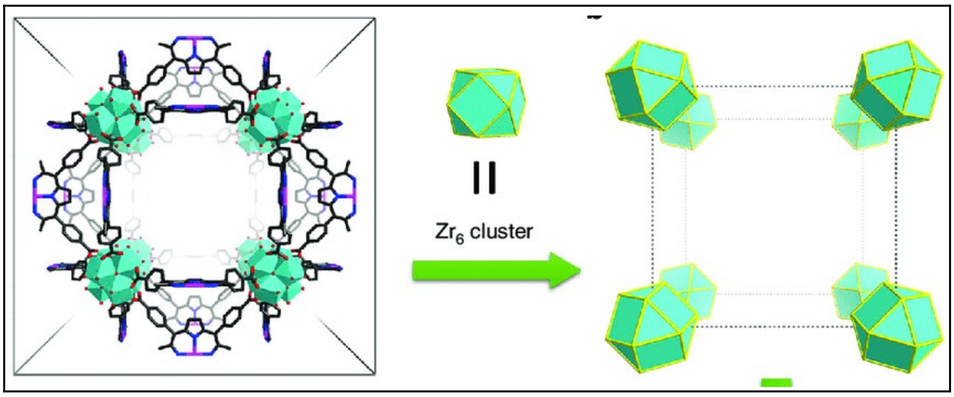


Synthesis of hollow silica nanoparticles

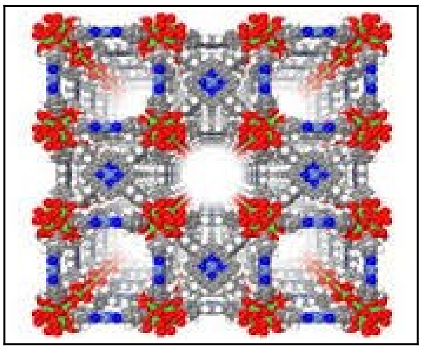


Hollow mesoporous silica nanoparticles

Among the thousands of different compounds, Zr4+-based MOFs clearly occupy an outstanding position. These MOFs often exhibit an extremely high thermal and chemical stability while having large specific surface areas and being excellent catalysts in various reactions.With uniform but tunable pore sizes, MOFs provide a special platform for the effective utilization of the porphyrinic catalytic centers. Recently, porphyrin derivatives have been introduced into MOFs by either linker extension or encapsulation. Catalytic activities and optical properties have been investigated in such porphyrinic MOFs. However, most of these MOFs are constructed by the combination of soft acids (low-oxidative transition metal ions) and hard bases (carboxylates), and consequently have relatively weak chemical stabilities while Zr (IV)-based MOFs, because the strong interaction between Zr(IV) and carboxylate will make the resultant MOFs chemically stable. Combing the versatility of metalloporphyrins and the stability of Zr-carboxylate MOFs, there has been reported an iron porhpyrin zirconium MOF, PCN-224(Fe) (PCN stands for porous coordination network), which exhibits extraordinary stability and peroxidase-like catalytic activity.[16,17]



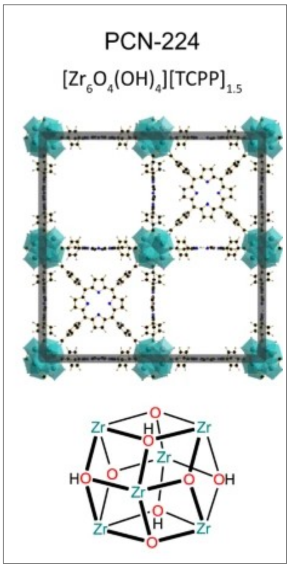
Zirconium metal organic frameworks



PCN-224(Fe)

Synthesis of PCN-224(Fe). ZrCl4, FeTCPPCl and benzoic acid in DMF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in 120 °C oven for 12 h. After cooling down to room temperature, a mixture of dark brown square and needle shaped crystals (PCN-222) was harvested. PCN224(no metal) and FeCl2·4H2O were heated at 120 °C with stirring for 12 h. After that, the mixture was centrifuged. The liquid was decanted and the remaining solid washed with fresh DMF twice and acetone twice. The acetone was decanted, and the sample was dried in an oven. Brown crystals were obtained and demonstrated to be PCN-224 pure phase by PXRD.[18,19,20]

Synthesis of PCN-224(No Metal): ZrCl4 (30 mg), H2TCPP (10 mg), and 400 mg of benzoic acid in 2 mL of DMF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in 120 °C oven for 24 h. After cooling down to room temperature, cubic dark purple crystals were harvested by filtration (10 mg, 71% yield).



PCN-224

CONCLUSION

The increased use of battery power is expected to play a major role in facilitating the shift from the worlds reliance on fossil fuels towards clean energy sources. The use of HSPs has been demonstrated in several applications, especially drug delivery and catalysis.However, most of the applications are still at the lab scale and have not yet gone beyond publication of results. Si has been regarded as one of the most promising next generation lithium-ion battery (LIB) anodes due to its exceptional capacity and proper working voltage. However, the dramatic volume change during lithiation/delithiation processes has caused severe detrimental consequences, leading to very poor cyclic stability. It has been one of the central issues to improve the cyclic performance of the Si-based anode for real practical applications. By systematically reviewing the academic research on the Si-based anodes this idea of embedding MOFs on hollow silica particles would overcome this and take away the whole market of lithium batteries.These batteries will present an opportunity to transform the transportation sector, which currently contributes significant amounts of carbon to the atmosphere. [21,22]

BIBLIOGRAPHY

1. Cheng H, Shapter JG, Li Y, Gao G. Recent progress of advanced anode materials of lithium-ion batteries. J Energy Chem. 2021;57. doi:10.1016/j.jechem.2020.08.056
2. Zubi G, Dufo-López R, Carvalho M, Pasaoglu G. The lithium-ion battery: State of the art and future perspectives. Renew Sustain Energy Rev. 2018;89. doi:10.1016/j.rser.2018.03.002
3. Yu X, Manthiram A. Sustainable Battery Materials for Next-Generation Electrical Energy Storage. Adv Energy Sustain Res. 2021;2(5). doi:10.1002/aesr.202000102
4. Goutam S, Omar N, Van Den Bossche P, Van Mierlo J. Review of Nanotechnology for Anode Materials in Batteries. In: Emerging Nanotechnologies in Rechargeable Energy Storage Systems. ; 2017. doi:10.1016/B978-0-323-42977-1.00002-9
5. Miyazaki R. High-Capacity Anode Materials for All-Solid-State Lithium Batteries. Front Energy Res. 2020;8. doi:10.3389/fenrg.2020.00171
6. Chae S, Ko M, Kim K, Ahn K, Cho J. Confronting Issues of the Practical Implementation of Si Anode in High-Energy Lithium-Ion Batteries. Joule. 2017;1(1). doi:10.1016/j.joule.2017.07.006
7. Manthiram A. An Outlook on Lithium Ion Battery Technology. *ACS Cent Sci*. 2017;3(10). doi:10.1021/acscentsci.7b00288
8. Nitta N, Wu F, Lee JT, Yushin G. Li-ion battery materials: Present and future. *Mater Today*. 2015;18(5). doi:10.1016/j.mattod.2014.10.040
9. Edfenergy. Benefits of electric cars on the environment. edfenergy.
10. Tao W, Wang P, You Y, et al. Strategies for improving the storage performance of silicon-based anodes in lithium-ion batteries. Nano Res. 2019;12(8). doi:10.1007/s12274-019-2361-4
11. Sharma J, Polizos G. Hollow silica particles: Recent progress and future perspectives. Nanomaterials. 2020;10(8). doi:10.3390/nano10081599
12. Kim J, Lee C, Suh YJ, Chang H, Roh KM, Jang HD. Synthesis and characterization of highly reflective hollow silica particles. *Mater Res Bull*. 2015;70. doi:10.1016/j.materresbull.2015.04.046
13. Pal N, Lee JH, Cho EB. Recent trends in morphology-controlled synthesis and application of mesoporous silica nanoparticles. Nanomaterials. 2020;10(11). doi:10.3390/nano10112122
14. Freudensprung I, Joe D, Nietzel S, Vollmer D, Klapper M, Müllen K. Spherical Polyolefin Particles from Olefin Polymerization in the Confined Geometry of Porous Hollow Silica Particles. Macromol Rapid Commun. 2016;37(20). doi:10.1002/marc.201600295

15. Bao Y, Shi C, Wang T, Li X, Ma J. Recent progress in hollow silica: Template synthesis, morphologies and applications. Microporous Mesoporous Mater. 2016;227. doi:10.1016/j.micromeso.2016.02.040

16. Kong XJ, Li JR. An Overview of Metal–Organic Frameworks for Green Chemical Engineering. Engineering. 2021;7(8). doi:10.1016/j.eng.2021.07.001

17. Reinsch H, Bueken B, Vermoortele F, et al. Green synthesis of zirconium-MOFs. CrystEngComm. 2015;17(22). doi:10.1039/c5ce00618j

18. Feng D, Chung WC, Wei Z, et al. Construction of ultrastable porphyrin Zr metal-organic frameworks through linker elimination. *J Am Chem Soc*. 2013;135(45). doi:10.1021/ja408084j

19. Zheng J, Wu M, Jiang F, Su W, Hong M. Stable porphyrin Zr and Hf metal-organic frameworks featuring 2.5 nm cages: High surface areas, SCSC transformations and catalyses. Chem Sci. 2015;6(6). doi:10.1039/c5sc00213c

20. Sun L, Xie J, Chen Z, Wu J, Li L. Reversible lithium storage in a porphyrin-based MOF (PCN-600) with exceptionally high capacity and stability. Dalt Trans. 2018;47(30). doi:10.1039/c8dt02161a

21. Zuo X, Zhu J, Müller-Buschbaum P, Cheng YJ. Silicon based lithium-ion battery anodes: A chronicle perspective review. Nano Energy. 2017;31. doi:10.1016/j.nanoen.2016.11.013

22. Liang B, Liu Y, Xu Y. Silicon-based materials as high capacity anodes for next generation lithium ion batteries. J Power Sources. 2014;267. doi:10.1016/j.jpowsour.2014.05.096