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# Novel conductive binder for high-performance silicon anodes in lithium ion batteries



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## ABSTRACT

A novel polymer is designed to serve as the conductive binder for high-capacity silicon anodes in lithium ion batteries (LIBs), aiming to address fast capacity fade and poor cycle life of silicon anodes caused by large volume change during repeated cycles. Abundant carboxyl groups in the polymer chain can effectively enhance the binding force to Si nanoparticles (NPs) and the n-type polyfluorene backbones of the polymer significantly promote the electronic conductivity under the reducing environment for anodes, dual-features of which can maintain electronic integrity during lithiation/delithiation cycles. Notably, the polymer can react with the polar groups on the surface of Si NPs to form strong chemical bonds, thus truly maintaining the electrode mechanical integrity and good electronic conductivity after repeated charge/discharge process. The as-assembled batteries based on the polymer without any conductive additive exhibit a high reversible capacity (2806 mA h g<sup>-1</sup> at 420 mA g<sup>-1</sup>) and good cycle stability (85.2% retention of the initial capacity) after 100 cycles.

## 1. Introduction

Lithium ion batteries (LIBs) are widely used in portable electronic products, however, there are still some concerns for their applications in electric vehicles and renewable energy storage grids, including energy density, cost, and safety [1–4]. Therefore, development of LIBs with high energy density and long cycle life is extremely important. Enormous efforts have been focused on high capacity silicon anodes for increasing energy density of LIBs. Silicon anodes possess a high theoretical capacity (ca. 4200 mA h g<sup>-1</sup>), which is about ten times higher than that of the currently available commercial graphite anodes (ca. 370 mA h g<sup>-1</sup>). However, fast capacity fade and poor cycling stability of Si anodes caused by volume expansion (400%) and shrinkage during repetitive lithiation and delithiation cycles have seriously restricted the application of Si anodes in high energy LIBs [5].

Tremendous efforts have been devoted to addressing the above mentioned problem of silicon anodes, by preparing nanostructured Si [6,7], controlling voltage [8,9], and using novel binder [10–12]. For nanoscale Si anodes, the main issue is that Si NPs easily lose electronic connection during cycling because the conductive additive has no mechanical binding force with the active materials. The cycling performance of nanoscale Si anodes can be easily improved by using high performance binders, including carboxymethylcellulose sodium

(CMCNa) [10], alginate [11], poly(acrylic acid) (PAA) [12], styrene butadiene rubber (SBR) [13], dopamine modified alginate [14], gum arabic [15], hyperbranched  $\beta$ -cyclodextrin polymer [16], guar gum [17], polyimide [18], polysaccharide [19]. Compared with conventional polyvinylidene fluoride (PVDF) binder, these polymeric binders possess higher Young's moduli and higher contents of functional groups, such as hydroxyl, carboxyl and catechol. These functional groups can increase the binding force between the binder and Si surface, and significantly improve the cycle stability of silicon anodes. Besides novel binders, cross-linked reaction [20,21], host-guest chemistry [22] and self-healing chemistry [23] were also used for improving the cyclic performance of silicon anodes.

In conventional approach, the electrode consists of three components which include active material, conductive additive and polymeric binder. But use of both conductive additive and binder significantly reduces the volumetric and gravimetric capacity of the electrode. Liu et al. [24] first reported a novel conductive polymer as a bi-functional binder instead of separate conductive additive and conventional binder. They found that Si anodes based on this conducting polymer without any conductive additive showed high capacity and excellent cycling performance. Afterwards, other conductive polymers including poly(2,7-9,9-dioctylfluorene-2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene-co-2,7-fluorenone-co-2,5-1-methylbenzoate ester) (PFEM) [25]

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and poly(1-pyrenemethyl methacrylate-co-triethylene oxide methyl ether methacrylate) (PPyE) [26] were reported. Furthermore, polyaniline (PANI) hydrogels [27], poly(phenanthrenequinone) (PPQ) [28], poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [29,30], and conductive gels [31] were also used as binders for improving the cycling performance of Si based anodes. In comparison with three-component electrode systems, these two-component electrode systems based on conducting polymeric binders can increase the volumetric capacity of Si anodes via decreasing the proportion of high specific area and inactive conductive additive in the electrodes. More importantly, conductive binders combine the functionality of both binder and conductive additive, avoiding the use of nonconductive binders. Thus, the electrical connectivity problem of the Si electrode is mitigated and the cycling performance is noticeably improved because of its good flexibility and mechanical property. Although considerable progress has been achieved in conducting polymeric binder, developing novel conducting polymeric binders for high capacity silicon anodes remains a challenge.

Conventional water-soluble binders (such as CMC-Na) significantly improve the electrochemical performance owing to their favorable interactions with the surface of Si NPs. But their insulating nature leads to poor electrical connections mainly because the conductive additive tends to be pushed away from Si NPs due to huge volume expansion of Si anodes during charging (Fig. 1a). Herein, we report a water-soluble multiple-carboxyl polymer as a conductive binder for improving the electrochemical performance of the silicon anodes. The polymer consists of an n-type polyfluorene backbones and abundant carboxyl

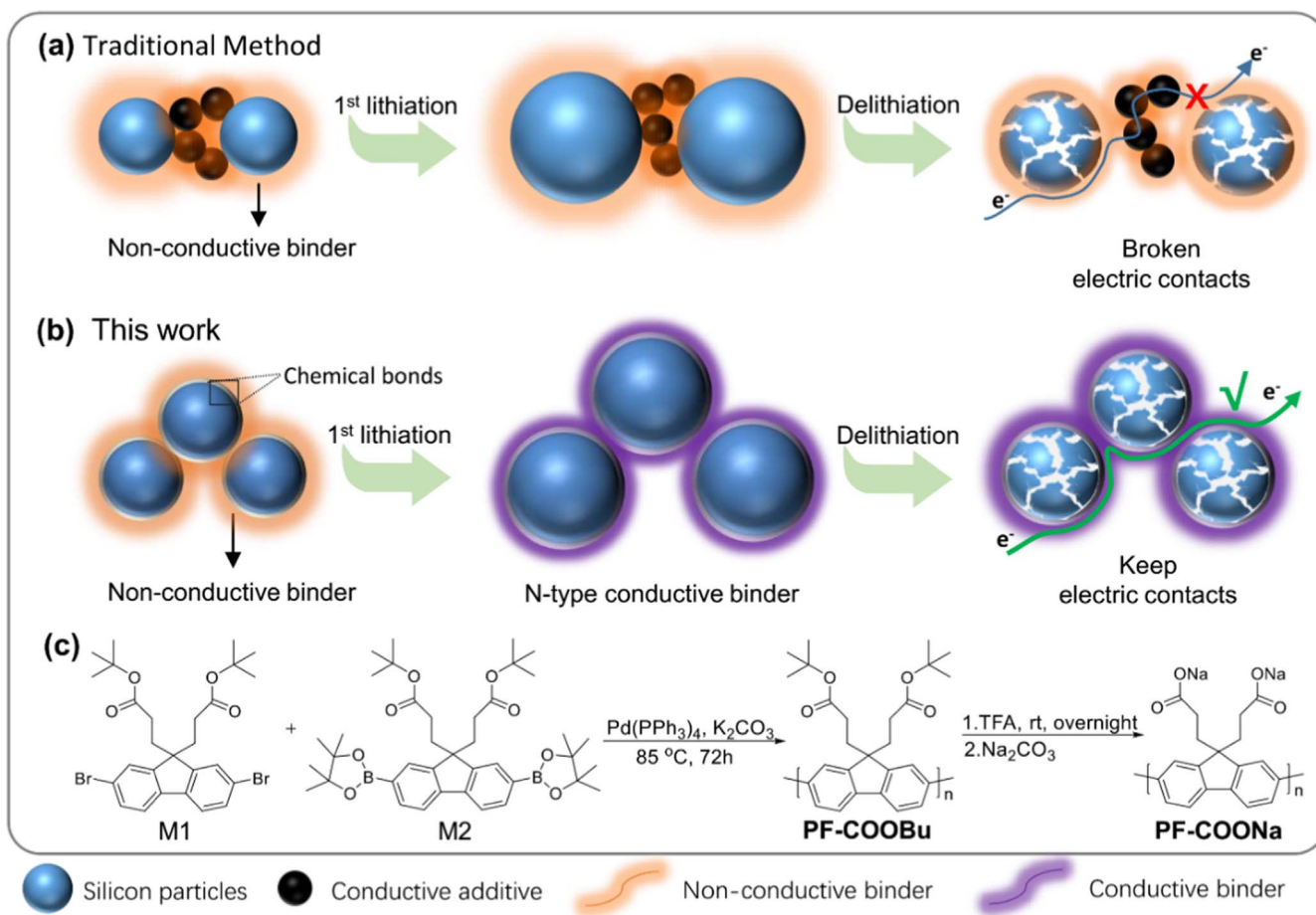
functional groups on the side chains. The polymeric binder shows excellent thermal stability due to its extremely simple structural design. In addition, the polymer backbone can be cathodically doped for enhanced electronic conductivity under the reducing environment for anodes. Abundant carboxyl groups on the side chains can considerably enhance adhesion force and electrolyte absorption. These properties are essential for an outstanding conductive binder. More importantly, these carboxylic sodium groups can react with the hydroxyl groups of SiO<sub>2</sub> on the surface of Si NPs, yielding new chemical bonds between silicon and binder. This can ensure constant electrical connections even as the Si particles disintegrate into pieces (Fig. 1b). Thus, this novel polymer can endure dramatic volume changes of active Si to achieve high capacity and excellent cycle life, which was demonstrated in assembled batteries using the polymeric binder.

## 2. Material and methods

### 2.1. Synthesis of conductive polymers

#### 2.1.1. Synthesis of poly(2,7–9,9-dioctylfluorene) (PFO)

A mixture containing 0.548 g (1 mmol) of 2,7-Dibromo-9,9-di-n-octylfluorene, 0.558 g of (1 mmol) 9,9-dioctylfluorene-2,7-diboric acid bis(1,3-propanediol) ester and several drops of Aliquat 336 in 13 mL of THF and 5 mL of 2 M Na<sub>2</sub>CO<sub>3</sub> solution was added into a Schlenk flask. The flask was degassed by three freeze–pump–thaw cycles, and then 0.057 g of [Pd(PPh<sub>3</sub>)<sub>4</sub>] was added quickly and refluxed with vigorous stirring for 72 h under a nitrogen atmosphere. After the



**Fig. 1.** Schematics of the approaches to address volume change issue in battery materials. (a) Traditional approaches using acetylene black (AB) as the conductive and non-conductive polymer as mechanical binder. (b) Replacing conductive additive and non-conductive binder, conductive binder could keep the electrical and mechanical integrity of the electrode during repeated charge/discharge cycles. (c) Synthetic scheme of the novel conductive polymer sodium poly(3,3'-(9H-fluorene-9,9-diyl)dipropionic acid) abbreviated as PF-COONa.

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