Conversion Reaction of Nanoporous ZnO for Stable Electrochemical Cycling of Binderless Si Microparticle Composite Anode

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ABSTRACT: Binderless, additiveless Si electrode design is developed where a nanoporous ZnO matrix is coated on a Si microparticle electrode to accommodate extreme Si volume expansion and facilitate stable electrochemical cycling. The conversion reaction of nanoporous ZnO forms an ionically and electrically conductive matrix of metallic Zn embedded in Li2O that surrounds the Si microparticles. Upon lithiation, the porous Li2O/Zn matrix expands with Si, preventing extensive pulverization, while Zn serves as active material to form Li2Zn to further enhance capacity. Electrodes with a Si mass loading of 1.5 mg/cm2 were fabricated, and a high initial capacity of ∼3900 mAh/g was achieved with an excellent reversible capacity of ∼1500 mAh/g (areal capacity ∼1.7 mAh/cm2) beyond 200 cycles. A high first-cycle Coulombic efficiency was obtained owing to the conversion reaction of nanoporous ZnO, which is a notable feature in comparison to conventional Si anodes. Ex situ analyses confirmed that the nanoporous ZnO coating maintained the coalescence of SiMPs throughout extended cycling. Therefore, the Li2O/Zn matrix derived from conversion-reacted nanoporous ZnO acted as an effective buffer to lithiation-induced stresses from volume expansion and served as a binder-like matrix that contributed to the overall electrode capacity and stability.

KEYWORDS: silicon microparticles, binderless electrode, lithium-ion battery, combustion reaction, composite electrode

Demand for next-generation energy storage devices for wearable electronics and electric vehicles has dramatically increased, culminating in the need for energy storage devices with higher energy density. However, conventional electrode materials such as graphite (375 mAh/g) demonstrate limited specific capacity and insufficient energy and power densities. In this context, Si is a promising candidate due to its unparalleled theoretical capacity (3578 mAh/g) and relatively low discharge potential (∼0.5 V versus Li+/Li0) while being one of the most abundant and inert materials on earth.1,2 Significant challenges still exist that limit the commercialization of Si, most serious of which is the extreme volume expansion (∼400%) during lithiation, which results in large lithiation-induced stresses that cause pulverization/delamination.2,3,5 Performance degradation due to pulverization over extended cycles is caused by the exposure of fresh Si surfaces that form thicker, unstable solid–electrolyte interphases (SEI) responsible for low initial Coulombic efficiency (CE, <80%).6 These issues arising from Si volume expansion lead to short electrode cyclic lifetime and rapid performance degradation, which prevent commercial application.7,8,9

Different approaches have been attempted in order to utilize Si as a high-capacity anode, including nanostructuring and using polymer binders to hold the fractured Si together. Nanostructuring improves the structural durability by enabling relaxation of lithiation-induced stresses and providing free space for easy volume expansion.9,10 However, large-scale production of Si nanostructures is difficult and costly, which limits commercialization. Alternatively, the use of com-
cially available Si microparticles (SiMPs) would have benefits in terms of processing costs, but challenges lie in the fact that SiMPs a few micrometers in size demonstrate extremely poor cyclic stability with a capacity loss of ∼80% over the first few cycles. Another approach using polymer binders has been developed and applied to Si nanostructures and Si microstructures to great effect. Most notably, Choi et al. reported a highly effective, elastic polyrotaxane-based binder to prevent delamination of pulverized SiMP to enhance capacity retention. Both approaches are effective but use complex and costly processes to nanostructure Si or synthesize functional polymers. Polymer binders, in particular, have the additional drawback of contributing to the electrochemical dead weight that can contribute up to 50 wt % of the electrode mass.

Another promising approach to enhance the performance of Si electrodes is through the application of surface coatings. Various carbon-based materials and metal oxides have been used to improve the mechanical integrity and electrochemical performance of active materials by enhancing the conductivity of electrodes, providing a rigid cage around the active material, and preventing direct electrolyte exposure. Carbon-coated Si electrodes have been the subject of in-depth investigation. However, although carbon coatings enhance conductivity and suppress uncontrolled SEI growth, carbon coatings demonstrate insufficient clamping effect to keep the SiMPs coalesced. By contrast, surface coating of metal oxides is a viable alternative but has been limited to atomic layer deposition (ALD) of inert oxides onto Si nanoparticles. For Si microparticles, however, the application of nonconductive surface coatings that themselves do not expand may not be an ideal choice as a coating material to suppress extreme volume expansion. It is also unfavorable that these coatings still result in low initial CE, which prevents practical application of Si electrodes.

As possible alternatives to inert metal oxide coatings, we consider metal oxide electrode materials. Metal oxide electrodes have been discussed as reasonable alternatives to conventional graphite anodes owing to their high theoretical capacities and smaller volume expansion compared to Si. Among potential metal oxide candidates, ZnO is considered as an attractive Li-ion battery anode due to its low cost, facile preparation, and chemical inertness in addition to its high theoretical capacity (978 mAh/g) if both alloying and conversion mechanisms occur during cycling. Unfortunately, the superior capacities of metal oxide electrodes, including ZnO, compared to the conventional graphite electrode are only possible when cycled in the voltage window of 0−3.0 V (versus Li0/Li+), which is unfavorable as an anode where a voltage window of 0−1.0 V (versus Li0/Li+) is favored. Therefore, metal oxide electrodes demonstrate insufficient capacities on their own in the anode voltage window. There has yet been a report on the application of metal oxide electrode materials, such as ZnO, on Si microstructures to the extent of the authors’ knowledge and has been limited to Si nanostructures. In this work, a polymer binderless and additiveless nanoporous ZnO-SiMP (np-ZnO/SiMP) electrode design is introduced. The np-ZnO/SiMP electrode takes advantage of the ZnO conversion reaction, which yields an ionically conductive Li2O matrix embedded with electrically conductive Zn nanograins that reversibly alloy with Li to form Li_xZn during cycling. The electrode is fabricated via a facile and scalable combustion reaction to spin-coat np-ZnO onto the SiMP electrode. The combustion reaction yields a highly porous np-ZnO that also provides free space, which helps accommodate SiMP volume expansion in addition to improving the CE of the composite electrode. A proof-of-concept methodology of air-spray fabrication suitable for large-scale fabrication is also demonstrated. The np-ZnO, therefore, serves as a binder-like matrix that facilitates the stabilization of
the Si SEI layer and functions as a compliant and mechanically robust matrix that accommodates Si volume expansion while also contributing to the electrochemical capacity. The developed electrode design takes advantage of characteristics of the ZnO conversion reaction to realize superior performance and stability without polymer binders and Si nanostructures.

**RESULTS AND DISCUSSION**

As a new binderless design with enhanced cyclic stability, the np-ZnO/SiMP anode is investigated. The role of the np-ZnO is to (1) provide a clamping effect, (2) participate in lithiation, (3) provide free space for volume expansion, and (4) form an ionically and electrically conductive matrix to facilitate stable cycling. A schematic of the fabricated np-ZnO SiMP electrode illustrates the electrode design concept where the np-ZnO and SiMPs are shown in light blue and gray, respectively (Figure 1a). Unlike conventional electrode designs, the proposed np-ZnO/SiMP electrode is binderless, which is favorable when considering the electrode energy density. The lithiation mechanism of the np-ZnO/SiMP electrode follows a two-step mechanism (Figure 1b). During the first lithiation cycle, np-ZnO undergoes a conversion reaction 1), which yields an ionically conductive np-Li2O matrix embedded with electrically conductive nanocrystalline metallic Zn. In the voltage window of 0.01−1.0 V (versus Li^0/Li^+), a conversion reaction occurs irreversibly consequentially followed by the reversible alloying reaction 2) of metallic Zn, which is similar to the Si alloying lithiation reaction.

\[
\text{ZnO} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{O} + \text{Zn} \quad (1)
\]

\[
\text{Zn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Zn} (x < 3),
\]

\[
\text{Si} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Si} \quad (2)
\]

The first conversion reaction that results in the decomposition of ZnO into Zn and Li2O occurs reversibly as the reverse reaction of ZnO formation from Zn and Li2O occurs at 1.34 V (versus Li^0/Li^+) 43,50 Therefore, the two-step reaction of np-ZnO with Li irreversibly yields a Li2O matrix embedded with metallic Zn nanograins that surround the SiMPs, where only the Zn nanograins and SiMPs participate in the subsequent electrochemical cycles between 0.01−1.0 V (versus Li^0/Li^+). The np-Li2O matrix facilitates Li-ion transport and diffusion into the SiMP electrode, and the Zn nanograins enhance the electric conductivity of the matrix for faster electron transport (Figure 1b).

Conformal coating of np-ZnO was achieved by adopting a solution-based, low-temperature combustion reaction process as reported by Park et al. 32 Conventionally, conformal deposition of thin films is carried out by sol−gel processes or by ALD. The sol−gel method is attractive due to its solution processability but is limited by the high process temperature, while ALD has limitations in terms of scalability. To achieve a low-cost, scalable, and conformal coating, a combustion reaction based process was elected due to its large scalability and low process temperature. Deposition of np-ZnO was carried out via combustion reaction at a low process temperature of ∼180 °C, which yielded a thin film with a sheet resistance of ∼20Ω/sq. A key benefit of the combustion reaction is the formation of a nanoporous ZnO thin film, which has sufficient porosity or free space to help alleviate lithiation-induced stresses from volume expansion and contraction. Another benefit of the np-ZnO matrix is the enhanced CE. Metal oxide electrodes in bulk or microscale demonstrate low CEs, which have been problematic for commercial applications. However, numerous reports demonstrated that ZnO can have high CEs when using nanostructured ZnO as the active material.37−44 Unfortunately, fabricating nanostructured ZnO in a facile, one-step process is difficult and conventionally requires the use of complex procedures that make large-scale application difficult. The combustion reaction process enables easy fabrication of np-ZnO, which serves as a monolithic nanostructure that conformally surrounds the SiMPs and improves the mechanical and electrochemical stability of the composite electrode.

The fabrication process of the np-ZnO/SiMP electrode is shown schematically (Figure 1c), where the Cu foil is first annealed to facilitate grain growth to reduce the yield strength, as shown in electron-backscatter diffraction (EBSD) (inset, Figure 1c). The softening behavior, as reported by Kim et al. 52 and observed via tensile testing (Figure S1, SI), is taken advantage of to embed SiMPs into the Cu foil by simple...
calendering. Then, the SiMP dispersion is drop-cast on the softened Cu foil and calendered. Finally, the np-ZnO combustion reaction solution is spin coated onto the SiMP electrode and reacted at \( \sim 180 \degree C \), and this is repeated until the desired thin film thickness is obtained. In the context of Li-ion battery manufacturing, temperatures around 200 \( \degree C \) are repeatedly used especially when drying electrodes of organic solvents, which makes combustion reaction a viable deposition method. Film thickness with respect to spin-coating number was optimized and is shown in Figure S2 in the SI.

Top view scanning electron microscopy (SEM) image and cross section transmission electron microscopy (TEM) images of the np-ZnO/SiMP (Figure 2a−c) confirm uniform deposition of \( \sim 100 \) nm thick np-ZnO on top of and in between the SiMPs. Infiltration between the SiMPs is critical to completely surround the SiMPs with Li$_2$O/Zn matrix during electrochemical cycling. Cross section TEM energy dispersive spectrometer (TEM-EDAX) mapping (Figure 2c) and high-resolution TEM images (Figure 2d,e) clearly highlight the high porosity of the np-ZnO structure, which also provides the free space for volume expansion. The X-ray photoelectron spectroscopy (XPS) survey spectra of the np-ZnO/SiMP electrode before and after np-ZnO coating (Figure 2f) show a distinct peak of Zn 2p and the decreased intensity of Si 2s and 2p peaks before and after np-ZnO deposition, suggesting that the SiMPs are well covered by the np-ZnO matrix.

The np-ZnO extends throughout the whole thickness of the SiMP electrode, and a composite structure demonstrates several advantages compared to conventional polymer binder based Si anodes. First, the high porosity of np-ZnO enables the electrolyte to penetrate and facilitate Li-ion transport throughout the entire thickness of the electrode, while conventional polymer binders rely on electrolyte swelling for Li-ion transport. Second, the lithiation of SiMPs occurs only by Li-ion diffusion across the Li$_2$O/Zn matrix, which prevents direct contact of SiMPs with the electrolyte. This is critical to suppress unstable SEI buildup on the SiMPs that is detrimental to Si electrode performance. Third, the alloying reaction of Zn

Figure 3. (a) Capacity retention and Coulombic efficiency of an np-ZnO SiMP electrode at C/5 rate with a potential window of 0.01−1 V (versus Li$/\text{Li}^+$). The first 10 cycles were performed at C/20 rate for activation and a further 200 cycles at C/5 rate. (b) Voltage profiles plotted for the 1st, 10th, 60th, 160th, and 210th cycles, where the latter three profiles represent the 50th, 150th, and 200th cycles at C/5 rate. (c) Areal capacity of the first discharge and after cycling discharge areal capacity of a SiMP-only electrode and electrodes coated with respective np-ZnO conditions. (d) Impedance spectroscopy measurements for an np-ZnO SiMP electrode before and after 210 cycles. The real and imaginary parts of the complex impedance \( Z \) are denoted by Re\((Z)\) and Im\((Z)\). (e) Rate capacity of an np-ZnO SiMP electrode at various C rates.
is accompanied by volume expansion of up to 100%, which allows the Li₂O/Zn coating to serve as a mechanically robust matrix that expands without contorting or fracturing the overall electrode structure and keeps pulverized SiMPs coalesced and in contact with the Cu foil. Fourth, the Li₂O/Zn serves as an ionically and electrically conductive matrix that also contributes to the overall electrochemical capacity. Last, as mentioned before, the high-porosity np-ZnO provides free space for volume expansion. Therefore, the application of a Li₂O/Zn matrix that results from np-ZnO conversion reaction provides functions that exceed conventional schemes for Si anodes.

Electrochemical performance was systematically investigated by varying the thickness of the np-ZnO coating to confirm the advantages of the np-ZnO/SiMP electrode. A 100 nm thick ZnO coating was elected due to its uniform infiltration on and in between SiMPs for characterization. Galvanostatic cycling with cutoff voltages between 0.01 and 1.0 V (versus Li⁰/Li⁺) was conducted. The first discharge capacity was 3900 mAh/g at a C/20 rate (Figure 3a), and discharge capacity was still maintained at 1500 mAh/g or 1.7 mA cm⁻² beyond 200 cycles at a C/5 rate. The higher than theoretical capacity can be attributed to the complex reaction mechanism of the ZnO metal oxide electrode, which also involves the reversible reaction of LiOH into Li₂O and LiH and provides additional capacity of up to ~400 mAh/g between 0 and 0.25 V (versus Li⁰/Li⁺), as reported by Hu et al. and Jang et al., where the CEs of conversion reaction metal oxides were investigated and reported that a complex reaction mechanism causes the high Coulombic efficiency. After the first cycle, CE remained above 100% throughout extended cycling, suggesting active participation of ZnO in the electrochemical reaction, which highlights the multifunctioning capability of the developed binderless electrode design. Most importantly, such high first-cycle CE values in a primarily Si electrode have yet been reported, with most investigations reporting a first-cycle CE of ~80% due to efficiency loss from the initial formation of SEI film. The conversion reaction from np-ZnO to Li₂O/Zn matrix prevents uncontrolled SEI formation of the SiMPs during initial electrochemical cycling, and the alloying reaction of Zn contributes to the high CE. This result hints at a potential solution in improving the problematic first cycle CE of Si electrodes.

Figure 4. SEM images and electrochemical cycling characterization of the np-ZnO thin film (a, c, e) and binderless SiMP electrode (b, d, f) indicating extensive pulverization and delamination of the respective single active material electrodes with extended cycling at a C/5 rate.
SiMP electrode and np-ZnO/SiMP electrodes with varying ZnO thickness were characterized to optimize the np-ZnO thickness for improved areal capacity. The first and last discharge capacities of the electrodes with varying ZnO thicknesses (Figure 3c) show that areal capacities as high as 3.2 mAh/cm² with an np-ZnO thickness of 200 nm can be obtained but with a trade-off in cyclic lifetime due to irregular coverage of np-ZnO (Figures S5, SI). Galvanostatic cycling results of the electrodes with different np-ZnO highlight the distinctly poorer cyclic lifetime of other electrodes, thereby confirming that the 100 nm thickness, with the most uniform SiMP coverage, is ideal for stable electrochemical cycling (Figure S6, SI). Impedance spectroscopy reveals a metallic, linear response of the pristine electrode arising from the binderless np-ZnO SiMP electrode, which is expected with a combination of the np-ZnO matrix demonstrating ∼20Ω/sq and metallic SiMP (Figure 3d). After cycling, however, the buildup of the SEI layer from the np-ZnO conversion reaction and formation of an SEI yields the characteristic semicircle portion at high frequencies.

Typically, a higher rate of charging results in buildup of higher lithiation-induced stresses to cause structural degradation of SiMPs, but rate capacity tests demonstrate that the performance of the np-ZnO/SiMP electrode design remains intact even at a faster (Figure 3e) charge/discharge rate of C/2. This is in accordance with the diffusion coefficient of the respective SiMP, np-ZnO, and np-ZnO SiMP electrodes (Figure S7, SI). The slope of the linear relationship between the CV curve peak current and scan rate¹/² can be used to estimate the diffusion coefficient of Li in the respective active materials. The results indicate that although the Li-ion diffusion coefficient of the np-ZnO/SiMP was smaller than bare SiMP electrode, it was still significantly larger than the np-ZnO-only electrode. Even compared to the conventional SiMP-PVDF electrode, the np-ZnO/SiMP was found to have a higher diffusion coefficient of Li. Therefore, the np-ZnO/SiMP electrode is able to facilitate charging at comparatively faster rates. Conversely, rate capability results could not be obtained for the SiMP-only electrode without np-ZnO due to extensive delamination of the SiMPs in the first initial cycles at C/20.

To fully understand the contribution of ZnO on the capacity of the final electrode, an electrode of 100 nm thick np-ZnO thin film and an electrode of only SiMPs were separately prepared and electrochemically characterized. Results confirm that, individually, the two materials show poor cyclic stability, in stark contrast with the synergy demonstrated by the np-ZnO/SiMP electrode. Pristine and after electrochemical cycling electrode SEM images first reveal that, on its own, the electrode consisting of only 100 nm np-ZnO thin film undergoes extensive delamination and pulverization (Figure 4a,b). With respect to electrochemical performance, np-ZnO on its own showed a ∼300 mAh/g capacity in the 0.01 and 1.0

Figure 5. Pristine np-ZnO SiMP electrode cross section SEM image of (a) SE and (b) BSE modes. Cross section images after (c) 2nd delithiation, (d) 60th delithiation, and (e) 210th delithiation. The electrode undergoes volume expansion during the first few cycles, and electrode thickness saturates to ∼8 μm. SiMPs remain coalesced throughout extended electrochemical cycling. Surface SEM images of (f) pristine np-ZnO SiMP and (g) np-ZnO SiMP after 210 cycles.
V (versus Li⁰/Li⁺) range (Figure 4e), thereby demonstrating that the np-ZnO coating actively participates in the voltage range and quantifying the additional capacity accrued by the np-ZnO to be ∼300 mAh/g, which explains the high specific capacity of the np-ZnO/SiMP electrode beyond the theoretical room-temperature capacity of Si.43–50 The first cycle CE is 109%, confirming that the high CE of the np-ZnO/SiMP is attributed to the ZnO conversion reaction. For comparison, the SiMP-only electrode was fabricated using the same drop-cast and calendering method and electrochemically characterized. The SiMP-only binderless electrode showed rapid capacity decay, losing 80% of its capacity within the first 10 cycles (Figure 4f). Note the drastically poorer CE values especially during the first few electrochemical cycles, indicating extensive SEI formation in the SiMPs. Detailed characterization results of the two electrodes support the introduced results (Figures S8 and S9, SI). In stark contrast, the excellent electrochemical cyclic stability of the np-ZnO/SiMP electrode indicates that the Li₂O/Zn matrix derived from np-ZnO conversion reaction was able to keep the SiMPs in contact with the current collector and kept the pulverized SiMPs coalesced even without the use of complicated polymeric binders or nanostructuring schemes.

The role of np-ZnO on the electrochemical performance was investigated ex situ using focused ion beam (FIB) and SEM imaging to analyze the electrode morphology before and after electrochemical cycling. The pristine electrode showed a thickness of about 3.5 μm throughout the electrode (Figures 5a,b). After the second delithiation, the entire electrode expanded by ∼220% to 7.8 μm with the np-ZnO matrix expanding with the SiMPs in the z-axis direction to help alleviate lithiation-induced stresses to maintain even pulverized SiMPs coalesced. Without the expansion of the np-ZnO matrix, the volume expansion of SiMPs will lead to the

Figure 6. (a) TEM-EDAX mapping of the np-ZnO SIIMP electrode after cycling showing carbon, fluorine, oxygen, silicon, and zinc elements, confirming that np-ZnO acts as a protective matrix to SiMPs. XPS (b) survey and (c) F 1s peak of the np-ZnO SIIMP electrode after cycling and (d) C 1s peaks of the np-ZnO SIIMP electrode and SIIMP-only electrode after cycling.
delamination of SiMPs from the electrode, causing a rapid capacity decay. Further electrode expansion becomes minimal after the initial expansion and stabilizes to about 8.2 and 8.5 μm after the 60th and 210th delithiation, respectively, which is ∼240% of the pristine electrode thickness (Figure 5d,e). Even after 200 cycles, SiMPs remain well embedded within the Li2O/Zn matrix and in contact with the current collector with the electrolyte forming SEI preferentially with the Li2O/Zn matrix. Note that the np-ZnO provides a sacrificial np-ZnO matrix to preferentially lithiate. In addition, the surface area of the SiMPs exposed to electrolyte is much smaller due to np-ZnO coverage; therefore, more controlled SEI formation on the SiMP surface is possible. This confirms the impedance spectroscopy results that indicate an increase in impedance after extended cycling resulting from SEI formation on the Li2O/Zn matrix. Most importantly, however, other elements were not detected within the Si domains, which confirms that the Li2O/Zn/SEI matrix successfully prevented extensive and unstable SEI formation on the SiMPs by serving as a physical barrier to direct electrolyte exposure. In addition, Si domains of several hundred nm are still observed embedded in the matrix, demonstrating that the matrix prevented delamination and electric contact loss of these pulverized SiMPs.

To confirm the SEI formation mechanism and unveil the changes of the np-ZnO/SiMP electrode after cycling, composition analyses through TEM-EDS mapping and XPS analysis were conducted. TEM-EDS mapping results show that carbon, oxygen, zinc, and especially fluorine are detected uniformly throughout the electrode (Figure 6a). The uniform dispersion indicates that the Li2O/Zn matrix had gradually reacted with the electrolyte to form a Li2O/Zn/SEI matrix. Most importantly, however, other elements were not detected within the Si domains, which confirms that the Li2O/Zn/SEI matrix successfully prevented extensive and unstable SEI formation on the SiMPs by serving as a physical barrier to direct electrolyte exposure. In addition, Si domains of several hundred nm are still observed embedded in the matrix, demonstrating that the matrix prevented delamination and electric contact loss of these pulverized SiMPs. XPS was conducted to further shed light on the composition of the SiMPs coalesced (Figure 5f,g and Figure S11, SI). All SEM images were obtained in fully delithiated states and in backscattered electron (BSE) mode, as BSE mode images particles up to 400 to ∼500 nm in depth compared to secondary electron mode with a limited analysis depth of ∼50 nm. BSE mode imaging visualizes objects with high atomic numbers with enhanced brightness, thereby clearly imaging SiMPs even when surrounded by an SEI layer.

Figure 7. (a) Schematic of the air-spray process adopted for large-scale production. (b) Photo of a 25 cm × 30 cm large-scale np-ZnO/SiMP composite electrode and (c) SEM image and SEM-EDAX mapping image of the composite electrode with Si and Zn shown in red and green, respectively. Thickness vs air-spray time (s) of (d) np-ZnO and (e) SiMP dispersions in ethanol in an air-spray setup as-sprayed and roll pressed. (f) Comparison of capacity retention between spin-coated and air-sprayed np-ZnO/SiMP composite electrode conducted at a C/5 rate.
matrix, which revealed the SEI components found in electrodes while confirming the TEM-EDS result (Figure 6b). An XPS spectrum survey of the SEI layer showed a strong presence of F 1s and O 1s peaks, while the F 1s and C 1s deconvolution showed the highest intensity in the LiPF 6 and Li 2 CO 3 species, which is widely known as the most stable SEI layer component. 56, 57 To highlight the benefits of np-ZnO, the C 1s peak was analyzed and compared between the SiMP electrode with and without the np-ZnO matrix (Figure 6d). A clear difference can be seen where the SiMP-only electrode showed predominantly C–F, C–O, and C–C bonds while the np-ZnO/SiMP electrode showed the presence of Li 2 CO 3 species, which are known to be a stable organic SEI component. ZnO was confirmed to act as an electrochemical and mechanical buffer layer during SiMP lithiation by facilitating the generation of stable SEI species (Figure 6d). Therefore, the abundance of stable Li 2 CO 3 SEI matrix and continued presence of an ionically and electrically conductive Li 2 O/Zn matrix confirm that the np-ZnO conversion reaction is behind the electrochemical and mechanical stability of the np-ZnO/SiMP electrode.

To demonstrate the large-scale production capability of the developed np-ZnO/SiMP composite electrode, the drop-cast combustion reaction methodology was modified into an air-spray setup with reference to the report by Yu et al. 58 The np-ZnO precursor solution with subsequent heat treatment at 180 °C was first air-sprayed onto the annealed Cu foil followed by roll pressing and air-spray of a 0.05 M np-ZnO dispersion in ethanol was then air-sprayed onto the annealed Cu foil with the nanoporous ZnO matrix undergoing a conversion reaction to form Li 2 O/Zn, which serves as an ionically and electrically conductive matrix, which also keeps pulverized SiMPs coalesced. The high porosity of np-ZnO also contributes to the enhanced stability by providing free space for SiMP volume expansion. In addition, the subsequent alloying reaction of Zn with Li makes np-ZnO an electrochemically active binder, which also contributes to capacity. Most importantly, the volume expansion of the np-ZnO matrix enables the entire electrode to expand during Si lithiation, thereby limiting Si delamination, and alleviates lithiation-induced stresses. In addition, the application of np-ZnO sheds light on a possible solution to improving the problematic first-cycle CE of Si electrodes, with the np-ZnO SiMP electrode demonstrating a first-cycle CE of 117% owing to the ZnO conversion reaction. Moreover, the electrode fabrication process is scalable and effective using a facile, low-temperature combustion reaction process as well as being applicable to air-spray deposition. Thus, the developed np-ZnO/SiMP electrodes combine the previously unpaired ZnO conversion reaction with a Si alloying reaction to suggest an approach to enhancing Si battery performance and stability without the need for complex nanostructuring and polymer additives.

**EXPERIMENTAL SECTION**

**Fabrication of the np-ZnO SiMP Electrode.** The SiMP electrode was fabricated by the drop-cast method. The SiMP dispersion was made by adding 0.2 g of SiMP (Alfa Aesar) into 10 mL of ethanol and sonicating for 1 h to obtain a homogeneous dispersion. Working electrodes were prepared by drop-casting the SiMP dispersion onto Cu foil that was annealed at 200 °C under H 2 exposure. Annealing the Cu foil encouraged grain growth and served as a softening mechanism that improved SiMP embedding after calendaring. After ethanol evaporation on a hot plate at 60 °C, the SiMP electrode was calendered, and uniform SiMP electrodes with a loading of ~1.5 mg/cm 2 were prepared. The SiMP-PVDF electrode was fabricated by a conventional slurry cast method. A slurry of SiMP/PVDF/CB with a ratio of 70:15:15 wt % was cast onto Cu foil, calendared, and dried overnight prior to electrochemical characterization.

A nanoporous ZnO matrix was coated using combustion reaction as detailed by Park et al. 71 A 1:1 molar ratio of zinc nitrate and zinc acetylatedonate (Sigma-Aldrich) was dissolved in 2-methoxyethanol at a total Zn concentration of 0.2 M. Undissolved residues were removed by a 0.45 μm syringe filter, and the solution was diluted to 0.1 M. The solution was spin coated onto the SiMP electrode and annealed at 180 °C for 1 min to deposit the np-ZnO matrix surrounding SiMPs. This process was repeated accordingly to obtain the desired ZnO thickness. For the 100 nm condition, ZnO made up 10 wt % of the active materials.

**Electrode Characterization.** Electrochemical properties were examined by galvanostatic cycling with 2032 stainless-steel coin cells with the nanoporous ZnO-SiMP (np-ZnO SiMP) electrode as the working electrode and Li metal as the counter electrode. LiPF 6 (1 M) in ethylene carbonate and fluoroethylene carbonate (1:1, v/v) and a monolayer polypropylene separator (Celgard 2400) were used as the electrolyte and separator, respectively. Cells were cycled between a potential window of 0.01–1.0 V. The first 10 electrochemical cycles were carried out at a C/20 rate for active material activation and subsequent cycles were carried out at a C/5 rate (VSP; Bio-Logic). Rate capacity was tested at different C rates corresponding to five cycles at C/20, C/10, C/5, and C/2 rates. An impedance analyzer (SP-200 Bio-Logic) was used to measure the alternating current impedance at frequencies from 100 mHz to 500 kHz, with a voltage...
amplitude of 10 mVrms. Specific capacity was calculated with respect to SiMP loading.

Surface and cross section morphologies were obtained using SEM (Magellan400, FEI) and FIB imaging (Helios Nanolab 450, FEI). FIB was also used to prepare TEM samples. SEM-EBSD was used to characterize Cu foil grain growth. TEM and energy-dispersive X-ray spectroscopy (EDS, Talos F200X, FEI) provided insight into the composition of np-ZnO SiMP before and after prolonged electrochemical cycling. XPS (K-alpha, Thermo VG Scientific) allowed deconvolution of the SEI layer after cycling.

ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b03951.

Tensile testing revealing Cu softening effect with annealing; nanoporous ZnO deposition optimization; CV curve results; air-spray setup proof-of-concept; nanoporous ZnO and SiMP-only electrochemical characterization; ZnO thickness effect on electrode morphology and electrochemical properties; diffusion coefficient; additional XPS results; Li metal counter electrode images (PDF)

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Notes

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