REVIEW

Opportunities to overcome the challenges of (high-performance) silicon anodes in Li-ion batteries

Silicon has a high theoretical charge capacity of 4200mAh g^{-1} which makes it an interesting potential anode material for Li-ion batteries. The major challenge is the volume expansion (400%) upon lithiation, which leads to subsequent problems in the battery. In this review, three technological approaches with the potential to overcome these challenges are presented. First, a polymer scaffold which accommodates the expansion of Si nanoparticles within the structure. Second, Si core-hollow shell nanocomposites which offer sufficient space inside each particle to manage the expansion of Si. Finally, an approach based on 1D nanowires controlling the Si swelling by individual radial expansion. The highest realized charge capacities are >3000mAh g^{-1} while other solutions showed cycle lifetimes of 150 cycles with ~1700mAh g^{-1}.

Introduction

In today's world, efficient energy storages continue to gain in importance to power all sort of mobile devices such as battery electric vehicles, smartphones, laptops, and other electrical devices. Currently, Li-Ion batteries are used for most of these applications because they offer the most reliable and efficient performance over their lifetime. Nonetheless, the search for smaller, lighter, safer and more efficient options is driving scientist's research all over the world.

One opportunity for improvement is the use of silicon (Si) as anode material due to its high theoretical charge capacity of 4200mAh g^{-1}. In comparison, commonly used carbonaceous materials like graphite offer a theoretical charge capacity of 372mAh g^{-1}, so even less than a tenth of silicon's theoretical capacity.[1] Unfortunately, Si also comes with some challenges. The major challenge is the volume expansion during lithiation. The volume changes during insertion and extraction of Li reaches up to 400%,[2] which is adverse to technical applications while additionally causing a series of other problems in the battery itself. These internal issues comprise pulverization of the electrode, loss of contact with conductive additives and the repeated breakage of the solid electrolyte interface (SEI).[1] The latter leads to the consumption of the electrolyte which again can initiate a multitude of other negative effects. All of the above cause rapid aging and thus a decrease in capacity until the active material loses the contact to the current collectors which is equivalent to the battery's death.

Fortunately, most of these problems can be avoided by controlling the volume expansion. Three promising approaches will be discussed in this review. First, a polymer scaffold binder that is able to accommodate the increase in the volume of Li particles during lithiation without demolishing the structure. Secondly, Si core-hollow shell nanocomposites with tuneable buffer voids which offer sufficient space inside each particle to allow the expansion of the Si during lithiation. Thirdly, an approach using nanotechnology to grow Si nanowires (NW) which cope with the expansion and shrinkage of Si on a nanoscale without the need for binders or conducting additives.

Results

Guo et al. [3] were experimenting with sodium carboxymethyl cellulose (CMC) binder to improve the Si anode with low nano-Si content (28-34 wt%). Less Si and more CMC binder means avoiding typical issues of Si anodes but at the same time, it also means lowering the overall anode capacity. This trade-off was circumvented by intentionally creating cavities in the CMC scaffold which gives space for Si particles to expand. The cavities in the CMC scaffold electrodes were created by the slurry spray technique, where the slurry (52 wt% Si nanoparticles, 12 wt% carbon black, 36 wt% CMC) is sprayed onto a heated copper foil. The water, used as the solvent for the slurry, evaporates when in contact with the hot copper foil, creating the desired porous scaffold. The Si nanoparticles (NP) in the slurry are coated with carbon black for two reasons. Firstly, it increases the electronic conductivity and secondly, it stabilizes the SEI.[3] Figure 1 shows the working principle of this approach. The 3D scaffold binder structure is offering sufficient space for Si nanoparticles to expand during lithiation thus preventing the volume increase of the overall anode.

Figure 2 shows the cycle stability for three different configurations of this novel anode in comparison to a conventional anode produced with the same materials. As shown, all scaffold solutions are outperforming the conventional approach in terms of specific capacity and cycle stability. Scaffold CMC-C/NanoSi 250mA/g (red) is offering a specific charge capacity of 1685mAh g^{-1} after 150 cycles at 250mA g^{-1} charge/discharge current. Expectedly, the performance is even better at lower C-rates confirmed with the same scaffold cycled at 100mA/g (green) which corresponds to 0.05C.
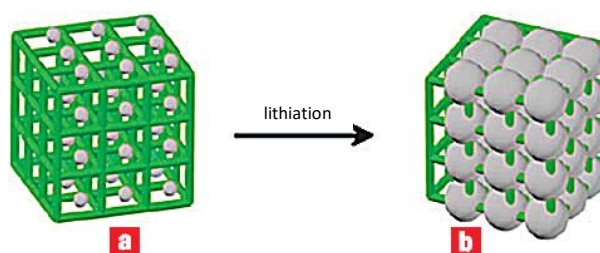

Figure 1 Theoretical structure of the 3D CMC scaffold at low state of charge (SoC) with minimal expansion of the Si NPs (a). After Li-ion insertion/ charging, the CMC scaffold is intact while accommodating the volume expansion of the Si NPs (b). Reproduced [3] and modified
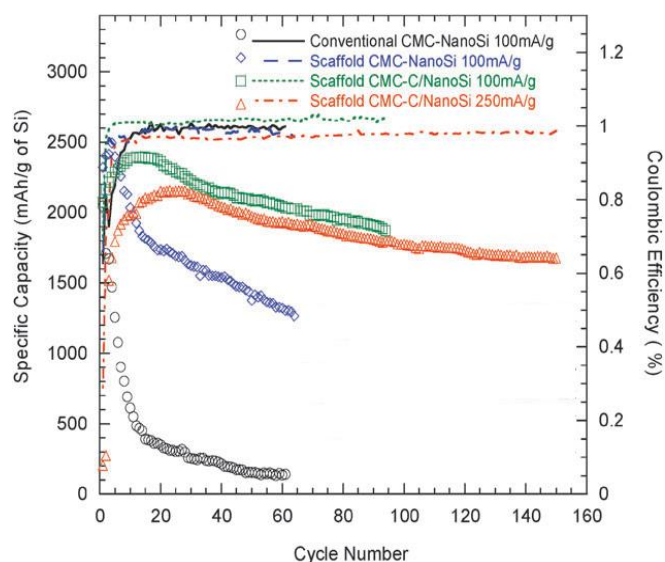
Figure 2 Discharge capacities (symbols), Coulombic Efficiencies (CE) (dashed lines) and cycle stabilities of Si nanoparticle electrodes with CMC scaffold binder. Reproduced [3]

Figure 4 Charge capacities (solid symbols) and CE (blank symbols) of Si core-hollow shell nanocomposites with tuneable buffer voids. Charged between 0.01 and 1 V, at 0.05 C. Showing the performance of different void/Si ratios denoted as Si@HC_1.5, Si@HC_3 and Si@HC_6. Reproduced [5]

Furthermore, the carbon-coated solution offers improved performance in comparison to the scaffold CMC-NanoSi 100mA/g (blue) without carbon coating, because the carbon is one factor to reduce the SEI film formation.[4] Apart from that, carbon is enhancing the conduction within the porous CMC structure and is thereby indispensable for a superior performance. It also needs to be mentioned that Guo et al. tested the anodes with Si micron-particles (average size ~ 2μm) instead of NPs which showed inferior capacity retention, leading to the conclusion that small particle diameters are essential to successfully implement Si as anode material.

Chen et al.[5] conducted research on hollow nano-structured materials, where Si NPs are encapsulated in hollow carbon spheres. This approach was not new, the new aspect, however, was to improve the void/Si ratio by introducing a synthesis method in which conformal carbon shells and tuneable built-in buffer voids can be realized. This synthesis was done in three steps (Figure 3). Starting with commercially available Si nano-particles, the first step is to grow a SiO_2 layer with a defined thickness using the Stöber method. In the second step, the particles are then coated with a poly-dopamine layer followed by carbonization, constructing the carbon shell. In the final step, the SiO_2 layer is removed by a hydrofluoric solution, creating a
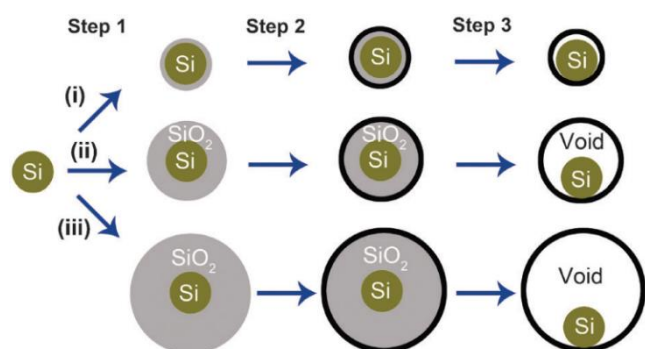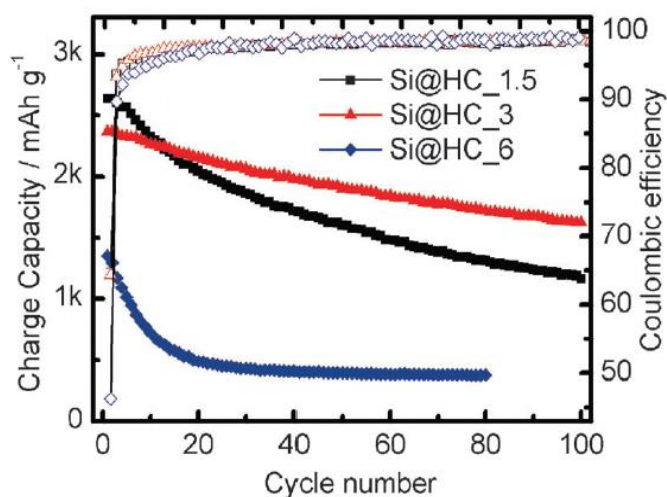

Figure 3 Three process steps for the synthesis of the silicon core–hollow carbon shell nanocomposites. i to iii show variation of sacrificial SiO_2 layer during the 1st step allowing for control of the void/Si ration. Step 1: Silicate (SiO^2) coating on Si NPs by Stöber method; Step 2: conformal poly-dopamine deposition and carbonization; and Step 3: creation of voids using hydrofluoric solution to etch off SiO^2. Reproduced [5]

void around the Si core without harming the outer carbon shell. The void/Si ratio can now be determined by controlling the thickness of the SiO_2 layer in the first step. Chen et al. created three different void/Si NP ratios (1.5:1 denoted as Si@HC_1.5, 3:1 denoted as Si@HC_3 and 6:1 denoted as Si@HC_6).

As shown in figure 4, the void/Si ratio of 3 (Si@HC_3) obtains the highest capacity of ~1700mAh g^{-1} after 100 cycles. Although Si@HC_1.5 has a higher Si fraction and thereby higher capacities, the capacity retention is worse due to insufficient void size, causing damage to the carbon shell and leading to loss of electrical contact and thus to capacity fading. Si@HC_6 however, with the lowest Si fraction shows a low charge capacity and weak cyclability as well. This may be attributed to the limited contact area between the Si core and the hollow carbon structure. The low CEs (high irreversible capacity loss) during the first cycles might originate in the increased surface area of the amorphous carbon. Larger surface area means more SEI formation and higher irreversible Li insertion into amorphous carbon. Si@HC_3 was also tested at different C-rates to proof the significance for technical application. The charge capacity drops significantly with higher C-rates. At 5C the stable charge capacity is approximately 500mAh g^{-1} which is still a good value in comparison to graphite anodes.

Another approach based on nanotechnology was done by Chan et al.[2] who grew Si nanowires (NW) directly onto current collectors which is advantageous because it assures that each NW is contributing to the battery's capacity.[2] Furthermore, voids between the NWs offer sufficient space for the volume expansion during lithiation and the direct 1D electron transport in axial direction of the NWs facilitates an improved electrical conductivity (Figure 5). Last but not least, the NW approach makes the use of binders and additives superfluous, reducing the overall weight and allowing higher specific charge capacities. The synthesis of 1D Si NWs was done using the vapor liquid solid method (VLS) with gold as a catalyst. The growth of the crystalline 1D structure is done through adsorption of a gas phase onto a solid surface. Since direct adsorption is very slow, golden nucleated seeds are used to create a catalytic liquid alloy phase which increases the growth rate of the NWs.
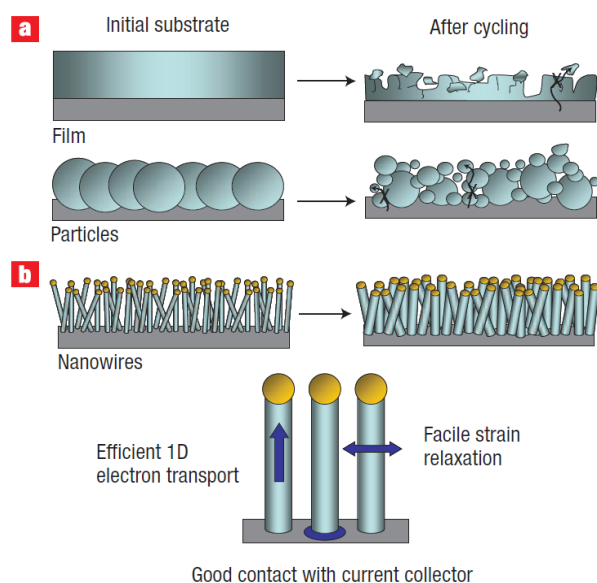
Figure 5 (a) The consequences of volume changes when cycling bulk or particle-based Si anodes. (b) Sketch of NWs grown with Au as catalyst. Highlighting (dark blue) the three advantages of Si NWs: good electron transport, direct contact with current collector and radial strain relaxation avoiding fractures in the structure. Reproduced [2]

The NWs were analyzed using scanning electron microscopy, transmission electron microscopy and X-ray diffraction. The researchers could confirm that the NWs expand by 400% without fracturing which indicates a good cycle stability. This cycle stability can be seen in figure 6 which also shows very high discharge capacities of >3000mAh g^{-1} at 0.05C for the first 10 cycles. According to the authors the capacity fade of the Si NWs after the first cycle does not originate in the build-up of the SEI because there is no significant capacity consumption in the voltage range of the SEI formation (0.5-0.7V).[2] The reason for the irreversible capacity loss remained uncertain to them, although they noticed an irreversible structural change of the Si NWs from crystalline before lithiation to amorph after the first cycle. Chen et al.[5] had noticed the same phenomenon in their experiment and could relate the capacity loss to the irreversible alloying of Si with Li.

Discussion

There is no doubt that the presented approaches offer improved charge/discharge capacities. However, the direct comparison of these new technologies is complicated due to variations in the testing condition. The NWs seem to be the most promising technology with a discharge capacity above 3000mAh g^{-1} but the authors are not revealing any capacity values for more than 10 cycles. Which leads to the assumption that the cycle lifetime of NWs based Si anodes might be limited. The second highest capacity is achieved by the polymer scaffold binder with a capacity of around 1900mAh g^{-1} at 0.05C after 100 cycles which is comparable to the core-hollow shell nanocomposites with a capacity of around 1700mAh g^{-1} at the same quantitative conditions. The capacities at different C-rates however, cannot be compared because in the case of the polymer scaffold binder the discharge rates were changed while the charging was continuously done at 0.05C. Besides the fact that this charging behavior makes the results incomparable to the other technologies, it is also not applicable for commercial Li-ion batteries since most applications require fast charging. It also needs to be
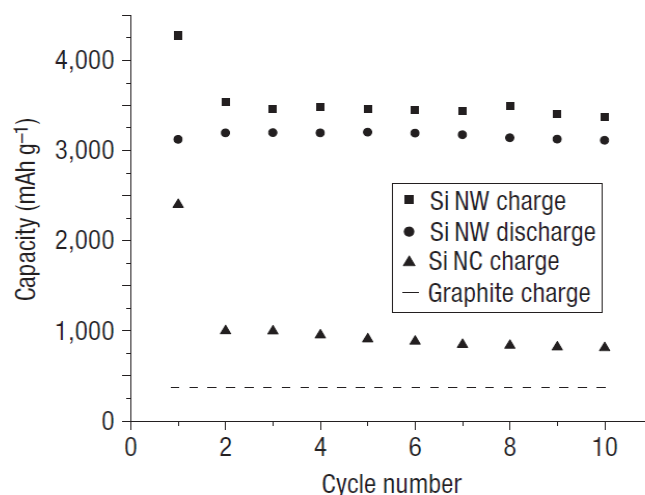

Figure 6 Charge and discharge capacities of Si NWs versus cycle number at 0.05C. In comparison, nanocrystals (NC) and graphite with significant lower performance. Reproduced [2]

mentioned, that none of these approaches were tested on a system level which most probably will significantly influence the performance of all technologies. Furthermore, the volumetric densities of the anodes are not considered for all three technologies which is another important measure for the commercialization of batteries. It would be interesting to see the volume increase that is required to mitigate the anode's expansion and shrinkage. Last but not least, the economic viability in terms of process cost plays a significant role for the future development of different approaches. Therefore, the comparison of key figures such as cost per capacity is one meaningful comparative value to decide which technology holds the highest future potential.

Conclusions

Si offers the highest theoretical potential for anodes in Li-ion batteries. The reduction of Si particles to the nanoscale while providing void space to accommodate the volume expansion during lithiation offers a way to overcome the related issues. Nonetheless, additional research is required to proof higher cycle stability, economic feasibility and the functioning on a cell level. In order to harvest the high theoretical capacity of Si further research will certainly be conducted to enable a broad mass market penetration of Si anode base Li-ion batteries.

References

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