UNIVERSITY OF CALIFORNIA SAN DIEGO

Graphite Based 3D Li Metal Anode for Stable Solid-State Batteries

A thesis submitted in partial satisfaction of the requirements

for the degree Master of Science

in

Nano Engineering

by

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Professor Zheng Chen
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2022

THESIS APPROVAL PAGE

The thesis of Zhaohui Liang is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego
2022

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ACKNOWLEDGEMENTS

Hereby, I would like to show my sincere acknowledgement to my advisor, Professor Ping Liu. His support has been invaluable for my study, research training and thesis defense preparation, and his talk with me has proven to be very helpful to my career and life. I would also acknowledge my committee member, Professor Zheng Chen, and Professor Jian Luo for their valuable time and comment.

I would also like to express my specific gratefulness to Dr. Jianbin Zhou for his kind help and inspiring discussion, which helped a lot with my research. I also appreciate Dr. Shen Wang, Victoria Petrova, and Mengchen Liu for their help within my experiments.

Finally, I want to show my special thanks to my family, for their strong support to me, their encouragement and conversations helped me to overcome the challenges I encountered.

My thesis, in part is currently preparing for publication: Zhaohui Liang, Jianbin Zhou, Shen Wang, Victoria Petrova, Mengchen Liu, and Ping Liu*, “Graphite Based 3D Li Metal Anode for Stable Solid-State Batteries”. The thesis author is the primary author for this publication.

ABSTRACT OF THE THESIS

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University of California San Diego, 2022

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As one of the most promising energy storage devices in the future, all solid-state lithium metal battery has attracted extensive attention. However, the Li dendrite growth and large volume change during cycling have limited the practical application of Li metal anode. Here, we apply a freestanding interlayer (IL) in between solid-state electrolyte (SSE) and anode to suppress the dendrite growth, and a freestanding 3D anode is designed coupling with excellent ion conductor inside to fabricated a 3D anode with both good ionic conductivity and electronic conductivity. In this work, large MCMB (graphite) particles are utilized as 3D anode host, which provide with free space for Li metal deposition, and KB is used as ion conducting agent, which drive Li metal away from the interface of SSE and make Li deposited in 3D anode. The

testing result of this 3D MCMB/KB anode design shows an improved critical current density of 5 mA cm^{-2}. The symmetric cells with both MCMB and MCMB/KB anode show very stable cycling performance with a capacity of 2 mAh cm^{-2} at 0.5 mA cm^{-2} for over 1,000h. However, when the capacity is increased to 4 mAh cm^{-2}, the symmetric cell with MCMB anode is shorted in 23 cycles, while the cell with MCMB/KB anode runs stably for over 50 cycles. This 3D anode design offers a promising approach for achieving high energy density and long cycle life solid state Li metal anode cells.

Introduction

All solid-state lithium batteries (ASSLBs) are considered as the next generation energy storage device due to their higher achievable energy density and safety compared to the lithium-ion batteries[1-13]. However, the growth of Lithium dendrite and large volume changes over cycling, which lead to the cell internal short circuits and shortened cycle life, remain to be addressed.[14-21] Lots of strategies has been proposed regarding these modification directions, such as applying highly mechanically strengthened solid-state polymer electrolyte (SSE), depositing an interlayer (IL) on the SSE and Li anode interface to induce the homogeneous deposition of Li, and utilizing 3D anode to host Li metal deposition during charging.[14-18,23-26]

As one of the promising solutions to the challenges, 3D anode hosts have been investigated in the past years.[14-18,23-29] Among the 3D anode hosts, metal foam, porous metal, metal oxides and carbon matrices have been investigated, which are highly electronically conductive, while ionically non-conductive. [15,17,26-30] In this case, Li metal must be infused into the structure with an ionic conductor, or Li dendrites will grow at the interface between SSE and 3D anode, where Li deposition initiated. Meanwhile, the high weight loading of the host material will decrease the overall energy density of full cell. On the other hand, specifically designed solid-state oxide electrolytes also have been investigated.[15,18,31] For solid-state oxide electrolytes, they have high Li ion conductivity, but electronically non-conductive. The electron transport inside the 3D will have to rely on Li metal itself. Apart from this, the solid-state oxide electrolyte 3D framework is so brittle. Based on these facts, a mixed electron conductor and ion conductor could be an ideal design of 3D anode.[1] Xing et al.[1] proposed to

make a 3D anode by mixing graphite and SSE, which provided both high electroconductivity and ionic conductivity. However, the severe side reaction between Li and SSE inside the 3D anode produced a low Coulombic Efficiency (CE) and low Li capacity retention, which resulted in a short cycle life.

In this regard, we report a 3D anode by mixing MCMB (graphite) and KB, after introducing CNTs, a free-standing and mechanically robust 3D anode is fabricated (Figure S1). As reported by many researchers, lithiated graphite is ionically conductive and the lithiophilic product of lithiated graphite, LiC_6, can promote Li metal deposition.[32-34] In order to further improve the ionic conductivity of the anode, we use KB as Li ion conducting agent, instead of using traditional SSE as ion conductor. MCMB itself can be used as both electron conductor and ion conductor, apart from that, the voids in between MCMB particles can be used as Li metal host. During cycling, Li metal can deposit in the voids or be stripped away. In this study, a 3D MCMB/KB anode with 4 mAh cm^{-2} areal capacity and 1 mA cm^{-2} current capacity was achieved, which provided with a promising design of 3D anode.

Results and discussion

To test the effect of the 3D anode, critical current density (CCD) was firstly performed. As shown in Figure 1a, the symmetric cell with a structure of Li/LPSCl/Li shows a shortage current density of 0.5 mA cm^{-2}, which coincides with previous reports[36]. In the CCD testing process, the increment is set as 0.1 mA cm^{-2}, and step length is 30min. To examine the effectiveness of our 3D anode and IL, cells with a structure of Li/3D Anode/LPSCl/3D

Anode/Li and Li/3D Anode/IL/LPSCl/IL/3D Anode/Li were fabricated, and the testing procedures were identical except for a pre-cycle for cells with 3D anode. This process is to guarantee that same amount and enough Li is on both sides. By comparing Figure 1b with Figure 1a, we find that CCD is improved by adding 3D MCMB anode into the cell structure from 0.5 mA cm^{-2} to 0.8 mA cm^{-2}, which indicates that by only applying 3D MCMB anode to the cell is insufficient to enhance the CCD of the cell. By comparing Figure 1b with Figure 1c, the CCD with IL is facilitated from 0.8 mA cm^{-2} to 2.4 mA cm^{-2}, which proves the effectiveness of the IL. To test our main point of this work, we performed CCD to the 3D MCMB/KB anode. The cell structure is set as Li/3D Anode/ IL/LPSCl/IL/3D Anode/Li. According to the CCD testing result, a result of 5 mA cm^{-2} CCD is obtained, which is dramatically improved comparing with previously reported data. These CCD testing shows that the 3D anode with KB as ion conductor can work effectively to enhance the cycling current density of the cell.

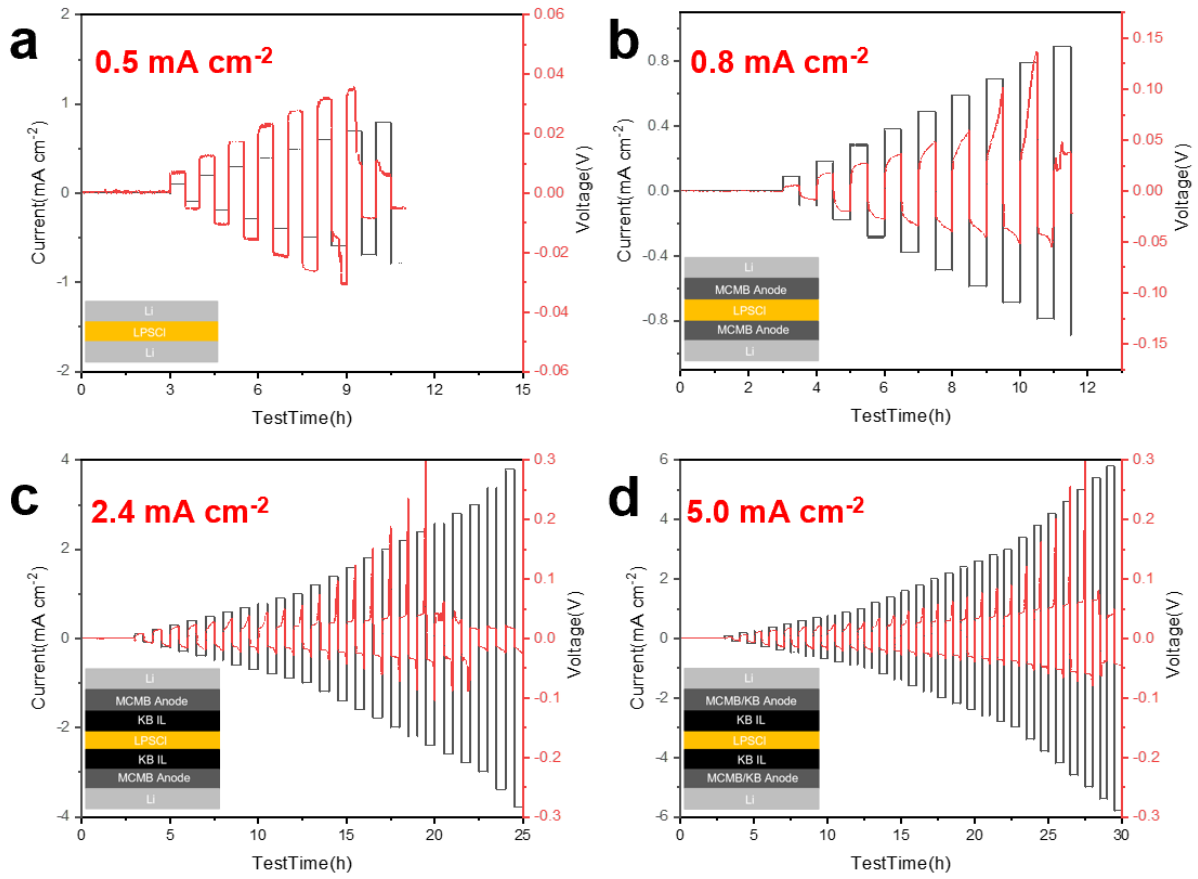

Figure 1: CCD testing result to symmetric cells with and without 3D anode. The cell structures are (a) Li/SSE/Li; (b) Li/MCMB Anode/SSE/MCMB Anode/Li; (c) Li/MCMB Anode/IL/SSE/IL/MCMB Anode/Li; (d) Li/MCMB+KB Anode/IL/SSE/IL/MCMB+KB Anode/Li.

To determine where Li metal deposited in the 3D anode, we did Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) to the 3D anode with only one discharging. As we can see from Figure 2a, there is a clear delamination between the IL and the 3D MCMB anode, and we can tell from the EDX mapping (Figure 2b) that the layer in between IL and 3D anode is Li metal, which obviously shows that Li metal deposits in a 2D manner. In Figure 2c, the gap between IL and 3D MCMB/KB anode still exists, but there is no separate layer of Li metal, which suggests that Li metal deposit does not deposit in a 2D manner. However, it is still unclear in the EDX mapping if the Li metal deposits in a 3D manner. To determine this, we did regular SEM and EDX to check where the Li metal deposited. As we see from Figure S3b, the 3D MCMB/KB anode after 4mAh cm^{-2} Li deposition, the oxygen signal inside 3D MCMB/KB

anode is very intense, while in the pristine MCMB/KB anode (Figure S3d), the anode without Li deposition, the oxygen signal inside the 3D MCMB/KB anode is sparse. This demonstrated that the Li deposited inside the 3D MCMB/KB anode in a 3D manner.

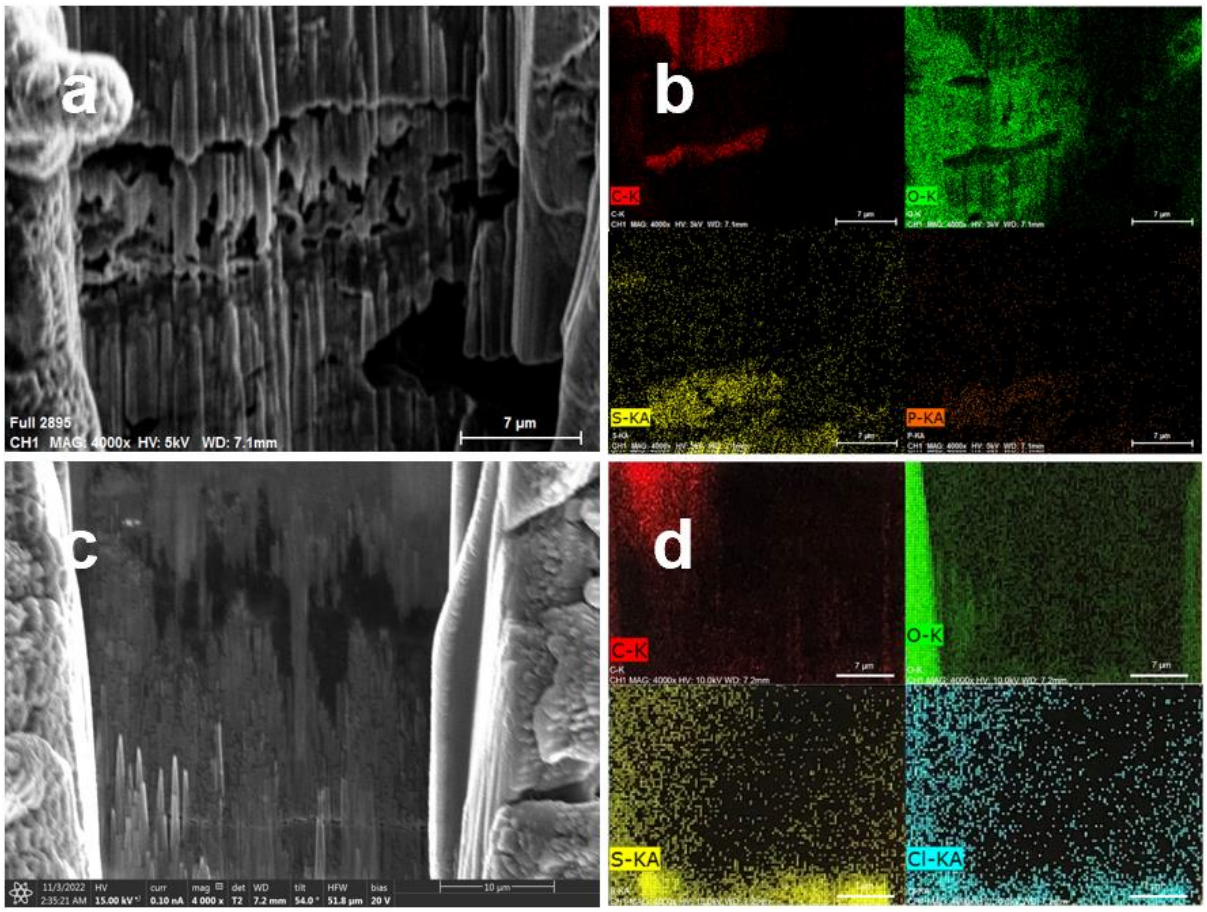

Figure 2: FIB-SEM test to the 3D anodes after depositing 4mAh cm^{-2} Li metal inside. (a) Cross-section of the 3D MCMB anode, a separated layer occurred between IL and MCMB anode; (b) The separated layer is determined to be Li; (c) Gap between IL and MCMB/KB anode exists, but no Li metal signal; (d) Determined that no Li metal deposited between IL and MCMB/KB anode.

Long-term cycling tests was performed to the 3D anode. As shown in Figure 3a, we made cells with a structure of Li/Super P/LPSCl/3D Anode, then the cell was set to run at a voltage range of 0 V ~ 2 V. We can see that the cell run stably at 0.1 mA cm^{-2} current density as a Li ion cell for over 50 cycles, and after 55 cycles, the discharge capacity is modified to 1.8 mAh cm^{-2}, corresponding 0.6 mAh cm^{-2} of Li metal is deposited into the anode. However, the cell shorts in 3 cycles. This coincides with our proposal that the Li metal first deposit on the

interface between SSE and 3D anode, and Li dendrites form on the interface penetrates through the SSE in 3 cycles. Then we tried the cell with IL, and the cell cycling data is shown in Figure 3b. While using the same loading of MCMB in the anode, by applying a KB IL into the cell, the cell run stably at a current density of 0.5 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2} for over 120 cycles (Figure 3c). However, when we tried to deposit more Li into the anode, which is 4 mAh cm^{-2}, the cell shorted in 23 cycles (Figure 3d). Then we tried the 3D anode with KB inside, as shown in Figure 3e, the cell run stably at a current density of 0.5 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2}. In the test to run the cell at an areal capacity of 4 mAh cm^{-2}, the cell still run stably for over 50 cycles (Figure 3f). This experiment proves the validity of KB as an ion conducting agent in the 3D anode.

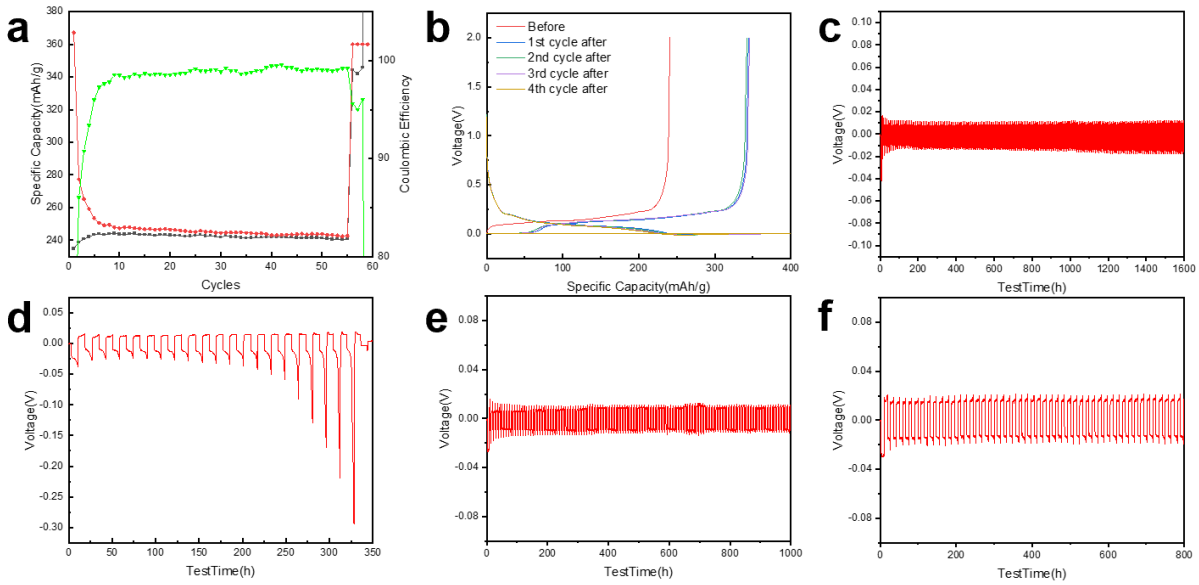

Figure 3: Long cycling performance of the cells with 3D anode. (a) Half cell performance with no IL between SSE and MCMB anode, after running for 55 cycles, 0.6 mAh cm^{-2} Li metal was deposited inside the anode, cell shorts in 3 cycles; (b) Voltage to Specific Capacity curve before and after depositing 50% more Li metal inside the MCMB anode; (c) Long-term cycling performance of symmetric cell with MCMB anode and IL at 0.5 mA cm^{-2} and 2 mAh cm^{-2}; (d) With the same cell structure to c, the cell ran at 0.5 mA cm^{-2} and 4 mAh cm^{-2}; (e) Long-term cycling performance of symmetric cell with MCMB/KB anode and IL at 0.5 mA cm^{-2} and 2 mAh cm^{-2}; (f) With the same cell structure to e, the cell ran at 0.5 mA cm^{-2} and 4 mAh cm^{-2}.

Conclusion

Overall, a freestanding, mechanically strong, flexible 3D MCMB/KB anode is fabricated, and we get a highly enhanced CCD of the anode compared with the 3D anode without KB inside. SEM imaging and EDX mapping proves that Li deposited inside the 3D MCMB/KB anode in a 3D manner, which indicates the validity of our 3D anode. These works also prove the validity of using KB as a Li ion conducting agent. By depositing more Li metal inside 3D MCMB/KB anode, we achieve a 4 mAh cm^{-2} capacity cycling stably for over 50 cycles, which has the potential to be practically utilized.[35] The design of a 3D MCMB/KB anode with KB as stable Li ion conducting agent inside, provides with a basis for further development of 3D host for Li metal anode.

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