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# Conductive polymer binder-enabled SiO-Sn<sub>x</sub>Co<sub>y</sub>C<sub>z</sub> anode for high-energy lithium-ion batteries

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**Abstract:** A SiOSnCoC composite anode is assembled using a functional conductive polymer binder for the application in next generation high energy density lithium ion batteries. A specific capacity of 700 mAh/g is achieved at a 1C (900 mA/g) rate. High active material loading anode with an areal capacity of 3.5 mAh/cm<sup>2</sup> is demonstrated by mixing SiOSnCoC with graphite. To compensate for the lithium loss in the 1<sup>st</sup> cycle, stabilized lithium metal powder (SLMP<sup>®</sup>) is used for prelithiation, when paired with a commercial cathode, a stable full cell cycling performance with an 86% 1<sup>st</sup> cycle efficiency is realized. By achieving these important metrics toward a practical application, this functional binder/SiOSnCoC anode system presents great promise to enable the next generation high-energy lithium ion battery.

**Keywords:** silicon anode, functional conductive polymer binder, lithium-ion battery, prelithiation

## Introduction

State-of-the-art lithium-ion technology uses graphite as an anode, with a theoretical gravimetric specific capacity of 372 mAh/g, while the alternative alloy anode materials such as tin (Sn, 994 mAh/g) or silicon (Si, 4200 mAh/g) have much higher gravimetric specific capacities.<sup>1</sup> However, almost 300% volume expansion occurs as the material transitions from Si to its fully lithiated phase.<sup>2</sup> Because of this large volume change, the electronic integrity of the composite electrode is disrupted, and high and continuous surface side reactions are induced, leading to a drastic capacity decay.<sup>3</sup> Associated with these problems is that most of the current approaches in Si materials research have only achieved an areal capacity of less than 1 mAh/cm<sup>2</sup><sup>4</sup> unless electrode architecture designs are integrated into the electrode fabrication process.<sup>5,6</sup> Instead of merely emphasizing the high specific capacities of Si-containing anode, recent focus in this field is on the fabrication of a thick and high-loading Si-containing electrode with high energy densities.<sup>7</sup> The drastic volume change of pure Si anode poses formidable challenges to build a high loading electrode. A well-designed nano-structure was employed to achieve an areal capacity of ~3 mAh/cm<sup>2</sup> at a C/20 rate.<sup>6</sup> An optimized binder network was applied to a Si/C material and an areal capacity of ~4 mAh/cm<sup>2</sup> was achieved at a C/10 rate.

The use of Si-containing anode such as Si/C, silicon oxide and silicon-containing alloy have intermediate capacities (800~1500 mAh/g) and volume changes (100~150%), a high-loading electrode is easier to fabricate based on these materials due to the intrinsically smaller volume change.<sup>8</sup> A new anode material was developed based on 50 wt% SiO and 50 wt% Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> composite (molecular composition: SiSn<sub>0.23</sub>Co<sub>0.23</sub>C<sub>0.3</sub>O).<sup>9</sup> This composite combines the advantageous properties of both SiO (high capacity) and SnCoC (stable cycling performance). In

this work, we develop an improved electrode based on this new SiO-SnCoC composite toward practical application in lithium-ion batteries.

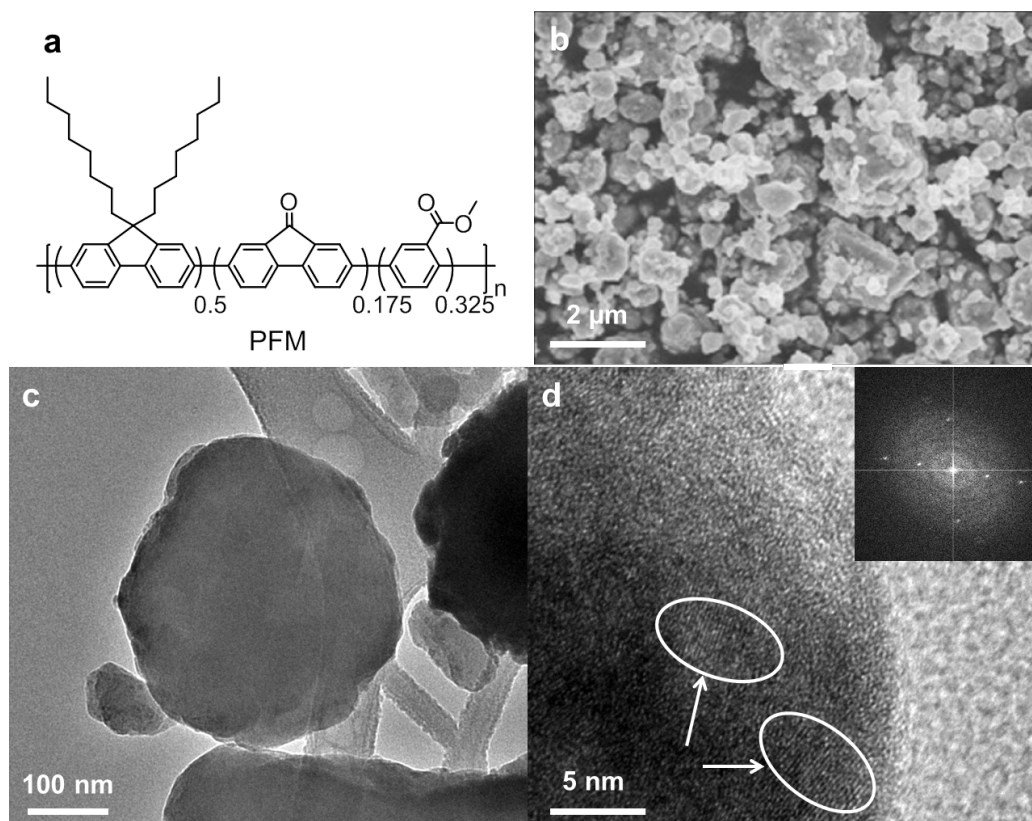
## **Experimental**

**Materials.** All reagents were purchased from Sigma-Aldrich or TCI America and used without further purification. SiOSnCoC anode material is a gracious gift from Argonne National Lab. Celgard 2400 separator is obtained from Celgard. Lithium-ion electrolyte were purchased from BASF, including 1 M LiPF<sub>6</sub> in ethylene carbonate, diethyl carbonate (EC/DEC=3/7 w/w) containing 30 wt% fluoroethylene carbonate (FEC).

**Electrode lamination and cell testing.** The slurry preparation, electrode coating and cell fabrication can be found in the literature.<sup>1</sup> All the electrode laminate in this study is composed of 5% binder, 15% Super P carbon black and 80% active anode materials. The performance of the assembled 2325 coin cells was evaluated with Maccor Series 4000 Battery Test system in a thermal chamber at 30 °C. The cut-off voltage of cell testing is between 1.0 V and 0.01V, assuming a theoretical value of 900 mAh/g for SiO.

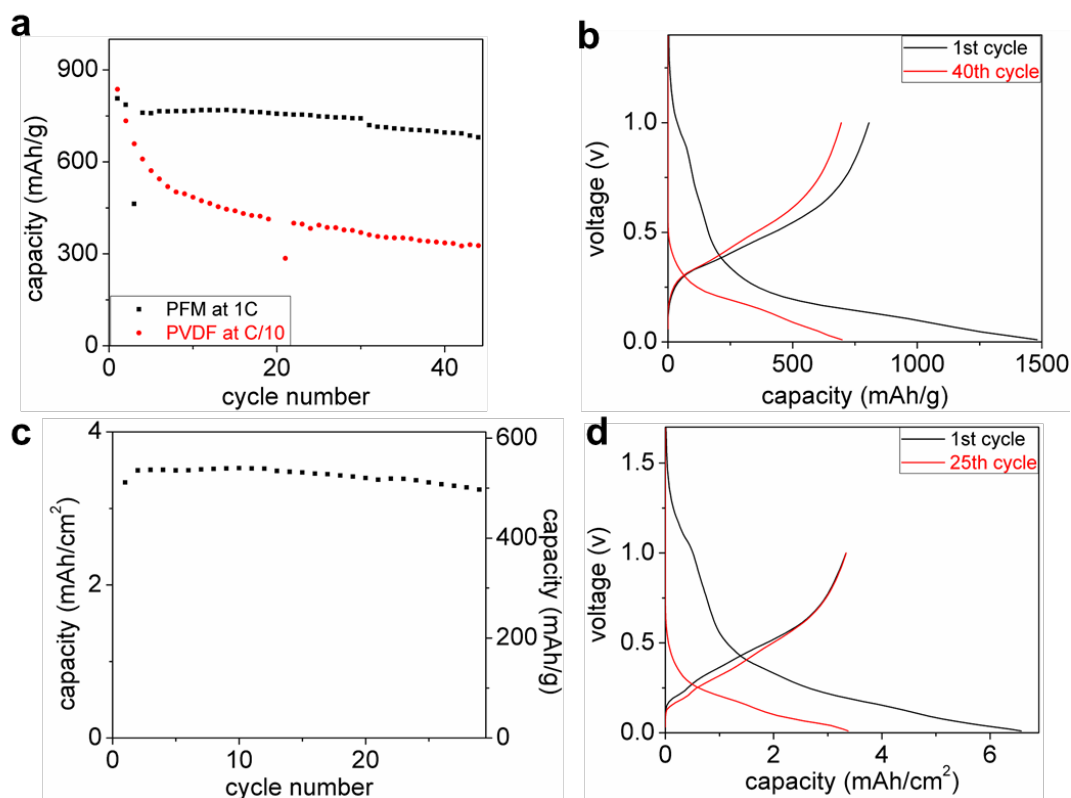
**Characterization.** A JSM-7500F scanning electron microscopy (SEM) was used to characterize the morphology of the electrode surface. Electrodes after cycling were washed with dimethyl carbonate (DMC) solvent to remove residual electrolyte inside the argon filled glove box. A homemade transfer system equipped with a gate valve and a magnetic manipulator are used for the transfer of the highly sensitive samples from the pure argon atmosphere of the glove box to the SEM system.

## **Results and Discussion**



**Figure 1.** (a) The chemical structure of PFM conductive polymer binder. (b) SEM morphology of the SiOSnCo pristine particles. (c) TEM image of the SiOSnCo particle. (d) High-resolution TEM image of the SiOSnCo, indicating the existence of the crystalline Si phases in nanodomain.

A functional conductive polymer binder, Poly (9,9-dioctylfluorene-co-fluorenone-co-methyl benzoic ester) (PFM, Figure 1a), was developed by combining adhesion and electrical conduction to provide molecular-level electronic connections between the active material and the conductive polymer matrix.<sup>10,11</sup> Figure 1b shows the SEM image of the pristine SiOSnCoC particles, indicating a bimodal distribution of the particle size, a typical morphology of particle material synthesized by high-energy ball-milling method. The smaller particles have a diameter of typically several hundred nanometers, and bigger particles have diameter of several micrometers. The TEM images in Figure 1c and 1d further discloses some details on the anode structure. Crystalline Si phases exist as nanodomains, which contribute to most of the specific capacities when used in lithium ion batteries.



**Figure 2.** (a) Cycling performance of SiOSnCoC half cells using either PFM (at 1C, 900 mA/g) and PVDF binder (at C/10, 90 mA/g). (b) The 1<sup>st</sup> cycle and 40<sup>th</sup> cycle voltage curves of the SiOSnCoC/PFM half cell. (c) Areal capacity and specific capacity vs. cycle no. for the SiOSnCoC/graphite/PFM high loading electrode at C/10. (d) The 1<sup>st</sup> cycle and 25<sup>th</sup> cycle voltage curves of the SiOSnCoC/graphite/PFM high loading half cell.

When cycling the half cell at a 1C rate, the PFM-based half cell exhibits a stable cycling with a specific capacity of above 700 mAh/g for over 50 cycles (Figure 2a). PVDF binder, on the other hand, shows a drastic capacity decay even at a slow rate of C/10. The 1<sup>st</sup> cycle and 40<sup>th</sup> cycle voltage curves of the PFM/SiOSnCoC cell are shown in Figure 2b. Different from a lot of other Si-based anode with crystalline Si phases, the good conductivity of this SiOSnCoC realizes 1<sup>st</sup> cycle lithiation without much overpotential. Also comparing the delithiation voltage curves at 1<sup>st</sup> and 40<sup>th</sup> cycles, the minimum capacity decay is further confirmed.

To increase the Si material loading to a benchmark areal capacity of above 3 mAh/cm<sup>2</sup>, a graphite/SiOSnCoC composite electrode is assembled and tested. This composite electrode employs 5% PFM binder, 15% carbon black, 20% graphite and 60% SiOSnCoC. As shown in

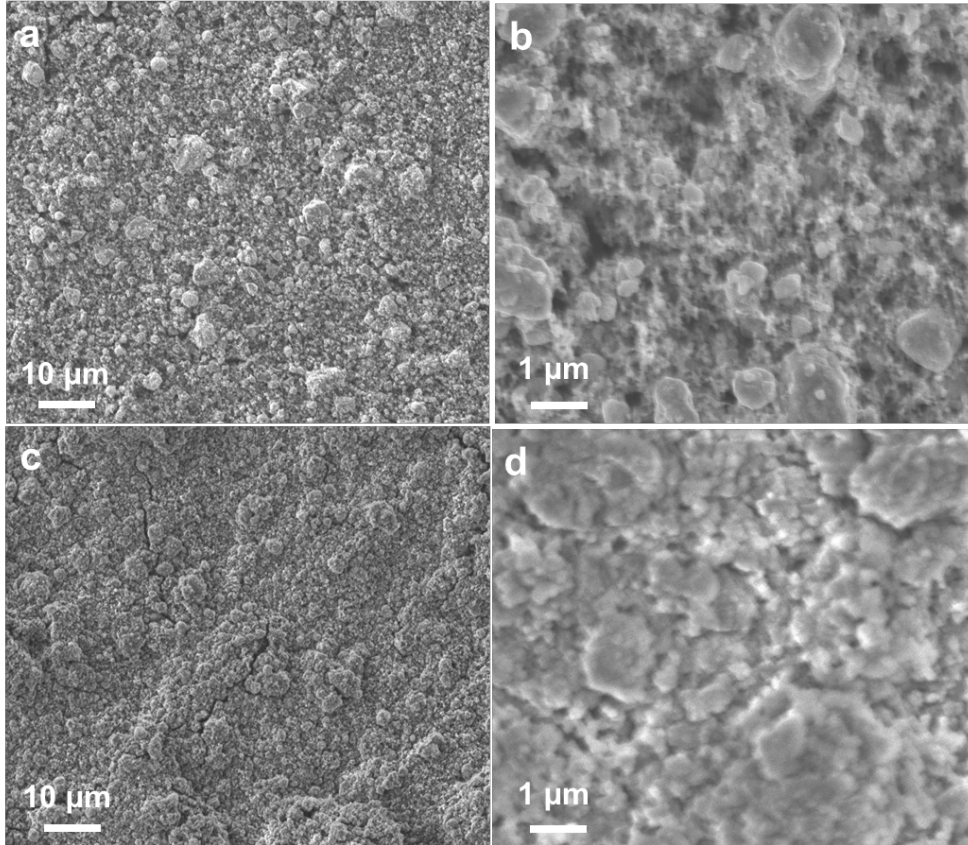
Figure 2c, an areal capacity of 3.5 mAh/cm<sup>2</sup> is achieved using this composite electrode at a C/10 rate. The 1<sup>st</sup> cycle and 25<sup>th</sup> cycle voltage curves shown in Figure 1d indicates minimum capacity loss during cycling of this high loading cell. Addition of Si-based material into the commercial cell anodes with a small portion represents a most promising route toward the commercial application of high capacity Si anode, the currents functional conductive polymer binder-based laminates exhibits a great potential toward the practical application.

		PVDF/SiOSnCoC	PFM/SiOSnCoC	PFM/SiOSnCoC/graphite
1 <sup>st</sup> cycle	$Q_c^a$ (mAh/g)	836.4	806.6	511.13
	$\eta^b$ (%)	59.77%	54.45%	50.77%
40 <sup>th</sup> cycle	$Q_c^a$ (mAh/g)	335.7	695.3	463.8
	$\eta^b$ (%)	99.35	99.49	99.27

<sup>a</sup> charge (delithiation) capacity    <sup>b</sup> Coulombic efficiency

**Table 1.** Electrochemical data of the half cells based on SiOSnCoC anode.

The electrochemical data of the cells based on PVDF and PFM, and the PFM/SiOCoC/graphite composite are shown in Table 1. With 20% graphite and 60% SiOSnCoC in the composite electrode, the specific capacity reaches 500 mAh/g, which is a much higher value compared to the state-of-the-art graphite anode (372 mAh/g). While the areal capacity of this high-loading cell reaches 3.5 mAh/cm<sup>2</sup>, this system proves to be a competitive alternative high energy anode.



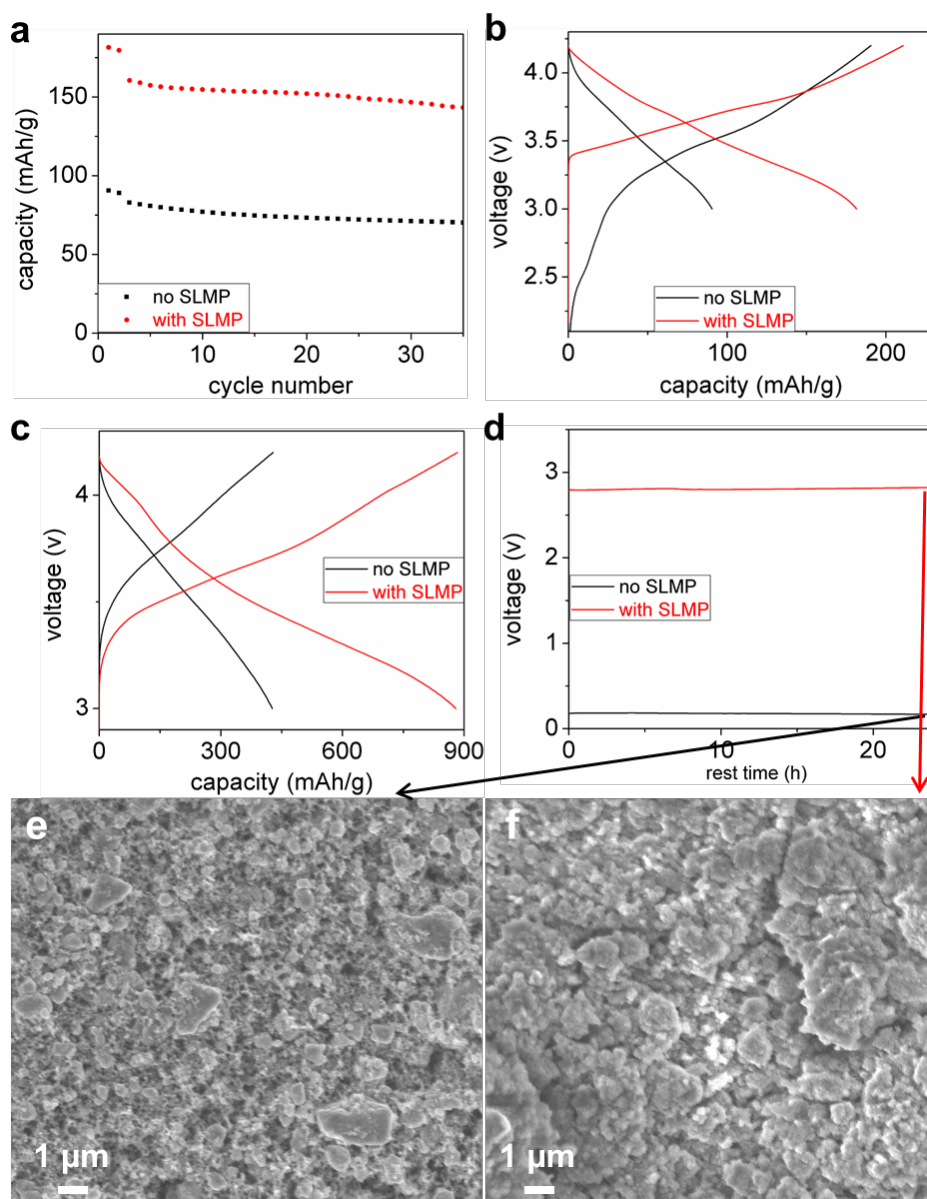
**Figure 3.** (a) (b) SEM images of the pristine SiOSnCoC/PFM electrode. (c) (d) SEM images of the SiOSnCoC/PFM electrode cycled at C/10 for 10 cycles.

The morphology of the pristine (Figure 3a and 3b) and cycled (Figure 3c and 3d) SiOSnCoC/PFM are shown in Figure 3. A very nice porosity is exhibited in the pristine electrode, which is critical for accommodating the volume expansion on the particle level, as well as to soak electrolyte for a good lithium ion transport. FEC-containing electrolyte is used for the cell testing, the cycled electrode shows a typical solid electrolyte interphase (SEI) formation in the FEC-containing electrolyte. No excessive SEI is visualized in the SEM images, this contributes to a good coulombic efficiency shown in Table 1.

To prove the application of this functional conductive polymer binder-based SiSnCoC high capacity anode in a full cell configuration, a commercial  $N_{1/3}M_{1/3}C_{1/3}$  is used to assemble the full cell. However, the efficiencies at 1<sup>st</sup> cycles shown in Table 1 is only around 50%, which irreversibly consumes the lithium in the cathode in the first cycle, this could be a detrimental



problem for practical application. A prelithiation method is needed for the full cell application.



**Figure 4.** (a) Full cell cycling performance of SiOSnCoC/PFM anode with NMC cathode with or without SLMP prelithiation. (b) The 1<sup>st</sup> cycle and (c) 30<sup>th</sup> cycle voltage curves of the SiOSnCoC/PFM full cell with or without SLMP prelithiation. (d) The open circuit voltage curves of the two full cells with and without SLMP. (e) SEM image of the SiOSnCoC/PFM anode in the full cell without SLMP after 24 hour equilibration, exhibiting similar morphology as the pristine electrode. (f) SEM image of the SiOSnCoC/PFM anode in the full cell with SLMP after 24 hour equilibration, indicating a complete SEI formation.

To compensate for the irreversible capacity loss in the first cycle, stabilized lithium metal powder (SLMP<sup>®</sup>) is used to prelithiate the SiOSnCoC anode in the full cell. SLMP is a micro-size lithium metal powder with ~2 wt% lithium carbonate surface coating.<sup>12,13</sup> SLMP was directly

loaded on the anode surface, which proved to be a simple and effective way of applying SLMP.<sup>14</sup> The amount of loaded SLMP was calculated to theoretically eliminate all the irreversible capacity in the first cycle. A calendar machine was used to pressure-activate the SLMP particles. This operation breaks the lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) shell and allows lithium to be in direct electrical contact with the SiOSnCoC materials in the anode.<sup>15</sup> A 24-hour rest period was used to allow the crushed SLMP to fully prelithiate the anode before current-driven charging of the cells. As a good control, the full cell without SLMP was also rested for 24 hours before cycling. Both full cells were put in a formation process consisting of two cycles at C/10 prior to C/3 cycling. Apparent improvement was shown for the SLMP-loaded full cells (Figure 4a). The first cycle CE increased from 48% to ~86% with the SLMP. SLMP enabled the NMC/SiOSnCoC full cell to maintain a reversible capacity of ~150 mAh/g after more than 35 cycles at C/3. The full cell without SLMP prelithiation started only with a capacity of ~90 mAh/g and dropped to ~65 mAh/g after 35 cycles.

The first cycle voltage curves of the full cells are shown in Figure 4b. Compared to the regular cell without SLMP, the voltage profile at both ends (start of charge and end of discharge) are distinctly different, indicating different lithiation and delithiation of SiOSnCoC during these two stages. In the first cycle charge process, SLMP eliminated the needs for SEI formation, so the curve goes directly to the anode lithiation voltage region. When SLMP is not used, this charging curve shows a long multi-plateau curvature accounting for a capacity of ~40 mAh/g, which is typical for SEI formation. The SEM image of the SiOSnCoC electrode rested for 24 hours in a full cell without SLMP is shown in Figure 4e and 4f. Compared to the pristine electrode (Figure 3a,b), no apparent morphology change occurred during this equilibration period. When the full cell is loaded with SLMP on the SiOSnCoC electrode, the SEM image in Figure 4f shows a clear SEI

formation due to the electrolyte decomposition after 24-hour rest period.

		Full cell without SLMP	Full cell with SLMP
1 <sup>st</sup> cycle	$Q_d^a$ (mAh/g)	90.6	181.5
	$\eta^b$ (%)	47.52%	86.05%
35 <sup>th</sup> cycle	$Q_d^a$ (mAh/g)	70.5	144.0
	$\eta^b$ (%)	99.57	99.49

<sup>a</sup> discharge (delithiation) capacity <sup>b</sup> Coulombic efficiency

**Table 2.** Electrochemical data of the full cells with or without SLMP prelithiation.

The electrochemical data of the full cells are shown in Table 2. The SLMP prelithiation successfully increases the 1<sup>st</sup> cycle efficiency from 47.52% to 86.05%, which is a comparable value to the state-of-the-art NMC/graphite full cells. Both cells show an efficiency around 99.5% at the 35<sup>th</sup> cycle, this indicates that SLMP prelithiation only affect the cell behavior at the 1<sup>st</sup> cycle, without much effect in the following cycles.

## Conclusions

By the combination of a new composite anode material SiOSnCoC with a special-design functional conductive polymeric binder, several key parameters for a commercial Si-based lithium ion battery are achieved, including high specific capacity (700 mAh/g at a 1C rate), high material loading (areal capacity of 3.5 mAh/cm<sup>2</sup>), fast charge/discharge without significant cell decay, stable cycling when paired with a commercial cathode, and a high 1<sup>st</sup> cycle coulombic efficiency (86%) in the full cell. This functional conductive polymer binder/SiOSnCoC anode system presents great promise to enable the next generation high-energy lithium ion battery.

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### **Notes**

The authors declare no competing financial interests.

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