Conductive polymer binder for nano-silicon/graphite composite electrode in lithium-ion batteries towards a practical application

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Abstract: The state-of-the-art graphite anode containing a small portion of silicon represents a promising way of applying high-capacity alloy anode in the next generation high energy density lithium-ion batteries. The conductive polymeric binders developed for Si anodes proved to be an effective binder for this graphite/nanoSi composite electrode. Without any acetylene black conductive additives in the electrode, a high areal capacity of above 2.5 mAh/cm² is achieved during long-term cycling over 100 cycles. This conductive polymer-enabled graphite/nanoSi composite electrode exhibits high specific capacity and high 1st cycle efficiency, which is a significant progress toward commercial application of Si anodes.

Keywords: conductive polymer binder, silicon nanoparticle, graphite, lithium-ion battery, practical application

1. Introduction

As human civilization advances, global energy consumption steadily increases. This necessitates a green method to effectively store energy, such as using fuel cells, flows batteries, and lithium-ion batteries (LIBs).[1] State-of-the-art LIBs use graphite as anode, with a theoretical gravimetric specific capacity of about 370 mAh/g. Alternative alloy anodes, such as silicon or tin, are shown as promising successors to graphite. Si has a gravimetric specific capacity over 10 times higher than graphite (4200 mAh/g), but a 300% volume expansion during lithiation prevents it from becoming commercially viable. The high volume changes during lithiation and delithiation cycles cause excessive electrolyte decomposition, leading to capacity decay. Another effect of the volume change is the difficulty to assemble electrodes with higher material loading for a stable cell performance. An area capacity of higher than 2.5 mAh/cm² is necessary and highly desirable towards a practical application of these high capacity alloy anodes in a commercial cell. New binders have been developed in recent years to achieve a high material loading in the silicon based anode, a cross-linked water soluble polymeric binder[2] and a conductive polymer binder[3], along with other types of binders, have shown that the right binder chemistry is critical toward a high-performance silicon anode.

Typically a high content of polymer binder and conductive additives are needed to enable a stable cycling of Si anode.[4] However, this unacceptably decreases the energy density due to the excessive non-active materials used to maintain a good cell performance. An electronic conductive polymeric binder developed for Si anodes achieved very stable cycling of Si anode with good active material loading.[5] Since no conductive additives are used, a high content of active material content is achieved. A conductive polymer binder compatible with both graphite

1 and nanoSi anodes are used to assemble a graphite/nanoSi composite electrode in this work. This
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4 conductive polymer-enabled composite electrode presents a promising opportunity for the
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6 practical application of high capacity alloy anodes for the next-generation lithium-ion batteries.
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10 11 **2. Experimental**

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13 All reagents were purchased from Sigma-Aldrich or TCI America and used without further
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15 purification. Synthesis of poly(1-pyrenemethyl methacrylate) binder was shown in a previous
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17 publication.[6] CGP-G8, purchased from ConocoPhillips, was used as the graphite anode. The
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19 nanoSi with a particle size of 50-70 nm is from Nanostructured and Amorphous Inc. Celgard 2400
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21 separator is obtained from Celgard. Lithium-ion electrolyte were purchased from BASF, including
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23 1 M LiPF₆ in ethylene carbonate, diethyl carbonate (EC/DEC=3/7 w/w) containing 30 wt%
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25 fluoroethylene carbonate (FEC). 2325 coin cells were prepared using lithium metal as a counter
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27 electrode. Slurry preparation, electrode coating, and cell fabrication were completed using
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29 standard techniques in the literature.[7] SEM images of the composite electrode surface were
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31 collected with a JEOL JSM-7500F field emission scanning electron microscopy with an
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33 accelerating voltage of 15 kV using the high vacuum mode at room temperature. High-resolution
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35 TEM images were obtained on a Philips CM200 field emission microscope operated at 200 kV at
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37 the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory
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52 53 **3. Results and Discussion**

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55 A pyrene-based homo-polymer poly(1-pyrenemethyl methacrylate) (PPy, Figure 1a) is
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57 synthesized and used as the conductive polymer binder for the graphite/nanoSi composite
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electrode. The graphite materials are composed of micron-size particles shown in Figure 1b. The micron-size particle with small surface area is the origin of its high Coulombic efficiency during cell cycling, which induces minimum electrolyte decomposition and formation solid electrolyte interphase (SEI).[8]

Figure 1. (a) Chemical structure of the PPy binder. (b) SEM image of the graphite particles. (c) and (d) High Resolution TEM (HRTEM) images of the nanoSi particles.

A typical nanoSi material is used to reduce the volume changes on the particle level and avoid particle cracking upon lithiation. The average particles size of the nanoSi is around 50-70 nm, with a high surface area of $\sim 50 \text{ m}^2/\text{g}$. [9] The nanoSi with high surface area needs significant electrolyte decomposition to form SEI and passivate the surface, the resulting low 1st cycle coulombic efficiency hinders a practical application of the high capacity nanoSi anodes. Even with a particle size in the nano-domain, Figure 1d still indicates crystalline silicon phase in this nanoSi particles. Overcoming the low initial efficiency is an intensive topic in recent literature.[10] The whole problem of stable cycling of Si anode is the 300% volume changes due to its high specific capacity (4200 mAh/g). However, compared to the state-of-the-art graphite anode (372 mAh/g),

an anode with an intermediate specific capacity at 700-1000 mAh/g could significantly enhance the energy density in the full cell configuration. Thus, in this work we mix graphite and nanoSi with PPy binder during slurry preparation process, only 20 wt% Si is used in the electrode assembly, which will only leads to 30% to 50% volume changes on the electrode level; on the other hand, the 70 wt% graphite material serves as a buffer to accommodate the volume changes on the electrode level, while maintaining a good electronic conduction channel throughout the whole electrode laminate.

Figure 2. (a) Specific capacity (left Y axis) and areal capacity (right Y axis) vs. cycle number using 10 wt% PPy binder with 20 wt% nanoSi and 70 wt% graphite. The initial two cycles were at C/25, then C/10 for the long-term cycling. (b) 1st, 30th, and 100th cycle voltage curves of the PPy/graphite/nanoSi mixture electrode. (c) Coulombic efficiency vs. cycle number from the second cycle (1st cycle efficiency is 69.79%). (d) Cell performance of graphite electrode based on PPy binder at a C/10 rate.

Previous work proves that the conductive PPy binder enables a very stable cycling of nanoSi material.[3] PPy also enables a stable cycling performance of the graphite anode.[6] Figure 2d shows the cell performance based on 10 wt% PPy and 90 wt% graphite at a C/10 rate. Almost full specific is achieved for this graphite anode material (around 310 mAh/g for CGP-G8,

ConocoPhillips), which is stable for several hundreds of cycles. Note that the initial decrease of specific capacity value in the initial 30 cycles is proposed due to electrolyte wetting, which self-recovers to a value of above 300 mAh/g after 50 cycles.

Targeting at a practical application in commercial cell, a relatively high loading electrode is assembled and tested. This specific cell shown in Figure 2a contains 0.87 mg nanoSi/cm² and 3.06 mg graphite/cm². The left Y axis in Figure 2a is plotted as mAh per gram of graphite & nanoSi, which exhibits twice as high as conventional graphite anode even after 100 cycles. Also, a signature areal capacity of 2.5 mAh/cm² is achieved and maintained stable for more than 100 cycles. The corresponding voltage curves at 1st cycle, 30th cycle, and 100th cycle are shown in Figure 2b. Consistent with the crystalline Si phase in the TEM morphology (Figure 1d), a large overpotential is shown in the 1st cycle lithiation curve, corresponding to the amorphization of the crystalline Si phase. The Si phase is kept amorphous in the following cycles, which is also reflected in the 30th and 100th cycle voltage curves.

		Graphite/PPy	nanoSi/PPy	nanoSi/graphite/PPy
1 st cycle	Q_c^a (mAh/g)	323.7	3482.4	899.9
	η^b (%)	87.12	69.79	82.59
30 th cycle	Q_c^a (mAh/g)	266.8	2868.8	700.8
	η^b (%)	99.78	98.21	98.91
100 th cycle	Q_c^a (mAh/g)	322.9	2907.6	625.1
	η^b (%)	99.83	98.93	99.39

^a charge (delithiation) capacity ^b Coulombic efficiency

Table 1. Electrochemical parameters of PPy conductive binder with different anode materials.

The main electrochemical parameters of the cell performance using 10 wt% PPy binders with different anode materials are shown in Table 1. It shows that PPy conductive polymer is compatible with the conventional graphite anode, with a high 1st cycle efficiency of 87.12%. The

efficiency value is enhanced to 99.83% after 100 cycles at a C/10 rate. A previous work established that PPy is a very good polymer binder for a long-term stable cycling of nanoSi anode,[6] with a typical 1st cycle efficiency of less than 70%. This low 1st cycle efficiency is typical for a nano-material electrode, which is due to the excessive side reaction and SEI formation from the high surface area. The low efficiency value at 1st cycle will consume excessive lithium in a full cell configuration, which is a major hurdle for the application of nanoSi anode. The compatibility of the PPy conductive polymer binder with both graphite and nanoSi is the foundation for the successful development of graphite/nanoSi mixture electrode. As shown in Table 1, mixing 20 wt% Si and 70% into the electrode formulation maintains a specific capacity value twice as high as the graphite anode even at 100th cycle, while enabling a 1st cycle efficiency as high as 82.59%. Simply mixing graphite with a small portion of nanoSi enhances the specific capacity while not sacrificing 1st cycle efficiency, together with a high areal capacity of above 2.5 mAh/cm², this approach represents a good way of using high capacity alloy anode in a the commercial application.[11]

Figure 3. SEM image (a) (b) pristine electrodes and (c) (d) cycled electrodes (10 cycles after C/10).

The morphology of the pristine and cycled PPy/graphite/nanoSi electrode is shown in Figure 3. Although there is only 20 wt% nanoSi in the electrode, the tap density for this nanoSi is quite small and the actual volume of added nanoSi is significant compared to the micro-size graphite anode material with high tap density. Thus, in the top-view SEM image of the pristine electrode in Figure 3a, a large portion of the material in the image is nanoSi. An expanded view on the nanoSi part in Figure 3b indicates good distribution of the nanoSi particles in the electrode with decent porosity. The electrolyte used in this work involves FEC additives, which results in a typical cycled electrode morphology shown in Figure 3c and 3d.

4. Conclusions

The state-of-the-art graphite anode containing a small portion of silicon represents a promising way of applying high-capacity alloy anode in the next generation high energy density lithium-ion batteries. Without any acetylene black conductive additives in the conductive polymer/graphite/nanoSi electrode, a high areal capacity of above 2.5 mAh/cm² is achieved during long-term cycling over 100 cycles. This conductive polymer-enabled graphite/nanoSi composite electrode exhibits high specific capacity and high 1st cycle efficiency, which is a significant progress toward commercial application of Si anodes.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

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