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Doped Si nanoparticles with conformal carbon coating and cyclized-polyacrylonitrile network as high-capacity and high-rate lithium-ion battery anodes

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Abstract

Doped Si nanoparticles (SiNPs) with conformal carbon coating and cyclized-polyacrylonitrile (PAN) network displayed capacities of 3500 and 3000 mAh g^{-1} at C/20 and C/10, respectively. At 1 C, the electrode preserves a specific discharge capacity of ~1500 mAh g^{-1} for at least 60 cycles without decay. Al_2O_3 atomic layer deposition (ALD) helps improve the initial Coulombic efficiency (CE) to 85%. The dual coating of conformal carbon and cyclized-PAN help alleviate volume change and facilitate charge transfer. Ultra-thin Al_2O_3 ALD layers help form a stable solid electrolyte interphase interface.

Keywords: doped Si, conformal carbon coating, cyclized-polyacrylonitrile network, atomic layer deposition

The great advancement in portable electronic devices and hybrid electric vehicles demands lithium ion batteries (LIBs) with high energy, high power densities, fast rate capabilities, prolonged lifetime, and low cost. The current commercial LIB anodes are made of graphite, which has a theoretical gravimetric capacity of only 372 mAh g^{-1}. Silicon alloys however, have shown a high degree of lithiation up to $Li_{15}Si_4$ [1, 2] at room temperature, resulting in a capacity of 3579 mAh g^{-1}, almost 10 times that of graphite. However, Si-based electrodes suffer from poor cycle life due to detrimental volume changes (i.e., theoretically up to 280% volume expansion [3]) of the host lattice upon alloying and de-alloying with Li. Extended fractures in the entire electrode structure can lead to a complete loss of electrochemical contact between active material, the current collector, and the rest of the electrode network.

Recently, several strategies have been applied to cope with Si cracking, such as replacing bulk Si with porous materials [4], engineering the empty space [5], reducing amorphization-induced mechanical stresses [1, 6, 7] during the first cycle by using non-crystalline silicon [8], and fabricating composite anodes where Si is mixed with other less-active materials that can buffer the volume change [9]. All of these strategies have helped overcome some of the challenges associated with Si electrodes. Despite these recent advances, the cracking and breaking of the composite electrode's microstructure, and thereby its conductive network, due to drastic volumetric change is still one of the biggest problems in realizing an electrochemically stable and long-lasting Si-based anode. We reported the use of cyclized-polyacrylonitrile (PAN) polymer as a binder and conductive additive by conformally coating SiNPs (~50 nm) and treated PAN at 300 °C [10]. At this temperature, the cyclization of PAN proceeds without carbonization, while maintaining its polymeric properties and introducing delocalized sp^2

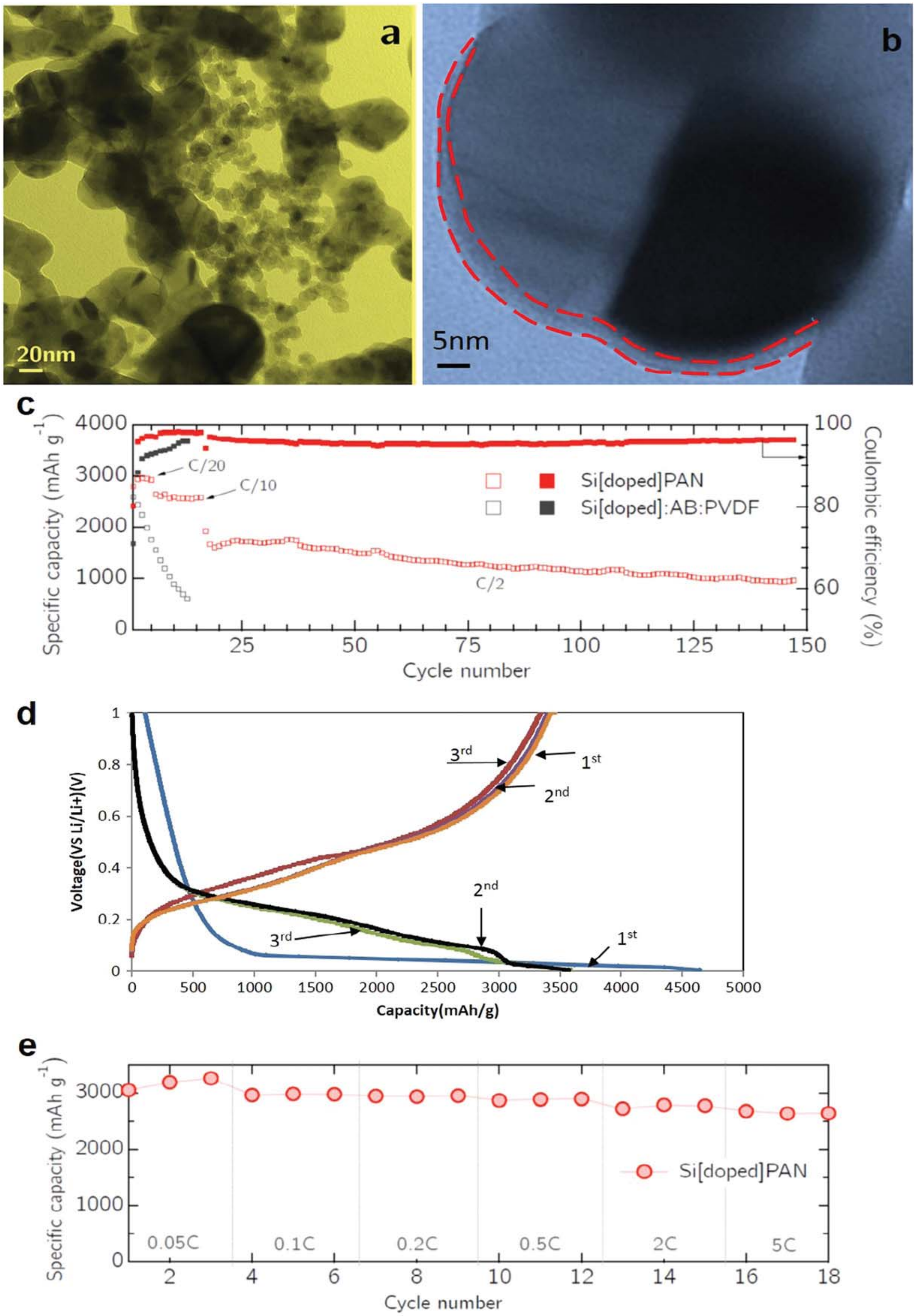

Figure 1. TEM of (a) silicon nanoparticle; (b) native oxide on silicon nanoparticles; (c) charge and discharge capacity of doped nano-Si/cyclized-PAN versus cycle number at C/20, C/10, and C/2 rate; (d) voltage profile of doped nano-Si/cyclized-PAN at C/20; (e) rate performance of doped nano-Si/cyclized-PAN.

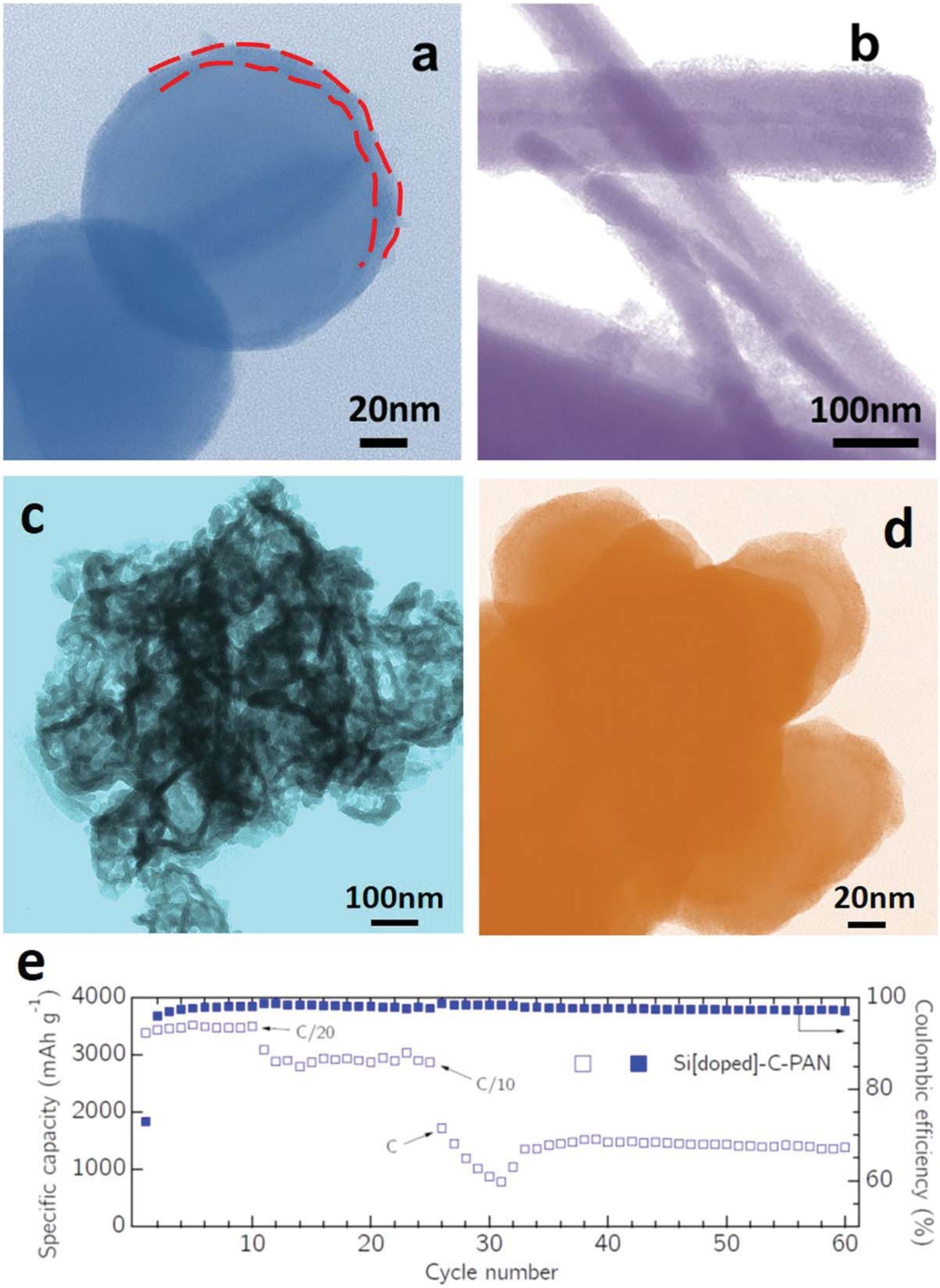

Figure 2. TEM of (a) carbon-coated silicon nanoparticle; (b) CNT found in carbon-coated silicon sample; (c) CNT embedded in nano-silicon/cyclized-PAN; (d) carbon coating remains on lithiated nano-silicon/cyclized-PAN; (e) discharge capacity of carbon-coated doped nano-Si/cyclized-PAN versus cycle number at C/20, C/10, and C rate.

Table 1. Summary of doped SiNPs at different conditions.

	C/20	C/10	Lifetime
Undoped SiNPs/cyclized-PAN at 50 mV	2585 mAh g^{-1}	2200 mAh g^{-1}	1500 mAh g^{-1} after 150 cycles at C/10
Doped SiNP with AB and PVDF at 50 mV	unstable	unstable	unstable
Doped SiNPs/cyclized-PAN at 50 mV	3000 mAh g^{-1}	2600 mAh g^{-1}	1100 mAh g^{-1} after 150 cycles at C/2
Doped SiNPs/cyclized-PAN at 10 mV	unstable	unstable	unstable
Carbon coated doped SiNPs/cyclized-PAN at 10 mV	3500 mAh g^{-1}	3000 mAh g^{-1}	1500 mAh g^{-1} after 60 cycles at 1 C

π-bonding for electrical conduction. The conformal cyclized-PAN coating on SiNPs is ~5 nm. Only 40% of electrode thickness change was observed after full initial lithiation of Si down to 50 mV [10]. However, SiNPs/cyclized-PAN still suffered ~15% capacity loss by the 50th cycle. In this work, we explored cyclized-PAN coating on commercially available doped SiNPs with higher intrinsic electrical conductivity, which showed a significant improvement in rate capability. In our recent study for silicon thin film as microbattery anode, chemical vapor deposition (CVD) carbon shows a dramatic improvement on stability and Coulombic efficiency [11]. Therefore, we conformally coated doped SiNPs with carbon by CVD, followed by creating a cyclized-PAN network to further improve the rate capability and stability at a lower cut-off voltage of 10 mV. Excellent cycling stability and high capacity at 1 C was obtained with this dual coating. These improvements are attributed to the synergistic effect of conformal carbon coating and a cyclized-PAN network on Si electrodes. At the end, Al_2O_3 ALD is applied to improve the CE to 85%, comparable to the commercial graphite anode.

Boron-doped SiNPs (p-type, with the primary particle size at 30 nm) was purchased from Meliorum Technologies. Doped SiNPs were uniformly spread onto an alumina boat. CVD carbon coating was performed by thermally cracking acetylene at 900 °C for 15 min Polyacrylonitrile (PAN, molecular weight = 150 000 g mol^{-1} from Sigma-Aldrich) was mixed with doped SiNPs in a 3:7 mass ratio with N, N-dimethylformaide (DMF, 99%). The mixture was stirred for 12 h, and then doctor-bladed onto a Cu current collector. After drying at 80 °C for 3 h, the electrode was then treated at 300 °C inside an Ar-filled glove box for 12 h. Al_2O_3 ALD was applied onto the electrode at 180 °C. The mass loading of Si is ~0.5 mg cm^{-2}. Detailed sample preparation and electrochemical testing procedures can be found in the experimental section.

Figure 1(a) presents a transmission electron micrograph (TEM) of doped SiNPs. The doped SiNPs has a wide size distribution from 20–50 nm. A native oxide layer (1 ~ 2 nm) can be seen on the surface in figure 1(b). Results of electrochemical characterization of doped SiNPs/cyclized-PAN without carbon coating are presented in figures 1(c)–(e). Doped SiNPs with acetylene black and PVDF were prepared using the doctor-blading technique. The electrodes were electrochemically tested at C/20 and C/10 for 10 cycles, respectively, and then at C/2 for all subsequent cycles. The cut-off voltage was limited to 50 mV. At C/20 and C/10, doped SiNPs have capacities of 3000 and 2600 mAh g^{-1}, respectively. When the rate is increased to C/2, the capacity is ~1600 mAh g^{-1}. At the 150th cycle, doped SiNPs/cyclized-PAN still exhibited a specific charge capacity of ~1100 mAh g^{-1}. This is almost equivalent to undoped SiNPs/cyclized-PAN at C/10, but at a five times higher rate [10]. This improvement is due to much higher electronic conductivity of doped SiNPs compared to the undoped SiNPs. On the other hand, doped SiNPs prepared by the conventional slurry-coating method start to decay immediately, much worse than SiNPs with a cyclized-PAN network. We believe this is due to a better adhesion within the cyclized-PAN network. Figure 1(d) displays the voltage profiles of our doped SiNPs/cyclized-PAN anode for the first three cycles at C/20. The first cycle shows a large irreversible capacity loss due to SEI formation. The first cycle delithiation profile shows a specific charge capacity of 3400 mAh g^{-1}, which is equivalent to the extraction of 3.55 moles of Li per mole of Si. This value is very close to its theoretical capacity of 3579 mAh g^{-1}, corresponding to 3.75 moles of Li per Si. The second and third cycles are nearly overlapped, indicating excellent stability. Furthermore, we conducted a rate capability test on doped SiNPs/cyclized-PAN as shown in figure 1(e). At 5 C, doped SiNPs/cyclized-PAN still maintain a discharge capacity over 2500 mAh g^{-1}, retaining ~75% of its capacity at C/20.

Although much improved capacity at various rates is obtained for doped SiNPs compared to the undoped SiNPs used in our previous work [10], the capacity still suffers some decay and the voltage is limited to 50 mV. When the cut-off voltage goes down further, more lithium will alloy with silicon, leading to a higher capacity but also causing more a dramatic volume change [12]. The CE for doped samples is only ~95%, indicating no stable SEI was formed. Large volume change exposes fresh surfaces of SiNPs to electrolytes every cycle, causing low CE and eventually structural degradation. In order to overcome these issues, a conformal carbon coating (~7 nm) was deposited by CVD (figure 2(a)) before cyclized-PAN coating. The color of the SiNPs changed from brown to black after CVD coating. No significant changes in particle size and agglomeration were seen. Interestingly, we observed some carbon nanotubes after carbon deposition (figure 2(b)). Only one hollow session per tube is observed, and there is no evidence that those are carbon nanotube (CNT) clusters. It is well known that carbon nanotubes can be grown with the assistance of

Table 2. Comparison of Columbic efficiencies (CE).

	Nano-silicon/cyclized-PAN at 50 mV [10]	Doped Nano-silicon/cyclized-PAN at 50 mV	Carbon coated doped nano-silicon/cyclized-PAN at 10 mV	ALD coated carbon coated doped nano-silicon/cyclized-PAN at 10 mV
The initial CE	70%	80%	75%	85%
CE after the first cycle	~99%	~95%	~98%	~99%

dielectric metal oxides, such as silicon oxide, even without using metal catalysts [13–15].

Carbon-coated doped SiNPs were first mixed with PAN, and then heat-treated in the same way as described previously for the doped SiNPs samples without carbon coating. The voltage window was extended to 10 mV, which would result in higher capacity but larger volume expansion. With carbon coating, the capacity of SiNPs/cyclized-PAN at C/20 and C/10 was improved from 3000 and 2600 mAh g^{-1} without carbon coating to 3500 and 3000 mAh g^{-1}, respectively. At 1 C, the electrode preserves a specific discharge capacity of ~1500 mAh g^{-1} for at least 60 cycles without decay. This indicates that the synergistic effect of the conformal carbon and cyclized-PAN coating stabilize SiNPs composite anodes at the extended cut-off voltage window of 10 mV with high rate capability. A summary of SiNPs with different conditions carried out in this work can be found in table 1.

After the 60th cycle, the coin cell was discharged to 10 mV and held for 2 h. The cell was then disassembled inside a glove box. A small piece of a lithiated Si-anode was scratched off for TEM analysis. CNTs embedded in the electrode are clearly visible in figure 2(c). CNTs form a conductive network to facilitate charge transfer. Figure 2(d) shows that the amorphous carbon coating is preserved on the surface of SiNPs after extensive cycling. We believe that the conformal amorphous carbon and cyclized-PAN dual coating isolates SiNPs from the organic electrolyte and inhibits SiNPs aggregation during cycling. Material aggregation is a frequent cause of capacity fade in electrodes utilizing nanoparticles [16, 17], but our carbon and cyclized-PAN dual coating technique helps maintain individual SiNP for good capacity retention.

An initial CE higher than 85% is usually required for Si-based electrodes. Limiting the cut-off voltage to 50 mV helps improve CE, as shown in table 2. When the cut-off voltage goes down to 10 mV, the initial CE of carbon-coated nano-silicon/cyclized-PAN is only 75%. However, from the second cycle, CE is improved to ~98%. ALD has been widely studied to improve the cycling life and CE of electrodes [18–20]. Here, we applied five cycles of Al_2O_3 ALD on carbon-coated doped SiNPs/cyclized-PAN electrodes. The initial CE was improved to ~85%, and the rest of CE was improved to ~99%. However, further improvement on CE over 99.99% is required to achieve prolonged cycle life. This could be achieved by using different electrolytes and additives, and will be addressed in our future studies.

Conclusions

In summary, we studied doped SiNPs with conformal carbon coating embedded in cyclized-PAN network as high-capacity and high-rate LIB anodes. We observed significant improvement in rate capability as compared to undoped SiNPs. At C/20 and C/10, doped SiNPs have capacities of 3000 and 2600 mAh g^{-1}, respectively. At the 150th cycle, they still exhibit a specific charge capacity of ~1100 mAh g^{-1} at C/2. In addition, the synergistic effect of carbon coating and the cyclized-PAN network helps extract more capacity from the lower cut-off voltage at 10 mV, and also improves the cycling stability at all rates. CVD carbon-coated SiNPs/cyclized-PAN at C/20 and C/10 are improved to 3500 and 3000 mAh g^{-1}, respectively. The electrode can maintain a specific capacity of ~1500 mAh g^{-1} for at least 60 cycles. Furthermore, its initial CE was improved to ~85% and the rest CE to ~99% with five cycles of Al_2O_3 ALD coating.

Acknowledgments

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