Enhanced Electrochemical Performances of Si/Graphite Composite Anode Using Commercial Promising Waterborne Conductive Binder

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Abstract. Silicon has attracted increasing attention as an anode material in Li-ion batteries (LIBs) owing to its high theoretical capacity. However, electrochemical properties of Si-based anodes are hindered by the electrode swelling during the charge/discharge process. In this paper, we developed a novel polymer binder with high electronic conductivity and self-healing function leading to stable cycling. These properties are attributed to the polymer structure which could provide more free Li+ leading to higher conductivity and capacity retention of the anodes. It is believed that this novel conductive binder could be a promising candidate for commercial application for the Si/graphite composite anodes in Li-ion batteries.

1. Introduction
Lithium ion batteries (LIBs) as an enabling energy storage technology present ever-increasing demands of high capacity and stable electrochemical performances [1, 2]. Silicon-based anode [3-8] has attracted increasing attention owing to its high theoretical capacity. Polymer binder [9], one of the major components of the electrode, is used to link active materials and conducting particles together onto the current collector and ensure the integrity of the electrodes during subsequent cycling. However, conventional poly (vinylidene fluoride) (PVDF) binder needs N-methyl-2-pyrrolidone (NMP) as the solvent which is toxic to the environment. In addition, the addition of polymer binders would restrict the electrochemical performances of electrodes for the poor conductivity. Thus, novel and effective waterborne binders with a low addition amount are urgently needed.

In recent years, waterborne polymer binders have particularly attracted more and more attention. Many researchers prepare conductive polymer as the binders for Si-based anodes to increase the conductivity of the electrodes leading to excellent electrochemical properties. Many studies focused on conductive polyamide imide (PAI) based polymer binder [10-12] presenting improved initial Coulombic efficiency and excellent retention for Si-based electrode for the high electronic conductivity upon cycling. Liu and his group prepared conductive polymer as the binders, such as PFFOMB [13] binders, PEFM [14, 15] conductive binder, conductive poly(9,9-diocylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) [16, 17] binder, poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA) [18] binder and aqueous poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [19], leading to enhanced cycle
stability and the specific capacity for Si-based anodes. Thus, the usage of conductive polymer binder could be an efficient way to enhance the performances.

In this paper, we report a novel conductive polymer binder, a kind of lithiated ionic polymer, for graphite anode materials through an in-situ hydrothermal method. The novel binder leads to the excellent cycling stability during the cycling and low impedance for Si/graphite composite anode which would be promising for further commercial application.

2. Experimental

2.1. Synthesis of the polymer binder
The aqueous binder was synthesized by styrene (Alfa Aesar), n-butyl acrylate (Alfa Aesar), methacrylate (Alfa Aesar) and lithium hydroxide (Alfa Aesar). For comparison purpose, the polyvinylidene fluoride (PVDF) solution of (NMP) was used as a control binder.

2.2. Preparation of electrodes and Li-ion cells assembling configuration
The prepared polymer binder was mixed with Si/graphite material (<100 nm, BTR Co., Ltd, China), and the weight ratio of the electrode was 96.5% Si/graphite, 1.5% CMC as the thicker and 2% binder for the anode. The composition of the PVDF electrodes was 96.5% Si/graphite and 3.5% PVDF (weight). The coin-type half cells were assembled with lithium metal as the counter electrode in Argon filled glove box. The electrolyte was consisted of 1 mol/L LiPF6 in a mixture of organic carbonates: 2:3:1 EC/DEC/EMC (volume).

2.3. Morphology and electrochemical characterization
Morphology test was used Hitachi S4800. Galvanostatic charge-discharge cycling of cells was tested between 0.01 and 1.5 V at 25oC using a Land battery tester (Wuhan, China) for 50 cycles at a current density of 0.1C. Electrochemical impedance spectroscopy (EIS) was tested on a CHI 660E electrochemical work station over the frequency range of 10-3-105 Hz with an amplitude modulation of 5 mV.

3. Results and discussion

3.1. Morphology test
The SEM image (Fig.1a) of the polymer emulsion particles shows that the emulsion particles are spherical and the average diameter of the particles is about 200nm. From Fig.1b and c, the appearance and interspace of the electrodes made by conductive binder and PVDF binder show no obvious difference which demonstrates that the conductive binder could prepare stable slurry with Si/graphite composite anode. In addition, Fig. 1b demonstrates that the conductive binder is dispersed uniformly in the slurry because black points which represent the conductive binder are equably distributed on the surface of the graphite particles. Thus, the conductive binder would be promising to improve the electrochemical performances.

![Figure 1](image-url) SEM images of (a) binder emulsion particles, (b) electrode using conductive binder before cycling, (c) electrode using PVDF binder before cycling.
3.2. Cycling performance

The cycling performances show that the electrode with conductive binder presents more stable cycling performance with the retention of 92.3% after 50 cycles even with a high rate of 0.1C compared to PVDF electrode with retention of 40.2%. Fig. 2b shows the rate capability of the graphite electrodes with the conductive binder and PVDF binders. The specific capacity of the conductive binder electrode performs no obvious decrease during the first 20 cycles owning to the conductivity of Li+. Thus, the conductive LIP binder could effectively enhance the cycling performance and the rate capacity because the improved conductivity of the electrode and the conductive binder could provide more free Li+ which would be beneficial to the electrochemical performances.

![Figure 2](image1.png)

**Figure 2.** (a) Cycling performances of the Si/graphite electrodes with conductive binder and PVDF binder. (b) Potential profiles of the Si/graphite electrodes using conductive and PVDF binder.

3.3. EIS spectroscopy

The electrochemical impedance spectroscopy (EIS) of graphite electrodes with conductive binder and PVDF were tested before cycling. From Fig. 3, the semicircle diameter of the conductive binder electrode is much smaller than PVDF binder electrode which indicates a lower impendence of the conductive binder electrode. The results demonstrated that the conductive binder could enhance the conductivity of electrode and would be beneficial to decrease the impendence and increase the properties for the following cycling.

![Figure 3](image2.png)

**Figure 3.** Nyquist plots for graphite electrode prepared with LIP and PVDF binder.
4. Conclusion
In summary, a conductive polymer binder has been prepared by using an in-situ thermal technique based on the low-cost for Si/graphite composite anodes. This conductive binder could effectively decrease impedance and enhance cycling stability owing to the increased conductivity and more free Li+ based on the polymer structure. In contrast, the cells using PVDF binder present fast capacity fading and PVDF binder needs NMP solvent which is toxic to the environment. Thus, this research demonstrates that waterborne polymer binder is not only environmental friendly but also beneficial to improve the electrochemical performances owning to the chemical structure of the polymer. The results of this study also provide a pattern for further researches and commercial application.

5. References
[1] S. W. Lee, S. W. Choi, S. M. Jo, B. D. Chin, D. Y. Kim, K. Y. Lee, Electrochemical properties and cycle performance of electrospun poly(vinylidene fluoride)-based fibrous membrane electrolytes for Li-ion polymer battery, J. Power Sources Vol. 163 (2006), P. 14-46
[2] N. Nitta, F.X. Wu, J.T. Lee, G. Yushin, Li-ion battery materials: present and future, Mater. Today Vol.18 (2015), P. 252-264
[3] M. Gu, Y. He, J.M. Zheng, C.M. Wang, Nanoscale silicon as anode for Li-ion batteries: The fundamentals, promises, and challenges, Nano Energy Vol. 17 (2015), P. 366-383.
[4] M. L. Terranova, S. Orlanducci, E. Tamburri, V. Guglielmotti, M. Rossi, Si/C hybrid nanostructures for Li-anodes: An overview, J. Power Sources Vol. 246 (2014) , P. 167-177.
[5] M. Ko, S. Chae, J. Cho, Challenges in Accommodating Volume Change of Si Anodes for Li-Ion Batteries, ChemElectroChem Vol. 2 (2015) , P. 1645-1651.
[6] M. Ashuri, Q.R. He, L.L. Shaw, Silicon as a potential anode material for Li-ion batteries: where size, geometry and structure matter, Nanoscale Vol. 8 (2016), P. 74-103.
[7] H. Wu, Y. Cui, Designing nanostructured Si anodes for high energy lithium ion batteries, Nano Today Vol. 7 (2012), P. 414-429.
[8] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R.P. Zaccaria, C. Capiglia, Review on recent progress of nanostructured anode materials for Li-ion batteries, J. Power Sources Vol. 257 (2014) , P. 421-443.
[9] S. L. Chou, Y. Pan, J. Z. Wang, H. K. Liu, S. X. Dou, Small things make a big difference: binder effects on the performance of Li and Na batteries, Phys. Chem. Chem. Phys. Vol. 16 (2014) , P. 20347-20359.
[10] N. S. Choi, K. H. Yew, W. U. Choi, S. S. Kim, Enhanced electrochemical properties of a Si-based anode using an electrochemically active polyamide imide binder, J. Power Sources Vol. 177 (2008) , P. 590-594.
[11] H. Wu, G. H. Yu, L. J. Pan, N. Liu, M. T. McDowell, Z. Bao, Y. Cui, Stable Li-ion battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles, Nat. Comms. Vol. 4 (2013), P. 1943.
[12] T. Yim, S. J. Choi, Y. N. Jo, T. H. Kim, K. J. Kim, G. Jeong, Y. J. Kim, Effect of binder properties on electrochemical performance for silicon-graphite anode: Method and application of binder screening, Electrochim. Acta Vol. 136 (2014), P. 112-120.
[13] G. Liu, S. D. Xun, N. Vukmirovic, X. Y. Song, P. O. Velasco, H. H. Zheng, V. S. Battaglia, L. W. Wang, W. L. Yang, Polymers with Tailored Electronic Structure for High Capacity Lithium Battery Electrodes, Adv. Mater. Vol. 23 (2011), P. 4679-4683.
[14] M. Y. Wu, X. C. Xiao, N. Vukmirovic, S. D. Xun, P. K. Das, X. Y. Song, P. O. Velasco, D. D. Wang, A. Z. Weber, L. W. Wang, V. S. Battaglia, W. L. Yang, G. Liu, Toward an Ideal Polymer Binder Design for High-Capacity Battery Anodes, J. Am. Chem. Soc. Vol. 135 (2013) , P. 12048-12056.
[15] M. Y. Wu, X. Y. Song, X. S. Liu, V. Battaglia, W. L. Yang, G. Liu, Manipulating the polarity of conductive polymer binders for Si-based anodes in lithium-ion batteries, J. Mater. Chem.
A Vol. 3 (2015), P. 3651-3658.

[16] H. Zhao, Z. H. Wang, P. Lu, M. Jiang, F. F. Shi, X. Y. Song, Z. Y. Zheng, X. Zhou, Y. B. Fu, G. Abdelbast, X. C. Xiao, Z. Liu, V. S. Battaglia, K. Zaghib, G. Liu, Toward Practical Application of Functional Conductive Polymer Binder for a High-Energy Lithium-Ion Battery Design, Nano Lett. Vol. 14 (2014), P. 6704-6710.

[17] H. Zhao, N. Yuca, Z. Y. Zheng, Y. B. Fu, V. S. Battaglia, G. Abdelbast, K. Zaghib, G. Liu, High Capacity and High Density Functional Conductive Polymer and SiO Anode for High-Energy Lithium-Ion Batteries, ACS Appl. Mater. Interfaces Vol. 7 (2015), P. 862-866.

[18] H. Zhao, Y. Wei, R. M. Qiao, C. H. Zhu, Z. Y. Zheng, M. Ling, Z. Jia, Y. Bai, Y. B. Fu, J. L. Lei, X. Y. Song, V. S. Battaglia, W. L. Yang, P. B. Messersmith, G. Liu, Conductive Polymer Binder for High-Tap-Density Nanosilicon Material for Lithium-Ion Battery Negative Electrode Application, Nano Lett. Vol. 15 (2015), P. 7927-7932.

[19] D. Shao, H. X. Zhong, L. Z. Zhang, Water-Soluble Conductive Composite Binder Containing PEDOT: PSS as Conduction Promoting Agent for Si Anode of Lithium-Ion Batteries, ChemElectroChem Vol. 1 (2014), P. 1679-1687.