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VGCF 3D conducting host coating on glass fiber filters for lithium metal anodes

In this paper, vapor grown carbon fiber 3D conducting host coating on a glass fiber filter has been demonstrated for its use as a lithium metal anode. The anode exhibits improved safety performance and cycling stability at a high area capacity (2 mAh cm<sup>-2</sup> and above).

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VGCF 3D conducting host coating on glass fiber filters for lithium metal anodes<sup>†</sup>

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We report a rational design of vapor grown carbon fiber (VGCF) 3D conducting host coating on a glass fiber filter for its use as a lithium metal anode to inhibit dendrite growth and enhance cycling stability. The high coulombic efficiency of 91.1% and stable cycling can be maintained after 100 cycles (965 h) at the current density of 0.5 mA cm<sup>-2</sup> for the capacity of 2.5 mAh cm<sup>-2</sup> in the carbonate electrolyte.

Since the successful commercialization of lithium ion batteries (LIBs) in 1991 by the SONY Corporation of Japan, LIBs are considered to be one of the most successful achievements of electrochemical power sources, and have been widely used in the portable electronic devices.<sup>1,2</sup> However, the energy density of conventional LIBs cannot meet the ever-increasing demand for electric vehicles and grid-scale energy storage.<sup>3</sup> The Li metal anode is a promising anode candidate due to the highest theoretical specific capacity (3860 mAh g<sup>-1</sup>) and the lowest electrochemical potential (-3.040 V vs. standard hydrogen electrode) among all present anode materials for Li-based batteries.<sup>4,5</sup>

Unfortunately, the poor safety and low coulombic efficiency (CE) during prolonged cycling impede the practical application of the lithium metal anode.<sup>6</sup> A Li metal anode has virtually infinite relative volume change during Li deposition/stripping owing to its hostless nature, generating cracks on the solid electrolyte interface (SEI).<sup>7,8</sup> The enhanced ion flux and low impedance in the regions with cracks lead to a rapid growth of Li dendrites (Scheme 1a). The side reactions between dendritic Li and the electrolyte and electrical disconnection to the current collector exacerbate the evolution of dead Li from dendrites, resulting in increased impedance and capacity loss.<sup>9</sup> The continuously growing Li dendrites also can penetrate the separator eventually, causing short circuits and thermal runaway of cells.

Extensive efforts have been made to solve the problems mentioned above. The additives such as vinylene carbonate (VC),<sup>10</sup>

fluoroethylene carbonate (FEC),<sup>10</sup> LiF,<sup>11</sup> LiBr,<sup>12</sup> N-propyl-N-methylpyrrolidiniumbis(trifluoromethanesulfonyl)amide (Py13TFSI),<sup>13</sup> and Li polysulfide<sup>14</sup> have been investigated to improve the stability of SEI. Constructing additional protective layers is another commonly adopted approach, which can act as a strong physical barrier to suppress the formation of Li dendrite.<sup>15</sup> The examples include SiO2@polymethyl methacrylate (PMMA) core-shell nanoparticle coating,<sup>16</sup> polyacrylonitrile (PAN) fiber array coating,<sup>17</sup> poly(dimethylsiloxane) film coating,18 and glass fiber cloth modification.<sup>19</sup> Building a three-dimensional (3D) conductive network is an effective way to improve the electrochemical performance of electrode materials.<sup>20-22</sup> And designing a 3D conductive host for Li plating has also attracted considerable attention recently. For example, the 3D Cu current collector,<sup>23</sup> fibrous metal felt (FMF) 3D interlayer,24 layered reduced graphene oxide,<sup>25</sup> and carbon nanotube (CNT) matrix<sup>26</sup> have been investigated. These abovementioned studies have shown that the 3D conductive host can greatly improve the CE of the Li metal anode by reducing the current density and thus delaying the potential dendrite onset. But the solution is usually employed singly in these studies. When electrodes are cycling at a low area capacity, the single solution may be effective. However, when cycling at a relatively higher area capacity (2 mAh  $cm^{-2}$  and above),



Scheme 1 Schematic diagrams of Li deposition/stripping processes: (a) on the Cu foil and (b) on the VGCF@GF electrode. (c) Schematic diagrams for the preparation of the VGCF@GF electrode. (d) Schematic illustration of the VGCF@GF electrode used as a lithium metal anode.



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the significant increase in the amount of deposited Li may penetrate the protective layer or grow outside the 3D-conductive host resulting in the formation of Li dendrites.

Here, we demonstrate a rational design of vapor grown carbon fiber 3D conducting host coating on glass fiber filters (VGCF@GF) by combining these two strategies (3D conductive host and protective layer) together to realize dendrite-free Li deposition at the high area capacity. The fabrication process is very simple (Scheme 1c). A thin film of Au is deposited onto the surface of GF via a magnetron sputtering process (Fig. S1, ESI<sup>+</sup>). Then the VGCF matrix is subsequently coated onto the surface to obtain the final VGCF@GF electrode, which can be directly used as the lithium metal anode (Scheme 1d). The previous report has indicated that there are many polar functional groups on the surface of GF which can cause strong interactions between the GF and Li ions, and then bring out the uniform redistribution of Li ions on the current collector.<sup>19</sup> And the high modulus of the chemically stable GF is likely to suppress the formation of Li dendrites. The VGCF 3D conducting host with many voids can alleviate the volume change of Li plating/stripping and maintain the electron transport pathways among the isolated lithium particles (Scheme 1b). Owing to the functional protective layer (GF) and the well-established conducting host, the VGCF@GF design is expected to inhibit dendrite growth and enhance the cycling stability of the Li metal anode.

The whole VGCF@GF electrode with the thickness of about 400  $\mu$ m (Fig. 1e, Fig. S2, ESI†) is designed to consist of a conductive layer (VGCF) and a nonconductive layer (GF); the Au layer is hard to be distinguished owing to its too little loading mass (only 0.07 mg cm<sup>-2</sup>). The top view SEM images of the pristine VGCF@GF electrode are presented in Fig. 1a and b. The glass fibers form a robust and porous structure, which can guarantee the unobstructed diffusion of Li ions and suppress

the formation of Li dendrites. The VGCFs with the length of  $6-10 \ \mu m$  are interconnected to each other to form a 3D conducting host (Fig. 1c). The VGCF layer not only serves as a "built-in" current collector, but also helps to form many voids (Fig. 1d and f) which can provide spaces for the deposition of the Li metal.

The Cu foil is a widely used current collector for Li deposition. Thus, the morphologies of deposited Li have been investigated after specified cycles of Li deposition/stripping galvanostatically on the Cu foil or the VGCF@GF electrode (Fig. 2). For the Cu foil after 10 cycles, the mossy-like Li dendrites can be clearly observed on the surface (Fig. 2a and b). By contrast, the surface of the VGCF@GF electrode after 50 cycles (Fig. 2c and d) is still very smooth, which is similar to the pristine one (Fig. 1a and b). The micrometer-sized deposited Li metal particles are uniformly distributed in voids formed in the VGCF host (Fig. 2e and f, Fig. S3, ESI†). And the Li metal does not appear in the glass fiber layer basically (Fig. 2g). The VGCF embedded in the deposited Li metal particles (Fig. 2h) is also helpful in maintaining the conductive network of the electrode.

For practical applications in batteries, the areal capacity of electrodes is usually needed to be more than 2 mAh cm<sup>-2</sup>. Thus, the cycling performances of Li deposition/stripping on the Cu foil and VGCF@GF electrodes for different capacities of 2.0, 2.5 and 3.0 mAh cm<sup>-2</sup> at the current density of 0.5 mA cm<sup>-2</sup> have been investigated (Fig. 3). For the Cu foil electrodes, the CE for different capacities exhibits a quick decay after about 35 cycles.



Fig. 1 (a and b) Top view, (c and d) bottom view and (e and f) side view SEM images of the pristine VGCF@GF electrode.



**Fig. 2** (a and b) Top view SEM images of Li deposition on a Cu foil for 2.5 mAh cm<sup>-2</sup> of Li deposition at the current density of 0.5 mA cm<sup>-2</sup> after 10 cycles. (c and d) Top view, (e and f) bottom view and (g and h) side view SEM images of the VGCF@GF electrode for 2.5 mAh cm<sup>-2</sup> of Li deposition at the current density of 0.5 mA cm<sup>-2</sup> after 50 cycles.



Fig. 3 Comparison of the coulombic efficiency (CE) of Li deposition/ stripping on the Cu foil and VGCF@GF electrodes at the current density of 0.5 mA cm<sup>-2</sup> for different capacities: (a) 2.0 mAh cm<sup>-2</sup>, (b) 2.5 mAh cm<sup>-2</sup> and (c) 3.0 mAh cm<sup>-2</sup>. Voltage profiles of (d) the Cu foil and (e) the VGCF@GF electrode at 0.5 mA cm<sup>-2</sup> for 2.5 mAh cm<sup>-2</sup>. (f) Voltage hysteresis of these two electrodes at 0.5 mA cm<sup>-2</sup> for 2.5 mAh cm<sup>-2</sup>. (g) Voltage stability of the VGCF@GF electrode at 0.5 mA cm<sup>-2</sup> for 2.5 mAh cm<sup>-2</sup>.

Because less and less Li can be stripped during repeated cycling, the continuously growing Li dendrites may penetrate the separator to result in an internal short-circuit of the battery. For the VGCF@GF electrodes, the CEs are maintained at about 89.3%, 91.1% and 91.7% after 100 cycles at the capacity of 2.0, 2.5 and 3.0 mAh cm<sup>-2</sup>, respectively. The much improved cycling stability can also be proved by the comparison of voltage profiles. The voltage plateau of the Cu foil (Fig. 3d) varies dramatically, compared with that of the VGCF@GF electrode (Fig. 3e). The voltage hysteresis of the VGCF@GF electrode is maintained less than 150 mV after 100 cycles (Fig. 3f), while the voltage hysteresis of the Cu foil increases to above 450 mV only after 40 cycles. Moreover, the cell voltage of the VGCF@GF electrode is very stable even after a very long cycling duration of 965 h (Fig. 3g). The comparison of the electrochemical performance of the VGCF@GF electrode in this work with those in some reported works employing the concept of a 3D conductive host or a protective layer is summarized in Table S1, ESI.<sup>†</sup> And the CE of the VGCF@GF electrode without Au coating is also investigated (Fig. S4, ESI<sup>†</sup>).

The electrochemical performance of the VGCF@GF electrode at the higher current density of 1.0 mA cm<sup>-2</sup> has also been investigated (Fig. S5, ESI<sup>†</sup>). After 100 cycles at 1.0 mA cm<sup>-2</sup> for 2.0, 2.5 and 3.0 mAh cm<sup>-2</sup>, all the CEs can be maintained at

above 89.0% (Fig. S5a, ESI<sup>†</sup>). And the cell voltage is very stable during the cycling duration of 530 h (Fig. S5b, ESI<sup>†</sup>). Even under the extremely high current densities of 2.0 and 5.0 mA cm<sup>-2</sup>, the VGCF@GF electrode still delivers stable CEs of 90.5% and 92.7% after 60 cycles, respectively (Fig. S6, ESI<sup>†</sup>). In order to further verify the cycling stability of the VGCF@GF electrode, the VGCF@GF electrode is assembled into a pouch cell with Li metal as the counter electrode. As shown in Fig. S5c and S5d, ESI<sup>†</sup>, a relatively high CE of 92.7% with a stable voltage hysteresis is maintained after 100 cycles at 1.0 mA cm<sup>-2</sup> for 2.0 mAh cm<sup>-2</sup>.

The wettability of the electrodes is also an important factor for Li deposition, because an electrode with good wettability can retain the liquid electrolytes easily and uniformly.<sup>27</sup> Thus, contact angle tests have been performed. The contact angle of the Cu foil is measured to be 18.4° (Fig. 4a and b). However, the contact angle of the VGCF@GF electrode significantly decreased to  $0^{\circ}$  (Fig. 4c and d) after the same contact time (1 s). The superior wettability of the VGCF@GF electrode is in favor of the uniform distribution of Li ions between the electrode and the electrolyte. Electrochemical impedance spectra are recorded on these two electrodes to further study the origin of the improved electrochemical performance (Fig. 4e). The semicircles in the high and medium frequency ranges are related to the interfacial resistance at SEI  $(R_{sei})$  and charge-transfer resistance  $(R_{ct})$ , and the inclined straight line in the lower frequency range is related to the diffusion of Li ions.<sup>25,28,29</sup> Obviously, the  $R_{\rm sei}$  (13.8  $\Omega$ ) and  $R_{\rm ct}$  (5.9  $\Omega$ ) values of the VGCF@GF electrode are much smaller than those of the Cu foil electrode (148.5  $\Omega$  and 68.3  $\Omega$ , respectively), indicating the more favorable Li stripping/plating kinetics for the VGCF@GF electrode.

The VGCF@GF electrode has several outstanding features that can improve the cycling stability of the Li metal anode: (1) the protective layer of GF can suppress the formation of Li dendrites and avoid the internal short-circuit of the battery. (2) Li metal can be accommodated in the VGCF 3D conducting host, and the structural strength and conductive connection can be well maintained. (3) The introduction of Au in the contact area of VGCF and GF layers can smoothen the deposition morphology of the Li metal grown on the interface.<sup>30,31</sup> (4) Homogeneous distribution of Li ions between the electrode and the electrolyte favors the uniform deposition of Li metal in the electrode.



**Fig. 4** Contact angle images of (a and b) the Cu foil and (c and d) the VGCF@GF electrode. (e) Nyquist plots and fitting results of the Cu foil and VGCF@GF electrodes after 15 cycles; the inset shows the equivalent circuit used for fitting.

In conclusion, we demonstrated a rational design of VGCF 3D conducting host coating on glass fiber filters for use as a lithium metal anode. The results reveal that Li metal is accommodated in the voids formed in the VGCF host, and no Li dendrites are observed on the surface layer of the glass fiber. Even cycling at a very high capacity of 3 mAh cm<sup>-2</sup>, the high CE of 91.7% can be retained. Besides, all the raw materials are commercial products and the fabrication process is simple and short time-consuming, and this design thereby offers a new potential possibility for improving the cycling stability of a Li metal anode.

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## Conflicts of interest

There are no conflicts to declare.

#### References

- 1 J. M. Tarascon and M. Armand, Nature, 2001, 414, 359-367.
- 2 J. B. Goodenough and Y. Kim, Chem. Mater., 2010, 22, 587-603.
- 3 M. V. Reddy, G. V. S. Rao and B. V. R. Chowdari, *Chem. Rev.*, 2013, **113**, 5364–5457.
- 4 D. Lin, Y. Liu and Y. Cui, Nat. Nanotechnol., 2017, 12, 194-206.
- 5 S. Matsuda, Y. Kubo, K. Uosaki and S. Nakanishi, *ACS Energy Lett.*, 2017, **2**, 924–929.
- 6 Y. Liu, D. Lin, Z. Liang, J. Zhao, K. Yan and Y. Cui, *Nat. Commun.*, 2016, 7, 10992.
- 7 K. Liu, A. Pei, H. R. Lee, B. Kong, N. Liu, D. Lin, Y. Liu, C. Liu, P.-C. Hsu, Z. Bao and Y. Cui, *J. Am. Chem. Soc.*, 2017, **139**, 4815–4820.
- 8 C. Wang, Y. Gong, B. Liu, K. Fu, Y. Yao, E. Hitz, Y. Li, J. Dai, S. Xu, W. Luo, E. D. Wachsman and L. Hu, *Nano Lett.*, 2017, 17, 565–571.
- 9 X.-B. Cheng, R. Zhang, C.-Z. Zhao and Q. Zhang, *Chem. Rev.*, 2017, 117, 10403–10473.

- 10 J. Guo, Z. Wen, M. Wu, J. Jin and Y. Liu, *Electrochem. Commun.*, 2015, **51**, 59–63.
- 11 Z. S. Wu, L. L. Xue, W. C. Ren, F. Li, L. Wen and H. M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 3290–3297.
- 12 Y. Lu, Z. Tu, J. Shu and L. A. Archer, *J. Power Sources*, 2015, 279, 413–418.
- 13 N.-W. Li, Y.-X. Yin, J.-Y. Li, C.-H. Zhang and Y.-G. Guo, *Adv. Sci.*, 2017, 4, 1600400.
- 14 X.-B. Cheng, H.-J. Peng, J.-Q. Huang, R. Zhang, C.-Z. Zhao and Q. Zhang, ACS Nano, 2015, 9, 6373–6382.
- 15 H. Wu, Y. Cao, L. Geng and C. Wang, Chem. Mater., 2017, 29, 3572–3579.
- 16 W. Liu, W. Li, D. Zhuo, G. Zheng, Z. Lu, K. Liu and Y. Cui, *ACS Cent. Sci.*, 2017, **3**, 135–140.
- 17 J. Lang, J. Song, L. Qi, Y. Luo, X. Luo and H. Wu, ACS Appl. Mater. Interfaces, 2017, 9, 10360–10365.
- 18 B. Zhu, Y. Jin, X. Hu, Q. Zheng, S. Zhang, Q. Wang and J. Zhu, *Adv. Mater.*, 2017, 29, 1603755.
- 19 X.-B. Cheng, T.-Z. Hou, R. Zhang, H.-J. Peng, C.-Z. Zhao, J.-Q. Huang and Q. Zhang, *Adv. Mater.*, 2016, **28**, 2888–2895.
- 20 X. Zhou, Y.-X. Yin, A.-M. Cao, L.-J. Wan and Y.-G. Guo, ACS Appl. Mater. Interfaces, 2012, 4, 2824–2828.
- 21 P. Lian, J. Wang, D. Cai, L. Ding, Q. Jia and H. Wang, *Electrochim.* Acta, 2014, **116**, 103–110.
- 22 P. Lian, Y. Dong, Z.-S. Wu, S. Zheng, X. Wang, W. Sen, C. Sun, J. Qin, X. Shi and X. Bao, *Nano Energy*, 2017, **40**, 1–8.
- 23 C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li and Y.-G. Guo, Nat. Commun., 2015, 6, 8058.
- 24 H. Lee, J. Song, Y.-J. Kim, J.-K. Park and H.-T. Kim, Sci. Rep., 2016, 6, 30830.
- 25 D. Lin, Y. Liu, Z. Liang, H.-W. Lee, J. Sun, H. Wang, K. Yan, J. Xie and Y. Cui, *Nat. Nanotechnol.*, 2016, **11**, 626–632.
- 26 S. Matsuda, Y. Kubo, K. Uosaki and S. Nakanishi, *Carbon*, 2017, **119**, 119–123.
- 27 P. Yang, P. Zhang, C. Shi, L. Chen, J. Dai and J. Zhao, J. Membr. Sci., 2015, 474, 148–155.
- 28 L. Fan, H. L. L. Zhuang, L. N. Gao, Y. Y. Lu and L. A. Archer, *J. Mater. Chem. A*, 2017, **5**, 3483–3492.
- 29 W. Luo, Y. Gong, Y. Zhu, Y. Li, Y. Yao, Y. Zhang, K. Fu, G. Pastel, C.-F. Lin, Y. Mo, E. D. Wachsman and L. Hu, *Adv. Mater.*, 2017, 29, 1606042.
- 30 K. Yan, Z. D. Lu, H. W. Lee, F. Xiong, P. C. Hsu, Y. Z. Li, J. Zhao, S. Chu and Y. Cui, *Nat. Energy*, 2016, 1, 8.
- 31 C. Yang, Y. Yao, S. He, H. Xie, E. Hitz and L. Hu, *Adv. Mater.*, 2017, 29, 1702714.