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An environmentally benign LIB fabrication process using a low cost, water soluble and efficient binder

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Here we report a green production process polymer binder, Eastman AQTM 55S (EAQ) polymer, which has plentiful active hydroxyl groups on its surface that is different from the chemical inertness PVDF binder for LIBs. The water soluble EAQ binder tuned the performance the oxidized graphite with carboxyl group for the maximum effect.

Since the lithium ion battery inception, very little research has been devoted to the binder materials.¹ As the statistics of the market research showed, polyvinylidene fluoride (PVDF) dissolved in organic solvents, typically N-methyl-2-pyrrolidinone (NMP), has been the binder of primary choice for cathodes in commercial Li-ion batteries. In addition to the PVDF binder, the styrene-butadiene copolymer (SBR) and carboxyl methyl cellulose (CMC) is now used in almost 70% of all anode materials as binder.²⁻⁴ The CMC and SBR provide a few advantages such as more flexible electrode, higher binding ability with a small amount, larger battery capacity and higher cycle performance. However, CMC and SBR can only be used for negative electrodes in the reduction atmosphere, it's not suitable for positive electrodes because of the double bonds exists in the binder, which are prone to be oxidized.⁵ PVDF has good electrochemical stability, adhesion to electrode and current collector materials, however, the absence of active functional groups such as carboxyl and hydroxyl make the PVDF can't have certain chemical linkage with the active materials. Moreover, PVDF requires the use of volatile organic compounds that are often toxic (like NMP) and are not easily disposable at the end of the battery production process.⁶⁻⁸

In order to cope with the increasing demand for environment-friendly and sustainable production technologies, water soluble synthetic and low cost Eastman AQTM 55S polymer (EAQ) is proposed here for the first time as an alternative to the conventional PVDF, CMC and SBR binders.⁹ The EAQ polymer is cheap, water soluble, and harmless. Initially, it was produced by Eastman Chemical Company as an ingredient for cosmetics and personal care applications. The EAQ polymer has a high viscosity in water with the inherent viscosity of 0.29-0.37 dL/g. Besides, the EAQ polymer is the certified biodegradable products. The polymer binder is found to be at least seventy percent biodegradable after just 28 days. Based on its molecular structure, EAQ has abundant active hydroxyl groups on its surface that can make it have the potential to be attached to the active materials with chemical bonds. Based on these advantages and the potential for the binder for various lithium ion battery electrode,¹⁰ we exploited the use of EAQ as binder based on the modified graphite in an aqueous suspension.^{11, 12}

So far, many anode materials such as silicon, titanium oxides, tin composite oxides, nitrides of lithium and transition metals, and some novel alloys have been investigated, but graphitic carbon is still proved to be the dominating material especially on the electronic products because it exhibits a high specific capacity, a

desirable charge potential profile, and superior cycling behaviour. Hence, we choose the graphite as the specific anode materials to investigate the performance of the EAQ polymer binder. It is generally known that there are a lot of structure imperfections and defects such as sp³-hybridized carbon atoms, edge atoms and carbon chains in graphite especially in natural graphite because of its incomplete graphitization during the natural formation process.¹³⁻¹⁵ These structures are prone to attack by oxidants and some of them would be removed after the oxidation reaction. Consequently, the surface structure of the natural graphite will be changed after the oxidation reaction. Natural graphite can be mildly oxidized by air, oxygen, carbon dioxide, and ozone, or fluorinated by fluorine gas. Here we introduce an effective liquid-solid interface oxidation reaction using nitric acid. The standard potentials of nitric acid partial decomposition products can be > 1.5 V. When its solution is heated, its oxidation capacity will increase further. Here, we use the heated nitric acid solution as the oxidant to modify the nature graphite.^{16, 17}

Initially, the natural and modified graphite/EAQ binder was used for the aqueous processing of graphite anodes without conductive additives. The aqueous slurry was mixed by a defined amount of the graphite and EAQ binder to meet the desired weight ratios. The galvanostatic discharge-charge cycling performance of the natural and oxidized graphite using EAQ and PVDF polymer binder separately is showed in Fig. 1 a and b. All the cell data reported are based on lithium metal as counter electrode in coin cells. The voltage range is 0.01-3 V for the full capacity cycling. The C-rate calculation of the graphite based electrode is assuming the graphite has the theoretical capacity of 372 mAh/g.

Fig.1 Galvanostatic charge discharge profiles of the natural graphite (a) and oxidized graphite (b) separately using EAQ polymer and PVDF binder (weight ratio 9:1 graphite:binder,) between a cycling voltage of 3 V and 0.01 V when at C/10. The graphite was oxidized by concentrated HNO₃ under stirring at 60 °C for 1 h. The FESEM images of the oxidized graphite before (c) and after (d) combined with the EAQ polymer binder on the copper foil.

A series of research work have been carried out to improve the cycle performance of graphite anode, such as employing smaller particles,¹⁸ preparing graphite/nanopowder composite,¹⁹⁻²¹ and oxidizing or purifying the graphite. Under the summarization of former works, the natural graphite without surface modification suffered both the lower capacity and the problem of long-term cycle performance.²²⁻²⁴ As showed in Fig. 1a, the reversible capacity of natural graphite was 210 mAh/g when using EAQ polymer binder compared to about 170 mAh/g when using PVDF binder during constant C/10 cycling. The coulombic efficiency of both electrodes all keep stable up to 99% after the first few cycles during the next 100 cycles. To explore the mechanism for the better performance of EAQ compare to PVDF, the oxidized graphite with more carboxyl group on its surface was used as the anode material as illustrated in Fig. 1b. As expected, the performance of EAQ polymer binder when using the oxidized carboxyl enrichment graphite is much better than natural graphite, which is stable at 370 mAh/g and closed to the theoretical capacity of graphite. Also, we can see the morphology of the obtained oxidized graphite before and after combined with the EAQ binder in Fig. 1c and d under field emission scanning electron microscopy (FESEM). The EAQ binder distribute uniformly on the surface of the oxidized graphite.

The higher current discharge-charge performance of the EAQ/Oxidized graphite is also showed here in Fig 2a, when the discharge-charge current increased to C/2 the capacity can be stable at about 330 mAh/g and 280 mAh/g when at the current density of

372 mA/g. The coulombic efficiency of each higher current density all can reach more than 99% during the whole 200 cycles. The detailed galvanostatic discharge-charge profiles of the EAQ/oxidized graphite electrode cycled at C/10 is also performed (Supplementary Fig. S1). The first discharge curve shows a sloping profile that can be mainly ascribed to the solid electrolyte interface (SEI) formation. Clearly, lithium ions can rapidly pass through the thin EAQ layer to reach the graphite active material throughout the 250 cycles. According to Fig 2a, we can also find that the thermal stability of the EAQ binder/oxidized graphite electrode is quite well since there is no decrease after the ambient temperature increased to 60 °C. To investigate the effect of the proportion of the EAQ binder, we vary the binder percentage from 5 wt% to 20 wt%. As illustrated in Fig. 2b, the capacity decreased to about 350 mAh/g when the percentage of the EAQ binder increased to 20 wt%. Simultaneously, when the percentage of EAQ binder decreased to 5 wt%, the capacity decreased a little to about 340 mAh/g. The first cycle coulombic efficiency of oxidized graphite anode with 10 wt% EAQ binder is 95.2 % which is higher than 5 wt% EAQ binder with the value of 85.1 %. This result indicates that an optimized binder percentage (10 wt%) is beneficial to the lithium diffusion and stability of the electrode (Supplementary Fig. S2). Furthermore, the electrochemical cycling performance of the CMC/oxidized graphite (1/9 weight ratio) was

evaluated using deep charge/discharge galvanostatic cycling from 3 to 0.01 V (Supplementary Fig. S3).

To clarify the better binder effect between the EAQ binder and the graphite materials, the surface structure is the key factor to investigate. As is well known, the binding mechanisms including the mechanical mosaic theory, adsorption theory, diffusion theory, electrostatic theory, and chemical bond theory. The chemical bond theory exists between the atoms including the ionic bond, covalent bond and metallic bond. Ionic bond force is generated between the positive ions and the anions. The covalent bond force is generated when the atoms share electron pair. The metallic bond is generated when the movement of the electrons of the metallic positive ions happens. The binding force will increase rapidly when the chemical bond generated on the surface of the binders and the active materials.

vibrations, a peak at around 1700 cm^{-1} corresponding to C=O vibrations. To evaluate the interactions of EAQ binder and oxidized graphite, we also explored the different active groups on the natural and oxidized graphite using the FTIR (Fig 4). On the basis of the previous literature,^{22, 25, 26} some reactive structural imperfections on the natural graphite surface were eliminated after oxidation, and therefore, the decomposition of electrolyte molecules was made less likely. The better performance of the oxidized graphite compared to natural graphite when we use either PVDF or EAQ is the sufficient proof as performed in Fig 1a and b. In the meantime, the surface of natural graphite was covered with a fresh and dense layer of oxides containing hydroxyl, ether oxygen, carboxylic oxygen in $-\text{COOR}$ ($\text{R} = \text{H}$ and alkyl) and carbonyl oxygen. After the oxidation, the increase of the absorbance peak indicates that the relative content of carboxylic oxygen and carbonyl oxygen

Table 1. Binder properties of AQTM 55S (EAQ) polymer and polyvinylidene fluoride (PVDF).

^a Minimum thermal decomposition temperature from TGA (10 mg sample, 5 °C/min heating rate, nitrogen atmosphere)

Fig.3 Fourier transform infrared (FTIR) spectra of the EAQ and PVDF polymer binder.

Fig.4 Fourier transform infrared (FTIR) spectra of the natural graphite and the graphite oxidized by HNO_3 .

increases as illustrated in Fig 4. Since more carboxylic groups in the surface of oxidized graphite have led to a larger number of possible binder-graphite bonds and, thus, better graphite electrode stability. The enhancement of the reversible capacity and stability can be attributed mainly to the chemical bonds between the EAQ polymer binder and graphite through the oxidation treatment.^{27, 28} Hence, we suppose that the prime mechanism for the superiority of the EAQ polymer binder is the chemical bonds formed in the electrode.

The electrochemical stability of EAQ polymer binder is experimentally verified through the cyclic voltammetry (CV) tests on pure EAQ polymer film (Supplementary Fig. S6). In order to compare with PVDF, both of these two polymer films were coated on the copper foil then fabricated into the coin cell under a mimic condition of anodes in lithium-ion environment. The EAQ binder has nearly the same profile with the PVDF except the first irreversible cycle. This promising stability varies from 0.01 V to 3.5 V imply a wide application in the future.

Conclusions

We demonstrate that the green Eastman AQTM 55S (EAQ) polymer, which has the potential for use as LIBs binder substitute for conventional LIBs binders. The EAQ polymer binder is operation-environment friendly because it uses aqueous solvent instead of N-methyl-2-pyrrolidinone (NMP) solvent for PVDF binder. Moreover, the EAQ polymer binder has plentiful active hydroxyl groups on its surface, which is different from the chemical inertness PVDF binder. We use the oxidized graphite with carboxyl group on its surface as the anode material. Concluded from the better performance of the EAQ polymer binder to PVDF, we demonstrate that the formation of the chemical bonds between the carboxyl group on the oxidized graphite surface and the hydroxyl group on the EAQ polymer surface is the key factor. The water soluble Eastman EAQ polymer binder have the potential to convert the tradition LIBs production process from organic solvent and binder based process into a green and water-based production technologies.

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Notes and references

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1. V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy & Environmental Science*, 2011, **4**, 3243.
2. S.-T. Myung, K. Amine and Y.-K. Sun, *Journal of Materials Chemistry*, 2010, **20**, 7074.
3. J. B. Goodenough and Y. Kim, *Chemistry of Materials*, 2010, **22**, 587-603.
4. C. Zonghai, L. Christensen and J. R. Dahn, *Journal of Applied Polymer Science*, 2004, **91**, 2949-2957.
5. H. Buqa, M. Holzapfel, F. Krumeich, C. Veit and P. Novak, *J. Power Sources*, 2006, **161**, 617-622.
6. G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang and W. Yang, *Adv Mater*, 2011, **23**, 4679-4683.
7. T. N. Danks, R. C. T. Slade and J. R. Varcoe, *J. Mater. Chem.*, 2002, **12**, 3371-3373.
8. S. Hietala, S. Holmberg, M. Karjalainen, J. Nasman, M. Paronen, R. Serimaa, F. Sundholm and S. Vahvaselka, *J. Mater. Chem.*, 1997, **7**, 721-726.
9. L. Jabbour, C. Gerbaldi, D. Chaussy, E. Zeno, S. Bodoardo and D. Beneventi, *Journal of Materials Chemistry*, 2010, **20**, 7344.
10. I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, **334**, 75-79.

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11. H. Zheng, R. Yang, G. Liu, X. Song and V. S. Battaglia, *Journal of Physical Chemistry C*, 2012, **116**, 4875-4882.
 12. M. Mancini, F. Nobili, R. Tossici, M. Wohlfahrt-Mehrens and R. Marassi, *J. Power Sources*, 2011, **196**, 9665-9671.
 - 5 13. E. Peled, C. Menachem, D. BarTow and A. Melman, *J. Electrochem. Soc.*, 1996, **143**, L4-L7.
 14. M. Yoshio, H. Y. Wang, K. Fukuda, Y. Hara and Y. Adachi, *J. Electrochem. Soc.*, 2000, **147**, 1245-1250.
 15. M. Yoshio, H. Y. Wang, K. Fukuda, T. Umeno, T. Abe and Z. Ogumi, *J. Mater. Chem.*, 2004, **14**, 1754-1758.
 - 10 16. Y. P. Wu, C. Jiang, C. Wan and R. Holze, *Journal of Power Sources*, 2002, **111**, 329-334.
 17. K. Takata, M. Okuda, N. Yura and R. Tamura, *Applied Physics Express*, 2012, **5**.
 - 15 18. S. R. Sivakkumar, J. Y. Nerkar and A. G. Pandolfo, *Electrochim. Acta*, 2010, **55**, 3330-3335.
 19. C. S. Chou, C. H. Tsou and C. I. Wang, *Adv. Powder Technol.*, 2008, **19**, 383-396.
 20. S. M. Jang, J. Miyawaki, M. Tsuji, I. Mochida, S. H. Yoon and F. Y. Kang, *New Carbon Mater.*, 2010, **25**, 89-96.
 - 20 21. Y. Wang and J. Y. Lee, *J. Power Sources*, 2005, **144**, 220-225.
 22. J. Shim and K. A. Striebel, *J. Power Sources*, 2007, **164**, 862-867.
 23. H. P. Zhao, J. G. Ren, X. M. He, J. J. Li, C. Y. Jiang and C. R. Wan, *Electrochim. Acta*, 2007, **52**, 6006-6011.
 - 25 24. L. Zou, F. Y. Kang, X. H. Li, Y. P. Zheng, W. C. Shen and J. Zhang, *J. Phys. Chem. Solids*, 2008, **69**, 1265-1271.
 25. Q. M. Pan, K. K. Guo, L. Z. Wang and S. B. Fang, *J. Mater. Chem.*, 2002, **12**, 1833-1838.
 - 30 26. T. Zhang, J. Gao, L. J. Fu, L. C. Yang, Y. P. Wu and H. Q. Wu, *J. Mater. Chem.*, 2007, **17**, 1321-1325.
 27. G. Liu, H. Zheng, X. Song and V. S. Battaglia, *Journal of The Electrochemical Society*, 2012, **159**, A214.
 28. G. Liu, H. Zheng, S. Kim, Y. Deng, A. M. Minor, X. Song and V. S. Battaglia, *Journal of The Electrochemical Society*, 2008, **155**, A887.
 - 35