This article can be cited before page numbers have been issued, to do this please use: Y. Wu, X. Xiong, R. Zhi, Q. Zhou, W. Yan, Y. Zhu, Y. Chen, L. Fu and N. Yu, Mater. Adv., 2021, DOI: 10.1039/D1MA00121C.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
1. Introduction

Developments in consumer electronics and electric vehicles have recently heightened the need for rechargeable batteries with high energy density and long cycling life\textsuperscript{[1,2]}. Compared with graphite anode of commercial lithium ion batteries, lithium metal anode has been attracting considerable interest for its high theoretical specific capacity (3860 mAh g\textsuperscript{-1}) and the lowest redox potential (-3.04 V vs. SHE)\textsuperscript{[3]}. However, the situation is that the low coulombic efficiency and the lowest redox potential originated from uneven lithium deposition during cycling hinder batteries with high energy density and long cycling life. Vehicles have recently heightened the need for rechargeable batteries, which mainly include modifying electrolytes such as adding additives\textsuperscript{[5,6]}, applying a protective coating on the separators\textsuperscript{[7]} or the surface of anode directly\textsuperscript{[8]}, and providing host materials\textsuperscript{[9]}. Normally, the enhanced SEI formed in situ by electrolyte modification cannot achieve ideal mechanical robustness to endure the dramatic volumetric change of lithium anode. While mechanically suppressing the dendrites by solid electrolyte is also subject to the poor interface contact. As a result, more recent attentions have focused on the electrode surface modification, and coating layers with great flexibility and mechanical strength exhibit the ability to stabilize the electrode interface\textsuperscript{[10,11]}. Generally, high ionic conductivity and sufficient mechanical robustness are the two essential properties for an ideal modified coating to accommodate the inhomogeneous Li\textsuperscript{+} ions distribution nearby the lithium anode surface and sustain the serious electrode inhomogeneity in the composition and structure of SEI would give rise to the uneven and loose lithium deposition layer due to the nonuniformity of lithium ion flux on the SEI surface, which is favorable for the evolution of lithium dendrites.

Metallic lithium is an promising next generation electrode material due to its ultrahigh specific capacity and the lowest redox potential. However, short cycling lifespan and safety hazards have hindered the practical application of it. To improve the cycling performance of lithium metal anode, a dendrite-free lithium deposition and stable electrode-electrolyte interface are of vital importance. Here, we prepared a thin PMMA/PVDF gel coating by electrospinning technique on the Cu substrate for anode directly, which can not only homogenize lithium ion flux, promoting the uniform lithium deposition, but also alleviate the dramatic volume change of the lithium anode, improving the stability of electrode interface. Owing to the excellent lithiophilic property and high mechanical flexibility of the binary blend polymer coating, stable cycling for over 1400 h is achieved in Li/Li symmetric cell using the modified coating at 1 mA/cm\textsuperscript{2} with a specific capacity of 4 mAh/cm\textsuperscript{2}. The binary blend polymer coating with complementary properties prepared by this facile method provides a new insight on lithium metal anode improvement.

Binary PMMA/PVDF blend film modified substrate enables superior lithium metal anode for lithium batteries

Xiaosong Xiong, Ruoyu Zhi, Qi Zhou, Wenqi Yan, Yusong Zhu,\textsuperscript{*} Yuhui Chen, Lijun Fu, Nengfei Yu,\textsuperscript{*} Yuping Wu\textsuperscript{*}

State Key Laboratory of Materials-oriented Chemical Engineering & School of Energy Science and Engineering, Nanjing Tech University, Nanjing 211816, China. E-mail: zhuys@njtech.edu.cn (Zhu); yufn@njtech.edu.cn (Yu); wyp@fudan.edu.cn (Wu)

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
deformation during cycling. However, it is still a challenge to reduce the additional interface resistance and deposition barrier introduced by the modified coating, and most improvement strategies are far away from application due to high cost and complex preparation process.

In this contribution, poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) are utilized to build an artificial protective coating on Cu substrate for lithium anode via electrospinning technique. The main PMMA polymer composition has the advantages of good electrochemically stability, low interfacial impedance and low cost. In addition, considering that the strong interaction between carbonyl (-CO-) group in methyl methacrylate (MMA) unit and liquid organic electrolyte, PMMA can contain a large amount of liquid electrolytes and shows superior affinity with the liquid electrolyte[14], significantly reducing the interface resistance and lithium heterogeneous nucleation barrier, which is conducive to the uniform deposition of lithium in the following deposition process. To improve the mechanical robustness of the ex-situ modified coating, polyvinylidene fluoride (PVDF) matrix is added. Its characteristics of high dielectric constant (~10) and relative low surface energy (~35 mJ/m²) are believed to reduce the overpotential and promote lithium to deposit compactly with smaller area in theory[15]. Also, -C-F- groups with strong electron-withdrawing capabilities endows the matrix highly resistant to electrochemical oxidation, ensuring the superior physical and chemical stability of the modified coating, and maintaining the integrity of the coating. Consequently, due to the synergistic effect of the composition and structure of the modified polymer coating, Li⁺ ions diffusing from the bulk electrolyte can be evenly distributed in the protective coating and depositing on the Cu substrate compactly and uniformly. As a result, in half-cells, the PMMA/PVDF modified Cu electrodes show an enhanced coulombic efficiency of 98.3% for over 260 cycles at 1 mA/cm², and the stable cycling life-span, which is four times than that of bare Cu electrodes. In addition, low overpotential (~20 mV) is also achieved in Li/Li symmetric cells cycled at 1 mA/cm² for over 1400 h when protected by the PMMA/PVDF modified coating, which is much better than that of the bare electrodes (~400h). Furthermore, dendrite-free lithium deposition morphology is observed on PMMA/PVDF coating modified electrodes and thus a stable electrode/electrolyte interface is ensured.

2. Results and discussion

As shown in Figure 1a, the PMMA/PVDF modified layer was directly collected on the copper substrate by electrospinning technique. Afterwards, the electrode foil was punched to obtain the electrodes with a diameter of 15 mm. The thickness of the modified layer was controlled by the electrospinning time. Measured by digital micrometer, the optimal thickness was about 50 μm for 5 h-electrospinning. After the cell was assembled, the modified layer was compressed to 4 μm (Figure S1a), which ensures no additional resistance for the migration of lithium ions. Figure 1b shows the top-view scanning electron microscope (SEM) image of electrospun PMMA/PVDF film. A 3D interconnected network structure with numbers of voids is obtained via electrospinning technique, which is beneficial to store massive electrolyte, facilitate the diffusion of lithium ions and restrict the lithium deposition[16]. The fibers are dispersed uniformly without beads, exhibiting an average diameter of 1.6 μm (Figure S1b). As is shown in the digital picture (Figure 1c), the modified layer adhering to the Cu foil presents white colour. Subsequently, it turns into a flexibility and transparent gelatinous substance as soon as it contacts with the electrolyte (Figure 1d). This result can be explained by the fact that the PMMA/PVDF macromolecules swollen after absorbing electrolyte[17]. Afterwards, the pristine electrospon modified coating was removed from the copper electrode for Fourier transform infrared spectra (FTIR) measurement (Figure 1e). The characteristic peaks of PMMA and PVDF are cleanly identified in the pristine PMMA/PVDF electrospon coating. The characteristic peaks of PMMA appear at 1726 cm⁻¹ (C=O stretching vibration), and 988 cm⁻¹ (CH₂ wagging mode). Also, the wide split bands at 1148 cm⁻¹ and 1191 cm⁻¹ are from C-O stretching vibration in PMMA. The bands at 1400 cm⁻¹ (CH₂, CF₂ deformation vibration), 877 cm⁻¹ (amorphous phase PVDF), 841 cm⁻¹ (-CH₂ in-plane deformation vibration) and 490 cm⁻¹ (wagging mode of CF₂) are from the PVDF. Both compounds do not present much interaction, and thus we can determine that a uniform binary PMMA/PVDF blend coating was prepared by electrospinning successfully. The affinity of current collector with electrolyte was evaluated by measuring the contact angle
on substrate (Figure 1f-g). The contact angle of ether-based electrolyte on the Cu foil surface is about 32°. As for the modified Cu foil, the electrolyte spreads out as soon as it contacts with the electrode surface. This result demonstrates an improved wettability for electrolyte on the modified anode, which is known to be able to mitigate the concentration gradient of lithium near the anode surface and decrease the cell resistance[14].

Li/Cu half cells were applied to investigate the influence of PMMA/PVDF modified coating on lithium deposition/dissolution behavior. Firstly, the cyclic voltammogram (CV) of the Li/modified Cu half cell during the first three cycle range in -0.2-1.5 V is given in Figure 2a. The reduction peak at 0.37 V in the first cycle represents the SEI formation process, and a couple of redox peaks near 0 V (vs. Li+/Li) are the characteristic of the lithium deposition/dissolution process, which means that the introduction of modified layer surely will not hinder the normal deposition and dissolution behavior of lithium. Furthermore, in the third cycle, the modified Cu exhibits a higher peak height (8.99 mA) than that of the bare Cu (4.76 mA)(Figure S2a), the increased peak height in CV curves of the cell using modified electrode indicates a faster lithium diffusion behavior on modified substrate surface[18], confirming a good SEI was achieved. In order to demonstrate the positive regulation of the modified coating on lithium deposition behavior, the overpotential of Li deposition in the first cycle was investigated, which is defined as the difference between tip voltage (lithium nucleation overpotential) and the later stable plateau voltage (mass transfer overpotential) in the voltage curve during the discharge process. As is shown in Figure 2b, the nucleation overpotential and mass transport overpotential in the first cycle for the control sample are -170 mV and -76 mV, respectively, that is, the lithium deposition overpotential was calculated as -94 mV. As for the modified samples, the nucleation and mass transport overpotential are -81 mV and -49 mV, respectively, and the corresponding lithium deposition overpotential is thus only -32 mV, which is obviously lower than that in control sample. The noteworthy decrease in lithium deposition overpotential demonstrates that there is no additional deposition barrier for lithium ions after the introduction of modified coating. Furthermore, originated from the good affinity between PMMA and lithium, a significant reduction in the lithium deposition overpotential was achieved[18]. In Li-Cu half cells, the coulombic efficiency (CE) is defined as the amount of lithium stripping from working electrodes over that of depositing on it, while the Li source is excessive at the anode side. The value of CE reflects the consumption of active lithium during the actual cycling. As shown in Figure 2c, the average coulombic efficiency of the cell with control electrode can keep stable at 97.2% only in the first 70 cycles, and then exhibits cell failure, which is mainly ascribed to the consumption accumulation of active lithium and electrolyte in the early stage during cell cycling, leading to large interface impedance[20,21]. In the case of electrode modified by the PMMA/PVDF coating, a high and stable coulombic efficiency of 98.3% was achieved over 260 cycles. Furthermore, similar results can be observed when the testing condition was restricted to 1 mA/cm²-3 mAh/cm² and 3 mA/cm²-1 mAh/cm², respectively (Figure S2b-c). The bare Cu electrode presents a more serious coulombic efficiency fluctuations when applied an increased current density or lithium deposition/dissolution capacity. By contrast, cells with the modified Cu electrode still remain a stable cycling performance with average coulombic efficiencies of 97.8% and 95.6%, respectively, confirming the flexible modified coating has good improvement effect under the condition of both high current density and more dramatic volume change. These remarkable improvements strongly indicate that the polymer modified coating prepared via electrospinning technique successfully stabilizes lithium metal anode and reduce the irreversible consumption of active lithium. To further investigate the stabilization effect of modified electrode toward
lithium deposition/stripping behavior, polarization voltage is utilized to evaluate the stability of electrode interface in lithium metal batteries because of the accumulation of dead lithium and poor interface SEI will increase the voltage polarization\textsuperscript{[22]}. Figure 2d and S2d show the voltage profiles of modified Cu/bare Cu at 1\textsuperscript{st}, 10\textsuperscript{th}, 50\textsuperscript{th} and 150\textsuperscript{th} cycles. The cell applying modified coating realizes a highly stable voltage profile with much smaller voltage polarization compared with the control sample. After 50 cycles, the polarization voltage of the cells with bare Cu and modified Cu are 62 mV and 32 mV, respectively, suggesting a PMMA/PVDF modified coating is beneficial to the formation of stable electrode interface. In contrast, at 150 cycles, the charging voltage of the control sample exhibited obvious fluctuation, which could be ascribed to the severe interfacial fluctuation occurs on the anode induced by the poor plating/stripping behavior\textsuperscript{[20]}. In addition, from the Tafel profile (Figure 2e), a higher exchange current density of 0.112 mA/cm\textsuperscript{2} was obtained in the cell using modified Cu, which was significantly higher than that of the control sample (0.0017 mA/cm\textsuperscript{2}), confirming a better Li\textsuperscript{+} ionic transmission in electrode interface after being modified. Furthermore, a significantly improved electrode interface can also be confirmed by electrochemical impedance spectra (EIS) analysis. Figure 2d shows that no additional resistance was observed for lithium-ion migration after introducing the modified coating, which is evidently attributed to the gelatinous PMMA/PVDF modified layer with fibrous and porous network structure preserving massive lithium migration pathways to ensure rapid Li\textsuperscript{+} ions transmission nearby the electrode interface. In addition, half cells with bare Cu electrode represents a charge transfer resistance (R\textsubscript{ct}) of 94.3 \Omega after the 1\textsuperscript{st} cycle and 28.4 \Omega at 40th cycles (Table S1). By contrast, the charge transfer resistance of the cells using modified Cu is much smaller, which is 48.8 \Omega after the first cycle and 5.98 \Omega after 40 cycles, indicating a promoted SEI with much less dead lithium, which is in line with the results from the polarization voltage\textsuperscript{[13]}

Lithium deposition behavior on bare Cu and modified Cu substrates are illustrated in Figure 3a. Due to the unstable electrode/electrolyte interface, lithium deposition is likely to show uneven morphology on bare Cu substrate, which will cause the growth of lithium dendrites, seriously shorten the life of lithium metal anode and reduce coulombic efficiency. As for the polymer fibers modified Cu substrate, the abundant functional groups on flexible polymer fibers can not only homogenize lithium ions flux by providing adhesion sites but also confine the lithium deposition behavior, and thus leading to uniform lithium deposition morphology. Figure 3b-e are the top and cross-section SEM images of lithium deposition on bare Cu after the first cycle. After 1 mAh/cm\textsuperscript{2} lithium deposition at 1 mAh/cm\textsuperscript{2}, the as-grown Li deposition presents a clear filamentary like Li morphology with diameters range from 2-10 \mu m, known as for the lithium dendrites\textsuperscript{[23]} (Figure 3b). From cross-section view, the loose and uneven lithium deposited layer has a thick-ness of ca. 13 \mu m (Figure 3c). By contrast, the deposition of lithium on the modified electrode shows a superior morphology. Firstly, it is clear that the flexible modified layer with superior mechanical robustness still retains the fibrous network structure (Figure 3d), and less lithium is adhered, that means the diffusion of lithium ions will not be hindered and a
low polarization is ensured. From the cross-section illustrated in Figure 3e, it can be seen that lithium is deposited in a very dense form with a thickness of about 9 µm. After 40 cycles, a large amount of flocculent dead lithium can be observed on the surface of the lithium deposition on bare Cu substrate (Figure 3f-g), which is mainly resulting from of the massive formation of lithium dendrites in previous cycles. For the modified Cu substrate, the protective coating still maintains the fibrous network structure and the lithium deposition morphology remains flat. There are two possible reasons for this: Lithiophilic PMMA can improve the initial lithium deposition density on the substrate by chemically anchoring Li⁺, so that the distribution of lithium ions will be more uniform in the subsequent process[16]. Besides, PVDF has moderate surface energy and high dielectric constant, which is believed to promote the formation of lithium deposition with large surface area[15]. In addition, LiF can be generated via the interface reaction between PVDF and lithium, which can favor a stable SEI due to its high ionic conductivity, low diffusing energy and excellent mechanical strength. As a result, the dense and uniform deposition morphology reduces the possibility for the formation of dendritic lithium, and is beneficial to enhance the cycling stability and prolong the cell lifespan[24]. As illustrated in Figure 3j, the FTIR spectra of the modified coating at different states were investigated. Compared with the initial state discussed above, the electrospun coating after soaking in electrolyte for 12 h loses the C=O characteristic peak at 1726 cm⁻¹ and forms new peaks centered at 1640 cm⁻¹ and 510 cm⁻¹, which are ascribed to the keto carbon group and Li-O bond of the reaction product of CH₂OLi[25], caused by the reaction between PMMA and lithium ions. The test results are consistent with the lithium anchoring process and chemical reaction mechanism of PMMA (Figure 3k)[26], the lithium ions trapped on the modified coating surface provides uniform nucleation sites and regulates the Li⁺ ions flux for the subsequent lithium deposition process, alleviating lithium ion aggregation due to inevitable roughness of electrode surface. Accordingly, the modified coating shows extremely low interfacial resistance and decreased lithium deposition barrier, which greatly stabilizes the electrode interface and is conducive to the uniform deposition of lithium. Meanwhile, the broad split bands at 1148 cm⁻¹ and 1191 cm⁻¹ also evolve to an absorption peak at around 1171 cm⁻¹, which is assigned to CF₂ stretching vibration, indicating the compound of PVDF remains stable in the modified coating and provides structural support. In the case of PMMA/PVDF coating layer cyclized in a Li/Cu half-cell for 25 cycles, no obvious change is observed in the characteristic peaks, indicating that the coating is quite stable during cycling. Figure 3m-n present the XPS high-resolution spectra of F 1s, the peaks at 685.1 eV and 688.6 eV for the modified Cu after cycling clearly show the existence of LiF and [CF₂-CF₂]ₙ. As for the control sample, the peaks at 685.2 eV and 686.3 eV can be assigned to the compound of LiF and CF₂-CF₂-CF₂-CF₂-CF₂. It is obvious that an increased proportion of LiF is obtained on the modified Cu, which is essential for uniform and stable SEI[27,28].

The Li/Li symmetric cell tests were carried out to evaluate Li plating/stripping performance during long cycling. Noteworthily, 4 mAh/cm² Li was pre-deposited on modified Cu or bare Cu at 1.0 mA/cm² (labelled as modified Cu@Li or bare Cu@Li), and the symmetric cells were assembled with two identical electrodes. As shown in Figure 4a, cycling at a current density of 1.0 mA/cm² with a fixed capacity of 1.0 mAh/cm², the cell with bare Cu@Li electrode presents higher voltage overpotential due to the continuous consumption of electrolyte and the accumulation of dead lithium[29]. After 400h, resulting from the depletion of electrolyte, the voltage hysteresis increases significantly[30]. While the cell using modified Cu@Li electrode exhibits stable cycling with low overpotential (~20 mV) for over 1400 h, indicating an improved electrode interfacial and successful inhibition on Li dendrites[31,32].

Figure 4. Electrochemical performance of Li/Li symmetric cells and Li/LiFePO₄ full cells. (a) Cycle stability comparison of bare Cu@Li and modified Cu@Li at a deposition capacity and current density of 1.0 mA/cm² and 1.0 mA/cm², cycling performance (b) and voltage-capacity curves (c-d) of bare Cu@Li/LFP and modified Cu@Li/LFP.

Practical application feasibility analysis was evaluated by the galvanostatic cycling performances of full cells, which were assembled with commercial LiFePO₄ as cathode while bare/modified Cu pre-deposited with 1 mAh/cm² lithium as the anode. In Figure 4b, the full cells cycled at 1C were labelled as LFP-Modified Cu@Li and LFP-Bare Cu@Li, respectively. The LFP-Bare Cu@Li full cell exhibits an initial coulombic efficiency of
77.87% with a charge/discharge capacity of 170.4/132.7 mA/h/g, much lower than the one which using the PMMA/PVDF modified Cu@Li, whose initial coulombic efficiency is 88.31% and the charge/discharge capacity is 162.5/143.5 mA/h/g. In the subsequent cycling, the control sample suffered a rapid capacity degradation during the first 10 cycles, which is mainly attributed to the excessive irreversible consumption of active lithium when the lithium source is fixed. By contrast, the full cell with modified electrode remains an average coulombic efficiency of 99.5% for over 250 cycles. In addition, Figure 4c-d shows the charge–discharge profiles of two kinds of full cells at 1°C when the lithium source is fixed. By contrast, the full cell with modified layer is favorable for stable electrode interface and high mechanical robustness is prepared and is proven to be effective in improving lithium metal anode with long cycling life.

3. Conclusions

In this work, a PMMA/PVDF porous coating was modified on the copper substrate directly by electrospinning technique. It acts as an artificial coating to obtain a uniform lithium deposition, protect the fragile SEI and relieve the dramatic volume change of anode. The affinity between Cu substrate and electrolyte is significantly improved due to the gel protection layer in situ formed on Cu current collector, which decreases the lithium deposition barrier and the probability of dendrite growth. Moreover, the synergistic effect of lithiophilic PMMA and robust PVDF can induce the homogeneous Li+ ions distribution and accomplish serious electrode volumetric change during cycling, which is favorable for stable electrode interface and uniform lithium deposition. Owing to the uniform lithium deposition and stable electrode interface achieved by the gel protection layer, a superior cycling performance is achieved by the resulting average coulombic efficiency reaches 98.2% for over 260 cycles at 1.0 mA/cm2 in ether-based electrolyte, and over 1400 h stable cycling lifespan is achieved in Li/Li symmetric cell at 1 mA/cm2 with a specific capacity of 1 mA/h/cm2. All in all, as an important aspect of electrode surface modification, a binary blend polymer modified coating with low interface resistance and high mechanical robustness is prepared and is proven to be effective in improving lithium metal anode with long cycling life.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

The authors gratefully acknowledge the financial support from the National Key R & D Program of China (2018YFB0104300), National Natural Science Foundation Committee of China (52073143), Distinguished Youth Scientists Project of 51425301, 21374021, 51573013, 51773092 and 51772147), State Key Lab Research Foundation (ZK201805, ZK201717), Jiangsu Distinguished Professorship Program (2016) and Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX20_1072).

References

1. W. Weng, J. Lin, Y. Du, X. Ge, X. Zhou and J. Bao, Journal of Materials Chemistry A, 2018, 6, 10168-10175.
2. Z. Zhang, Y. Du, Q.-C. Wang, J. Xu, Y.-N. Zhou, J. Bao, J. Shen and X. Zhou, Angewandte Chemie International Edition, 2020, 59, 17504-17510.
3. X. B. Cheng, R. Zhang, C. Z. Zhao and Q. Zhang, Chem Rev, 2017, 117, 10403-10473.
4. Z. Liu, Acta Physico-Chimica Sinica, 2019, 35, 1293-1294.
5. X. Xiong, W. Yan, C. You, Y. Zhu, Y. Chen, L. Fu, Y. Zhang, N. Yu and Y. Wu, Frontiers in Chemistry, 2019, 7, 365-377.
6. M. Zhao, B.-Q. Li, H.-J. Peng, H. Yuan, J.-Y. Wei and J.-Q. Huang, Angewandte Chemie International Edition, 2020, 59, 12636-12652.
7. X.-Q. Zhang, X. Chen, X.-B. Cheng, B.-Q. Li, X. Shen, C. Yan, J.-Q. Huang and Q. Zhang, Angewandte Chemie International Edition, 2018, 57, 5301-5305.
8. Y. Zhong, Y. Xie, S. Hwang, Q. Wang, J. J. Cha, D. Su and H. Wang, Angewandte Chemie International Edition, 2020, 59, 14003-14008.
9. C. Z. Zhao, P. Y. Chen, R. Zhang, X. Chen, B. Q. Li, X. Q. Zhang, X. B. Cheng and Q. Zhang, Sci Adv, 2018, 4, eaat3446.
10. N. Li, Q. Ye, K. Zhang, H. Yan, C. Shen, B. Wei and K. Xie, Angew Chem Int Ed Engl, 2019, 58, 18246-18251.
11. X. Ke, Y. Cheng, J. Liu, L. Liu, N. Wang, J. Liu, C. Zhi, Z. Shi and Z. Guo, ACS Appl Mater Interfaces, 2018, 10, 13552-13561.
12. A. A. Assegie, J. H. Cheng, L. M. Kuo, W. N. Su and B. J. Hwang, Nanoscale, 2018, 10, 6125-6138.
13. A. A. Assegie, C. C. Chung, M. C. Tsai, W. N. Su, C. W. Chen and B. J. Hwang, Nanoscale, 2019, 11, 2710-2720.
14. B. Liang, S. Q. Tang, B. Q. Jiang, C. S. Chen, X. Chen, S. L. Li and H. Y. Han, Electrochimica Acta, 2015, 169, 334-341.
15. J. Lopez, A. Pei, J. Y. Oh, G. N. Wang, Y. Cui and Z. Bao, J Am Chem Soc, 2018, 140, 11735-11744.
16. Z. Liang, G. Zheng, C. Liu, N. Liu, W. Li, K. Yan, H. Yao, P. C. Hsu, S. Chu and Y. Cui, Nano Lett, 2015, 15, 2910-2916.
17. S. Liang, W. Yan, X. Wu, Y. Zhang, Y. Zhu, H. Wang and Y. Wu, Solid State Ionics, 2018, 318, 2-18.
18. T. T. Beyene, B. A. Jote, Z. T. Wondimkun, B. W. Olbassa, C. J. Huang, B. Thirumalraj, C. H. Wang, W. N. Su, H. Dai and B. J. Hwang, ACS Appl Mater Interfaces, 2019, 11, 31962-31971.
19. X. Hu, P. Xu, S. Deng, J. Lei, X. Lin, Q. Wu, M.-s. Zheng and Q.-F. Dong, Journal of Materials Chemistry A, 2020, 8, 17056-17064.
20. Y. M. Liu, X. Y. Qin, S. Q. Zhang, L. H. Zhang, F. Y. Kang, G. H. Chen, X. F. Duan and B. H. Li, Journal of Materials Chemistry A, 2019, 7, 13225-13233.
21. K. Yan, B. Sun, P. Munroe and G. Wang, Energy Storage Materials, 2018, 11, 127-133.
22. G. Zheng, S. W. Lee, Z. Liang, H. W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu and Y. Cui, Nat Nanotechnol, 2014, 9, 618-623.
23. J. Steiger, G. Richter, M. Wenk, D. Kramer and R. Möning, Electrochemistry Communications, 2015, 50, 11-14.
24. Y. Zhao, D. Wang, Y. Gao, T. Chen, Q. Huang and D. Wang, Nano Energy, 2019, 64, 103893.
25. Y. Guo, Y. Ouyang, D. Li, Y. Wei, T. Zhai and H. Li, Energy Storage Materials, 2019, 16, 203-211.
26. Y. Wang, L. Zhang, L. Zhang, F. Zhang, P. He, H. Zheng and H. Zhou, Advanced Energy Materials, 2016, 6, 1601375.
27. T. Hagos, B. Thirumalraj, C. J. Huang, L. H. Abraha, T. M. Hagos, G. B. Berhe, H. K. Bezabih, J. Cherng, S. F. Chiu, W. N.
Su and B. J. Hwang, ACS Appl Mater Interfaces, 2019, 11, 9955-9963.

28 S. Sun, S. Myung, G. Kim, D. Lee, H. Son, M. Jang, E. Park, B. Son, Y.-G. Jung, U. Paik and T. Song, Journal of Materials Chemistry A, 2020, 8, 17229-17237.

29 Y. He, H. Xu, J. Shi, P. Liu, Z. Tian, N. Dong, K. Luo, X. Zhou and Z. Liu, Energy Storage Materials, 2019, 23, 418-426.

30 J. Xiao, P. Zhai, Y. Wei, X. Zhang, W. Yang, S. Cui, C. Jin, W. Liu, X. Wang, H. Jiang, Z. Luo, X. Zhang and Y. Gong, Nano Letters, 2020, 20, 3911-3917.

31 S. Liu, L. Deng, W. Guo, C. Zhang, X. Liu and J. Luo, Adv Mater, 2019, 31, e1807585.

32 S. Liu, X. Xia, Y. Zhong, S. Deng, Z. Yao, L. Zhang, X.-B. Cheng, X. Wang, Q. Zhang and J. Tu, Advanced Energy Materials, 2018, 8, 1702322.

33 W. Zhang, Q. Yi, S. Li and C. Sun, Journal of Power Sources, 2020, 450, 227710.