

ChemComm

Accepted Manuscript



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.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Binder effect on oxide-based anode in lithium and sodium-ion battery applications: the fastest way to ultrahigh performance

Jun Ming,^{a†} Hai Ming,^{ab‡} Won-Jin Kwak,^a Changdae Shin,^a Junwei Zheng^b and Yang-Kook Sun^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A positive effect of polyacrylic acid (PAA)/carboxymethyl cellulose (CMC) binder to enhance the performance of oxide-based anode was reported in batteries. A series of super high capacity and cycle ability of oxide powders rarely achieved before were obtained, particularly most of them without any specific carbon modification and/or morphology controlling.

Metal oxides have attracted great attention as anode material in the lithium-ion battery application owing to their higher theoretical capacity ($> 800 \text{ mAhg}^{-1}$) and reliable safe advantages than that of flammable commercial graphite ($\sim 372 \text{ mAhg}^{-1}$).¹ Most oxide-based anode such as Fe_2O_3 ,² Fe_3O_4 ,^{3a} Co_3O_4 ,^{3b} NiO ,^{3c,d} and CuO ^{3e} have the same lithium-storage mechanism *via* the reversible reaction of $\text{MO}_z + 2z\text{Li}^+ + 2z\text{e}^- \leftrightarrow \text{M} + z\text{Li}_2\text{O}$. Inevitably, the large volume change of the anode during the repeated charge/discharge always induce the pulverization of electrode and give rise to a poor cycle ability. Particularly, this problem could be further amplified in the current research of sodium-ion battery, because the volume variation of Na_2O is much larger than that of Li_2O due to the bigger radius of Na^+ ($\sim 102 \text{ pm}$) versus Li^+ ($\sim 76 \text{ pm}$). To date, especially in the field of lithium-ion battery, numerous excellent researches have been focused on preparing carbon coated (*e.g.*, $\text{Fe}_3\text{O}_4@\text{C}$,^{3a} $\text{SnO}_2@\text{C}^{4a}$), supported (*e.g.*, $\text{RGO}/\text{Fe}_2\text{O}_3$,^{2b} CuO/CNTs ,^{3e} $\text{CoO}/\text{Graphene}^{4b}$) and encapsulated metal oxide (*e.g.*, PC-CO_x ,^{4c} $\text{SnO}_2\text{-NiO-C}^{4d}$) to improve their cycling performance, owing to the protective ability and high electronic conductivity of carbon. However, the introduction of excess carbon would bring the flammable problem and also induce the lithium dendrite and reduce the capacity, let alone the complex procedures for carbon modification.^{3,4} Alternatively, the preparation of nano-structured metal oxides (*e.g.*, solid or hollow particles,^{5a,b} wires,^{5c} tubes,^{5d} arrays^{5e}) are also of great interest due to their improved performance in lithium storage application. However, it would better to consider the cost and energy consumption, as well as environmental problems for the process of preparing nanomaterials in the practical application. Guided by the same logical research trend, in the area of sodium-ion battery, more and more works are also aiming synthesis the nanostructured metal (oxide) and oxide-carbon composite, such as CuO arrays,^{6a} Sb_2O_4 film,^{6b} Sn fiber,^{6c} C/Sn ,^{6d} $\text{Fe}_2\text{O}_3/\text{graphene}$,^{6e} $\text{SnO}_2@\text{MWCNTs}$,^{6f}; however, the cycling ability and capacity could be further improved in a large space, particularly *via* other convenient ways.

Herein, we report a simple, fast but rather effective way to improve the electrochemical performance of oxide-based anode in batteries with using the PAA/CMC as binder. In this way, the metal oxides, such as Co_3O_4 and CuO thermally decomposed from metal nitrate, TiO_2 hydrolyzed from tetrabutyl titanate, as well as normal powders of $\text{Fe}_2\text{O}_3\text{-C}$ and NiO-C prepared *via* a simple ball milling, could show ultrahigh capacity and stability never reported before. This result should be a great breakthrough, because most oxides could exhibit excellent performance in batteries just varying a different kind of binder, rather than any complex carbon modification and/or any unique structure-controlling. It would be considerably significant for the commercialization of oxide-based anode and also largely prompting the investigations in recent sodium ion battery.

X-Ray diffraction (XRD) patterns confirmed that the crystalline structure of the powders belong to the normal Co_3O_4 , NiO , CuO , TiO_2 and Fe_2O_3 successively (Fig. S1). Scanning electron microscope (SEM) showed that they are aggregated particles without any uniform and ordered structure (Fig. S2), which were determined by the industrial scalable preparation method. Comparative capacity and cycling performance of metal oxide in lithium ion battery with using different kind of binders at the rate of 100 mA g^{-1} were demonstrated in Fig. 1. With using the traditional polyvinylidene fluoride (PVDF) as binder, the metal oxide, include Co_3O_4 , NiO and Fe_2O_3 decay seriously in the initial 50 cycles, except that of CuO and TiO_2 with a low capacity

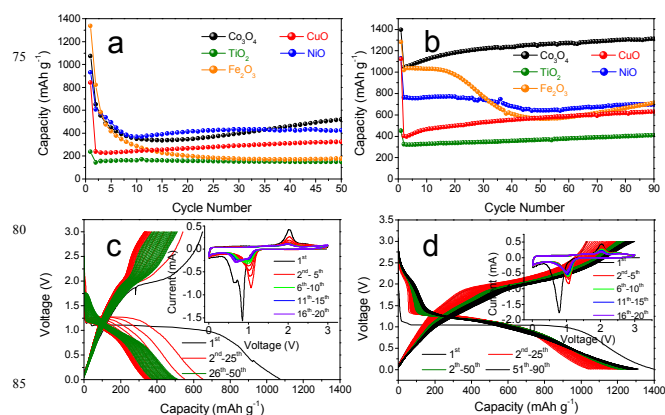


Fig. 1 Comparative capacity and cycling performance of metal oxide at the current density of 100 mA g^{-1} with using different kind of binders. (a) PVDF, (b) PAA/CMC. Typical charge-discharge curves and CV of (c) $\text{Co}_3\text{O}_4\text{-PVDF}$ and (d) $\text{Co}_3\text{O}_4\text{-PAA/CMC}$.

(Fig. 1a, Table S1). Alternatively using the PAA/CMC as binder, the capacity and stability of metal oxide, especially the Co_3O_4 , TiO_2 and CuO , become fantastic. They showed ultrahigh average capacities of 1216, 363 and 550 mAh g^{-1} correspondingly with capacity retention of 124%, 125% and 157% in the initial 90 cycles. Note that the capacities of Co_3O_4 (1311 mAhg^{-1}), TiO_2 (409 mAhg^{-1}) and CuO (630 mAhg^{-1}) at the 90th cycle were much higher than theoretical ones (i.e., Co_3O_4 , 897 mAhg^{-1} CuO , 600 mAhg^{-1} ; TiO_2 , 167 mAhg^{-1} versus 0.5Li^+) (Fig. 1b). They are the highest values never achieved before for pure metal oxide, especially without any carbon modification and structure-tailoring. While for the NiO and Fe_2O_3 , their second capacities were 762 and 1018 mAhg^{-1} with a capacity retention of 91.2% and 70.5% within 90 cycles (Fig. 1b). Clearly, the capacity and capacity retention were also largely increased compared to that of using PVDF (NiO , 607 mAhg^{-1} , 70% retention; Fe_2O_3 , 822 mAhg^{-1} , 22% retention within only 50 cycles), even the increased degree was little lower than those of Co_3O_4 , TiO_2 and CuO (Table S1).

The clear difference of charge-discharge with using different kind of binders was investigated. Taking the Co_3O_4 as an example, the plateau of discharge curves of the Co_3O_4 -PAA/CMC electrode around 1.07 V was much longer than that of Co_3O_4 -PVDF, demonstrating the high utilization of Co_3O_4 (Fig. 1c-d). This result was further confirmed by the comparative cyclic voltammetry (CV). As shown in inset of Fig. 1c, the peaks around 1.07 V, corresponding to the redox couple of $\text{Co}_3\text{O}_4/\text{Co}$, became weak and also moved toward low voltage till around 0.68 V, further confirming a low utilization of Co_3O_4 and a trend of hard to react. By contrast, the position and intensity of peaks around 1.07 V were almost the same in the electrode of Co_3O_4 -PAA/CMC (Fig. 1d), which were well accordance with the high capacity and stable cycling performance. Moreover, comparing the two anodic peaks (i.e., 1.07 & 0.68 V, corresponding to the reduction of Co_3O_4 to Co) in the Co_3O_4 -PVDF electrode, the single peak around 1.07 V in the electrode of Co_3O_4 -PAA/CMC fully demonstrated that the reduction of Co_3O_4 was much easier to occur with using the PAA/CMC as binder, thereby also promoting its good utilization.

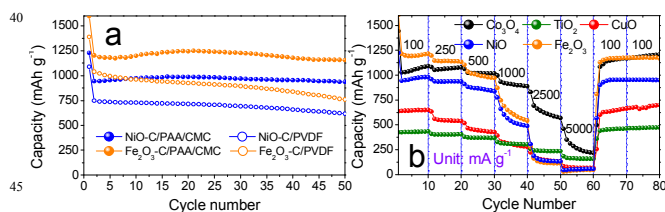


Fig. 2 (a) Cycling performance of NiO-C and $\text{Fe}_2\text{O}_3\text{-C}$. (b) Rate capability of different kind of metal oxide with using PAA/CMC as binder.

Stimulating by the positive effect of carbon modification in previous literatures and also pursuing a convenient way to make the commercialization of all the possible oxide in practical application, the Fe_2O_3 and NiO powders with 10 wt% of carbon was ball milled simply, and we find that the capacity and stability of $\text{Fe}_2\text{O}_3\text{-C}$ and NiO-C were further improved in the case of using PAA/CMC. As shown in Fig. 2a, the average capacities of $\text{Fe}_2\text{O}_3\text{-C}$ and NiO-C could achieve as high as 1204 mAhg^{-1} and 964 mAhg^{-1} with a capacity retention of 96.0% and 99.3% in the

initial 50 cycles. Such high capacity for Fe_2O_3 and NiO were hard to achieve previously,^{2, 3} and also they are much better than that of using PVDF binder (Fig. 2a). Except a superior cycle ability, the rate capability were also tested, and they showed very promising performance (Fig. 2b). For example, the sample of Co_3O_4 and TiO_2 , have capacities of 1057, 1065, 1018, 905, 618, 262 mAhg^{-1} and 428, 402, 370, 307, 236, 160 mAhg^{-1} under the current density of 100, 250, 500, 1000, 2500, 5000 mA g^{-1} (Fig. S3, Table S2). After the high rate test, all the electrode could work back to the high values of 1171, 684, 462, 974, 1169 and 1100, 980 mAhg^{-1} at 100 mA g^{-1} , demonstrating the high stability of electrode. In this way, at least five kind of metal oxide, without or with a simple carbon ball milling, showed an extremely high capacity, superior cycling ability and good rate capacity. Note that the capacities of TiO_2 around 160 mA g^{-1} at 5000 mAhg^{-1} (30C, where define 1C = 167 mA g^{-1}) and 462 mAhg^{-1} at 100 mA g^{-1} was the highest value among all the TiO_2 materials reported to date.⁷

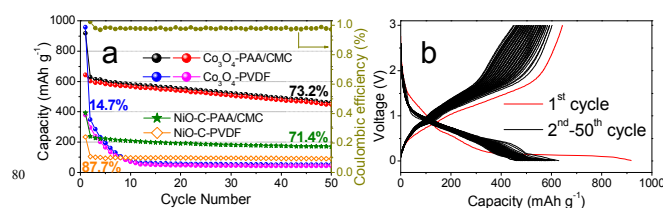


Fig. 3 (a) Comparative cycling performance of Co_3O_4 and NiO-C in the sodium ion battery with using different kind of binders under the current density of 50 mA g^{-1} . (b) Typical charge-discharge curves of Co_3O_4 -PAA/CMC.

Compare to the previous literatures about the anode,¹⁻⁶ it should be a great revolution to enhance their performance *via* such a simple but rather effective way to achieve the industrial requirement. Moreover, it could be further expanded to other kind of oxide in lithium and current sodium/sulfur/air batteries. Herein, we continually applied the electrode of Co_3O_4 and NiO-C in the sodium ion battery for the first time to investigate the effect of binders. The performance of electrode with using PAA/CMC binders were much better than that of using PVDF (Fig. 3). Under the current density of 50 mA g^{-1} , the capacity and coulombic efficiency of Co_3O_4 and NiO-C were 600 mAhg^{-1} (98%) and 237 mAhg^{-1} (99%) with a capacity retentions of 73.2% and 71.4% (vs. the 2nd cycle) in the initial 50 cycles. While for the electrode of using PVDF as binder, their capacity were only 300 and 150 mAhg^{-1} with a capacity retention of 14.7% and 87.7%. Clearly, the positive of binder effect to increase the capacity and maintain the cycling ability was also obvious in the sodium ion battery. Although a slow decay still exist due to the large volume variation in the repeated discharge/charge process, this is the first time to introduce the metal oxide of Co_3O_4 and NiO in the sodium battery with such high capacity, which are much higher than typical reported TiO_2 ⁸ and most carbon-based materials.⁹

Except the factor of different utilization that demonstrated in discharge/charge and CV curves (Fig. 1c, d), we further compared the electrode before and after cycling to study the reasons of improved performance with using PAA/CMC binder. For the electrode of Co_3O_4 -PAA/CMC, there is no obvious pulverization after 90 cycles test comparing to the pristine one (Fig. 4a, Fig. S4a-d). However, in the case of using PVDF, a

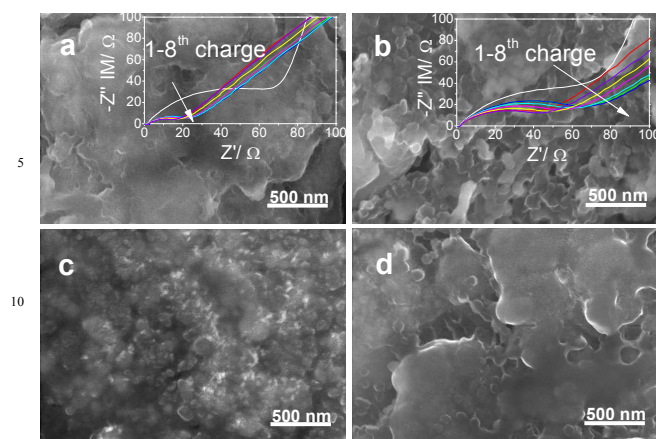


Fig. 4 Comparative SEM images of electrode (a) Co_3O_4 -PAA/CMC, (b) Co_3O_4 -PVDF, (c) Fe_2O_3 -PAA/CMC and (d) Fe_2O_3 -C-PAA/CMC after cycling. Inset of (a) and (b) are EIS in the initial eight cycles.

collapse and pulverization of electrode could be observed clearly after 50 cycles (Fig. 4b, Fig. S4e-h). The pulverization could also be found for the electrode of Fe_2O_3 -PAA/CMC due to the larger volume expansion as compared with the pristine one (Fig. 4c, Fig. S5a). But it was largely decreased for the sample of Fe_2O_3 -C (Fig. 4d, Fig. S5b), in which the carbon could act as a buffer to protect the integrity of electrode. Preliminary result confirmed that the layer of PVDF around the oxide particles seems difficult to endure the large volume-variation of oxide, and therefore an obvious collapse and pulverization of particles occurred, followed which the solid electrolyte interphase (SEI) layer could be continually formed on the new naked sites of oxide, finally giving rise to a low utilization, capacity and poor stability.

This result was confirmed by the fourier transform infrared spectroscopy (FTIR) (Fig. S6). The SEI layer, mainly consisting of Li_2CO_3 ($\sim 891\text{ cm}^{-1}$), LiOH ($\sim 3625\text{ cm}^{-1}$), ROCO_2Li (765 cm^{-1} , and the peaks around $1700\text{--}1578\text{ cm}^{-1}$ ascribed to the stretching vibration of $\text{C}=\text{C}\&\text{C}=\text{O}$),¹⁰ were clearly observed on the electrode. Besides, the typical peaks and intensity of Co_3O_4 , around $645\text{--}678\text{ cm}^{-1}$ and $525\text{--}588\text{ cm}^{-1}$,¹¹ become more obvious and stronger after cycling, clearly demonstrating the pulverization of Co_3O_4 . The Co_3O_4 -PVDF electrode after cycling demonstrated the stronger peaks of SEI layer and Co_3O_4 than that of Co_3O_4 -PAA/CMC, confirming the formation of thicker SEI on the Co_3O_4 -PVDF electrode and the serious pulverization of Co_3O_4 due to the lower adhesion ability of PVDF. As a result, the collapsed electrode was easily separated from the copper foil after disassembling the cell (Inset of Fig. S4f, Fig. 5a).

While the polymer film of PAA/CMC around the oxide particles could largely endure the repeated volume-variation during the charge and discharge, therefore mainly keeping the integrity of electrode and promising a high utilization of oxide and stability (Fig. 5b). With using PAA/CMC as binder, the electrode were always close adhered on the copper foil after cycling (inset of Fig. S4b). The stronger adhesion could also be directly observed in the experiment of using the electrode contact with lithium metal (Fig. S7). For example, the electrode of Co_3O_4 -PAA/CMC could be well preserved when it was directly contact with lithium metal for 10 min (Fig. S7a-b), but the electrode of Co_3O_4 -PVDF collapsed and dropped fast from the

copper foil (Fig. S7c-d). Moreover, the high stability of electrode-PAA/CMC were also confirmed by the electrochemical impedance spectroscopy (inset of Fig. 4a-b). Detail information relate to the molecular structures, average molecular weight and specific functional groups of polymers deserve to be further investigated and expanded in future. Although the binder of PAA and/or CMC have been used in lithium ion battery before,¹² all of them only focused on the Si-based anode and this is the first time to introduce them for the oxide-based anode with such ultrahigh performance rarely reported, particularly further expanding them into the current sodium ion battery. And also, preliminary results showed that the composite binder of PAA/CMC behaviors better than single PAA or CMC in the case of Co_3O_4 , and the coulombic efficiency of 98.8% was always close to 100% (Fig. S8).

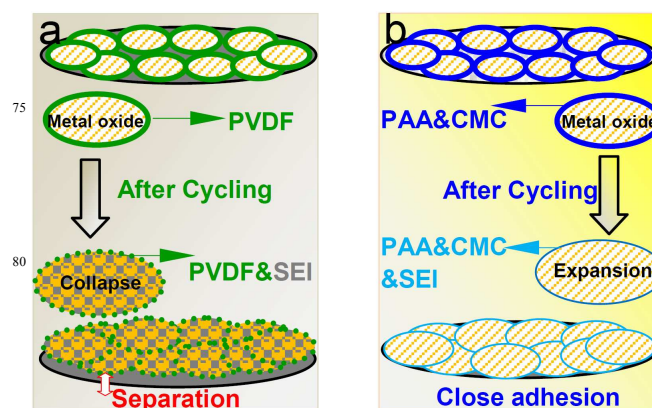


Fig. 5 Probable behaviours of metal oxide electrode on copper foil prepared from different kind of binders (a) PVDF and (b) PAA/CMC before and after the cycling.

Conclusions

We the first time reported the unexpected positive effect of PAA/CMC binder to the metal oxide anode for getting an ultrahigh capacity and stability, rather than mainly paying attention to the carbon modification or structure/composition-tailoring. It is a much simpler, faster but more effective way to promise the performance. With using this kind of binder, one part of metal oxide (*e.g.*, Co_3O_4 , TiO_2 , CuO) could directly demonstrate fantastic behaviors, and the capacity were much higher than those reported before. Although another part of metal oxide (*e.g.*, Fe_2O_3 , NiO) still showed little decay, a higher capacity and stability could be also achieved combining with a simple ball-milling of oxide and carbon. This intriguing effect of binder was also obvious in the sodium-ion battery when the electrode of Co_3O_4 and NiO-C were used. Based on the results, we take an investigation on the reasons of such positive effect, and one part of plausible reason could be ascribed to the strong tolerate and adhesion ability of polymer films around the oxide particle from collapse. More importantly, herein we opened an alternative gate of choosing appropriate binders for oxide-based electrode to improve their performance; undoubtedly a series of researches concerning the binders could be progressed worldwide in the battery field. Together with the way of possible carbon modification and structure/composition-tailoring, a much higher capacity and cycle ability could be well achieved.

Acknowledgment

This work was supported by the Global Frontier R&D Program (2013-073298) on Center for Hybrid Interface Materials (HIM) funded by the Ministry of Science, ICT & Future Planning and the Human Resources Development program grant (No. 20124010203310) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Korean government Ministry of Trade, Industry and Energy. Industry-Academia Cooperation Innovation Fund Projects of Jiangsu Province (Nos. BY2011130) are gratefully acknowledged.

Notes and references

^a Department of Energy Engineering, Hanyang University, Seoul 133-791, South Korea. Fax: +82 2 2282 7329; Tel: +82 2 2220 0524; E-mail: yksun@hanyang.ac.kr.

^b College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

† Electronic Supplementary Information (ESI) available: XRD and SEM images of metal oxide and electrode. A detail compare of capacities and charge-discharge curves of metal oxide. See DOI: 10.1039/b000000x/

‡ These authors contributed equally to this work.

- (a) Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa and T. Miyasaka, *Science*, 1997, **276**, 1395.; (b) M. V. Reddy, G.V. Subba Rao and B.V.R. Chowdari, *Chemical Reviews*, 2013, **113**, 5364.; (c) Z. L. Wang, D. Xu, H. G. Wang, Z. Wu and X. B. Zhang, *ACS Nano*, 2013, **7**, 2422.
- (a) L. Zhang, H. B. Wu and X.W. Lou, *J. Am. Chem. Soc.*, 2013, **135**, 10664.; (b) X.J. Zhu, Y.W. Zhu, S. Murali, M.D. Stollers and R.S. Ruoff, *ACS Nano*, 2011, **5**, 3333.; (c) L. Zhou, H. Xu, H. Zhang, J. Yang, S. B. Hartono, K. Qian, J. Zou and C. Yu, *Chem. Commun.*, 2013, **49**, 8695.; (d) D. Ma, Z. Cao, H. Wang, X. Huang, L. Wang and X. Zhang, *Energy Environ. Sci.*, 2012, **5**, 8538.
- (a) J. Ming, Y. Q. Wu, G. F. Liang, J. B. Park, F. Y. Zhao and Y. K. Sun, *Green Chem.*, 2013, **15**, 2722.; (b) W. Y. Li, L. N. Xu and J. Chen, *Adv. Funct. Mater.*, 2005, **15**, 851.; (c) G. W. H. Liu, J. Liu, S. Qiao, H. Ahn, *J. Mater. Chem.*, 2011, **21**, 3046.; (d) Y. Huang, X. Huang, J. Lian, D. Xu, L. Wang and X. Zhang, *J. Mater. Chem.*, 2012, **22**, 2844.; (e) S. Ko, J. I. Lee, H. S. Yang, S. Park and U. Jeong, *Adv. Mater.*, 2012, **24**, 4451.;
- (a) X. W. Lou, C.M. Li and L.A. Archer, *Adv Mater*, 2009, **21**, 2536.; (b) X. Huang, R. Wang, D. Xu, Z. Wang, H. Wang, J. Xu, Z. Wu, Q. Liu, Y. Zhang and X. Zhang, *Adv. Funct. Mater.*, 2013, **23**, 4345.; (c) J. Ming, J. B. Park and Y.K. Sun, *ACS Appl. Mater. Inter.*, 2013, **5**, 2133.; (d) M. F. Hassan, M. M. Rahman, Z. P. Guo, Z. X. Chen and H. K. Liu, *J. Mater. Chem.*, 2010, **20**, 9707.
- (a) X. W. Lou, L. A. Archer and Z. C. Yang, *Adv. Mater.*, 2008, **20**, 3987.; (b) J. Ming, Y.Q. Wu, J. B. Park, J. K. Lee, F. Y. Zhao and Y. K. Sun, *Nanoscale*, 2013, **5**, 10390.; (c) C. C. Li, Q. H. Li, L. B. Chen and T. H. Wang, *J. Mater. Chem.*, 2011, **21**, 11867.; (d) C. J. Jia, L. D. Sun, Z. G. Yan, Y. C. Pang, L. P. You and C. H. Yan, *J. Phys. Chem. C*, 2007, **111**, 13022.; (e) H. Liu, Y.S. Meng and Q. Li, *RSC Adv.*, 2013, **3**, 11586.
- (a) S. Yuan, X. L. Huang, D. L. Ma, H. G. Wang, F. Z. Meng and X. B. Zhang, *Adv. Mater.*, 2014, **26**, 2273.; (b) Q. Sun, Q. Q. Ren, H. Li and Z. W. Fu, *Electrochem. Commun.*, 2011, **13**, 1462.; (c) H. L. Zhu, Z. Jia, Y. C. Chen, N. Weadock, J. Y. Wan, O. Vaaland, X. G. Han, T. Li and L.B. Hu, *Nano Lett.*, 2013, **13**, 3093.; (d) Y. J. Zhu, X. G. Han, Y. H. Xu, Y. H. Liu, S. Y. Zheng, K. Xu, L. B. Hu and C. S. Wang, *ACS Nano*, 2013, **7**, 6378.; (e) Z. Jian, B. Zhao, P. Liu, F. Li, M. Zheng, M. Chen, Y. Shi and H. Zhou, *Chem. Commun.*, 2014, **50**, 1215.; (f) Y. Wang, D. W. Su, C. Y. Wang and G. X. Wang, *Electrochem. Commun.*, 2013, **29**, 8.
- (a) W. Li, F. Wang, S. Feng, J. Wang, Z. Sun, B. Li, Y. Li, J. Yang, A. A. Elzatahry, Y. Xia and D. Zhao, *J. Am. Chem. Soc.*, 2013, **135**, 18300.; (b) J. Ming, Y. Wu, S. Nagarajan, D. J. Lee, Y. K. Sun and F. Zhao, *J. Mater. Chem.*, 2012, **22**, 22135.; (c) J. S. Chen and X. W. Lou, *Mater. Today*, 2012, **15**, 246.; (d) Y. Ren, Z. Liu, F. Pourpoint, A. R. Armstrong, C. P. Grey and P.G. Bruce, *Angew Chem. Int. Ed.*, 2012, **51**, 2164.; (e) H. Ming, Y. Yan, J. Ming, X. Li, Q. Zhou, H. Huang, J. Zheng, *RSC Adv.* 2014, **4**, 12971.
- (a) H. Xiong, M. D. Slater, M. Balasubramanian, C.S. Johnson and T. Rajh, *J. Phys. Chem. Lett.*, 2011, **2**, 2560.; (b) K. T. Kim, G. Ali, K.Y. Chung, C.S. Yoon, H. Yashiro, Y.-K. Sun, J. Lu, K. Amine and S. T. Myung, *Nano Lett.*, 2014, **14**, 416.; (c) Y. Xu, E. Memarzadeh Lotfabad, H. Wang, B. Farbod, Z. Xu, A. Kohandehghan and D. Mitlin, *Chem. Commun.*, 2013, **49**, 8973.
- (a) Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L.V. Saraf, Z. Yang and J. Liu, *Nano Lett.*, 2012, **12**, 3783.; (b) J. Ding, H. Wang, A. Kohandehghan, K. Cui, Z. Xu, B. Zahir, X. Tan, E. M. Lotfabad, B. C. Olsen and D. Mitlin, *ACS Nano*, 2013, **7**, 11004.; (c) H. Wang, S. Yuan, D. Ma, X. Huang, F. Meng and X. Zhang, *Adv. Energy Mater.* 2014, **4**, 1301651.
- (a) J. Ming, C. Wu, H. Cheng, Y. Yu and F. Zhao, *J. Supercrit. Fluids*, 2011, **57**, 137.; (b) Y. K. Choi, K. Chung, W. S. Kim, Y. E. Sung and S. M. Park, *J. Power Sources*, 2002, **104**, 132.; (c) Y. C. Yen, S. C. Chao, H. C. Wu and N. L. Wu, *J. Electrochem. Soc.*, 2009, **156**, A95.
- (a) G. C. Yi, X. Yong, W. Q. He, S. Zhao, Y. J. Wu, Y. L. Liu, D. S. Yuan, L. H. Huang and S. Z. Tan, *Chin. J. Inorg. Chem.*, 2011, **27**, 162.; (b) J. A. Gaddsdon, *Infrared-spectra of minerals and related inorganic compounds*. London: Butterworth, 1975, **44**.
- (a) A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C.F. Huebner, T.F. Fuller, I. Luzinov and G. Yushin, *ACS Appl. Mater. Inter.*, 2010, **2**, 3004.; (b) J. S. Bridel, T. Azais, M. Morcrette, J.M. Tarascon and D. Larcher, *Chem. Mater.*, 2010, **22**, 1229.; (c) H. Wu, G. H. Yu, L. J. Pan, N. A. Liu, M. T. McDowell, Z. A. Bao and Y. Cui, *Nat Commun*, 2013, **4**, 1.