Si-Based Anode Materials for Li-Ion Batteries: A Mini Review

Delong Ma · Zhanyi Cao · Anming Hu

Received: 3 April 2014 / Revised: 24 May 2014 / Accepted: 10 June 2014 / Published online: 27 September 2014
© The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract Si has been considered as one of the most attractive anode materials for Li-ion batteries (LIBs) because of its high gravimetric and volumetric capacity. Importantly, it is also abundant, cheap, and environmentally benign. In this review, we summarized the recent progress in developments of Si anode materials. First, the electrochemical reaction and failure are outlined, and then, we summarized various methods for improving the battery performance, including those of nanostructuring, alloying, forming hierarchic structures, and using suitable binders. We hope that this review can be of benefit to more intensive investigation of Si-based anode materials.

Keywords Li-ion batteries · Anode · Si · High capacity · Nanomaterials

1 Introduction

In the last two decades, the Li-ion batteries (LIBs) have successfully captured the portable electronic market. However, when it is proposed to conquer the upcoming markets of electric vehicles, storage of energy from renewable energy sources, such as photovoltaic plants and/or wind turbines and other KWh levels load, great improvements in storage capacity, which is currently mainly limited by their electrode materials, are urgently needed [1–5]. It is well known that the commercial graphite anode cannot meet these challenges due to its low theoretical capacity (372 mAh g⁻¹). There is a consensus that the breakthrough in capacity can be achieved by moving from classical intercalation reaction to alloying reaction because the alloying reaction can store more Li compared with intercalation reaction. For example, Li can react with Si to form Li₂₂Si₅ alloy, but with graphite only, to form LiC₆ alloy. Since Dey demonstrated that Li metal can electrochemically alloy with other metals (Sn, Pb, Al, Au, Pt, Zn, Ag, Mg, and Cd) at room temperature [6], Li-alloying reactions with metallic or semi-metallic elements and various compounds have been investigated during the past few decades, such as Sn, P, Ge, Pb, and Sb. Wen et al. showed that Sn reacted with lithium to yield different Li–Sn phases: Li₂Sn₃, LiSn, Li₃Sn₃, Li₅Sn₂, Li₁₃Sn₄, Li₇Sn₂, and Li₂₂Sn₅. A black P/C nanocomposite also showed high capacity (about 2,000 mAh g⁻¹) [3]. Among the various Li alloy elements, Si has been considered as one of the most attractive anode materials for LIBs, not only because of its high gravimetric (4,200 mAh g⁻¹) and volumetric capacity (2,400 mAh cm⁻³), but also due to its abundance, cheapness, and environmentally benign property, as shown in Table 1. However, it suffers from fast capacity fading, which greatly hampers the application of Si anode materials.
1.1 The Mechanism of Electrochemical Lithiation

LIBs are mainly composed of anode (generally graphite), a carbonate-based organic electrolyte, and a cathode (generally LiCoO₂). Li ions are intercalated and deintercalated between graphite and LiCoO₂ through the electrolyte during discharge and charge. The theoretical capacities of anode and cathode are 372 mAh g⁻¹ (graphite) and less than 160 mAh g⁻¹ (LiCoO₂), respectively, which are too low, especially for anode material. Si anode is very attractive because of its high theoretical capacity of 4,200 mAh g⁻¹ which is 10 times more than that of commercial graphite [3]. Moreover, the discharging potential is about 0.2 V with respect to Li/Li⁺, which is lower than most of other alloy-type and metal oxide anodes [7]. Furthermore, it is safer and stabler than graphite (lithiated silicon is more stable in typical electrolytes than lithiated graphite) [8].

The mechanism of electrochemical lithiation of Si is critical to improve the performance of Si anode, which has been investigated by several groups [9–16]. It is found that the reactions follow the equilibrium Li–Si binary phase diagram at high temperature, forming different intermetallic compounds and showing distinct voltage plateaus for each two-phase region [17]. However, there is only a two-phase region at about 0.1 V at room temperature during first discharge process [18], as shown in Fig. 1. It should be noted that the two-phase region disappears after first cycle. In order to find out the lithiation mechanism, X-ray diffraction (XRD) analysis was performed to investigate the phase transition [13–15], and the reaction mechanism is explained as follows:

During discharge

\[
\text{Si (crystalline)} + \alpha \text{Li}^+ + \alpha e^- \rightarrow \text{Li}_x\text{Si (amorphous)} \\
+ (3.75 - x) \text{Li}^+ + (3.75 - x) e^- \\
\rightarrow \text{Li}_{15}\text{Si}_4 (\text{crystalline}) \tag{1}
\]

During charge

\[
\text{Li}_{15}\text{Si}_4 (\text{crystalline}) \rightarrow \text{Si (amorphous)} + y\text{Li}^+ + y e^- \\
+ \text{Li}_{15}\text{Si}_4 \text{(residual)} \tag{2}
\]

In the two-phase region, crystalline Si becomes amorphous Li–Si alloy during the first lithiation (1), and the highly lithiated amorphous LiₙSi phase is suddenly found to crystallize into Li₁₅Si₄ phase around 60 mV (vs. Li/Li⁺) (2). Another two-phase region appears during the first delithiation process, and the final product is amorphous Si (3). There are also amounts of residual Li₁₅Si₄ phase after the first delithiation, which can be avoided if the potential of the Si electrode is controlled above 70 mV during cycling. When Li ions react with the amorphous Si during the second cycle, the two-phase region disappears, and sloping voltage plateaus are observed, which indicates single-phase region. After the second cycle, reactions (2) and (3) were repeated, show the above features repeatedly, and reversible capacity faded quickly.
1.2 The Failure Mechanism

Although Si has the highest theoretical capacity, its cycling performance is very poor. Figure 2 shows the charge–discharge profiles of Si powder anode at a current density of 100 mA g\(^{-1}\). It could be found that a large amount of irreversible capacity appears in the first cycle. The first discharging capacity is about 3,260 mAh g\(^{-1}\) but that of the charging is only 1,170 mAh g\(^{-1}\). After 10 cycles, only very low capacity (about 200 mAh g\(^{-1}\)) can be retained.

To understand the reasons for the poor cycling stability of Si anode, the failure mechanism has been investigated by several groups [16, 19]. The conclusions can be drawn as follows:

a. The large change in the volume of Si anodes, which increases internal resistance and loss of contact area between Si and conductive materials, is considered to be the main reason for their rapid capacity loss. Figure 3 shows the schematic of morphologic changes that occur in Si during electrochemical cycling [20]. The volume of Si anodes changes by about 400% during cycling. As a result, Si films and particles tend to undergo pulverization during cycling. Most of the material loses contact with the current collector, resulting in poor transport of electrons.

b. Solid electrolyte interphase (SEI) stability at the interface between the silicon and the liquid electrolyte is also responsible for the failure of the Si anode. The SEI layer is formed during battery discharging, due to electrolyte decomposition on the surface of anode at the low potential. As shown in Fig. 4, a thin layer of SEI is formed in the lithiated and expanded state [21]. During delithiation, the Si particle shrinks, and the SEI layer breaks down into separate pieces, and fresh Si surface is exposed to the electrolyte. In later cycles, new SEI layer continues to be formed on the newly exposed silicon surfaces. The SEI is an electronic insulator but a Li–ion conductor, and so the growth of the SEI layer is eventually terminated at a certain thickness. The thick SEI layer is harmful for the cycle life, because it can cause a rise of the electrode impedance/polarization and decrease of the electrode’s electrochemical reactivity. As discussed above, a large volume change and unstable formation of SEI film are the main issues for the failure of Si anode.

2 The Methods to Improve the Battery Performance

2.1 Si Nanostructures

Tremendous efforts have been made to improve the batteries performance of Si anode. In order to overcome the volume change during electrochemical reaction, many researches are focused on accommodating the volume changes in the earlier studies. Nanomaterials have the genuine potential to make a significant impact on the electrochemical performance of Si anode [22], as their reduced dimensions enable far higher intercalation/deintercalation rates. In addition, the volume change can be
also buffered after downsizing the Si particle to nano-size. The significance of nano-sized Si on battery performance was demonstrated by several groups. Li et al. reported that a nano-Si (78 nm) powder anode showed better capacity retention than bulk Si powder [23]. Kim et al. also synthesized Si nanoparticles with various sizes (5, 10, and 20 nm) and studied their battery performance [24]. The results indicated that 10-nm-sized Si showed the highest capacity retention among the samples, as shown in Fig. 5.

![Voltage profiles of 5, 10, and 20-nm-sized Si and 10-nm-sized Si after carbon coating during the first cycle in coin-type half-cells at a rate of 0.2 C between 0 and 1.5 V.](image1)

![Cycle performances at a rate of 0.05 and 0.2 C (square: 0.05 C, circle: 0.2 C) [25](image2)

![SEM and TEM images (insets) of the sealed tip of a Si nanotubes.](image3)

![Cycle performances at a rate of 0.05 and 0.2 C (square: 0.05 C, circle: 0.2 C) [25](image4)
One-dimensional (1D) nanowires and nanotubes are also intriguing structures with good cycle stability. Cui et al. synthesized Si nanowires which were grown directly on the metallic current collector substrate [20]. The limited nanowire diameter allows for better accommodation of the large volume change and provides 1D electronic pathways allowing for efficient charge transport. The Si nanowires display high capacities at higher current density. Even at the 1 C rate, the capacities remain 2,100 mAh g$^{-1}$, and a reversible capacity of over 3,000 mAh g$^{-1}$ is maintained after 10 cycles. An array of sealed Si nanotubes is also prepared by CVD of Si on to ZnO nanorods and selective removal of ZnO (see Fig. 6) [25]. It shows discharge capacities of 3,360 and 2,500 mAh g$^{-1}$ at the rates of 0.05 and 0.2 C respectively, and high capacity retentions (about 81 and 82 % at 0.05 and 0.2 C, respectively) after 50 cycles.

Two-dimensional (2D) Si thin film is another promising nanostructure with improved cycle stability and rate capabilities, which can minimize the volume variation and retain structural integrity [26–29]. Of course, the battery performance depends on the film thickness as thinner films deliver larger accommodation capacity. For example, a 50-nm-thick Si film is found to deliver a higher discharge capacity and better cycling performance compared with 150-nm-thick Si film [26]. Although Si thin film offers high specific capacity, good capacity retention and fast charge/discharge rate, the practical application is hampered because of their prohibitively high synthesis costs and low active material content.

Recently, three-dimensionally macroporous (3DM) structure materials used in LIBs have attracted more attention, due to their special nature [30–35], as shown in Fig. 7. First, the wall thicknesses are on the order of nanometers to tens of nanometers, which can shorten both electronic and ionic pathways. Second, macropores with a size range of several hundred nanometers enable easy infiltration of electrolyte and fast liquid-phase Li ion diffusion, reducing the concentration polarization and increasing rate performance and capacity of the cell. Third, the continuous network of electrode material may provide better electrical conductivity than aggregates of loosely connected particles. Finally, macroporosity should help in accommodating volume change during cycling without losing the structural integrity of the electrode. Esmanski et al. synthesized several types of silicon-based inverse-opal films and studied their electrochemical performances [36]. These electrodes demonstrated significant improvement both in capacity retentions and rate capabilities.

Bang et al. reported a simple route for synthesizing 3DM bulk Si materials by combining an electroless metal deposition via a galvanic reaction, with a metal-assisted chemical etching process using commercially available bulk Si powders (Fig. 8). The as-prepared materials exhibited a high reversible capacity of approximately 2,050 mAh g$^{-1}$ with a remarkable initial coulombic

---

**Fig. 8** Upper: schematic illustration of the preparation of macroporous Si powders. Ag nanoparticles were deposited onto the surface of bulk silicon via a galvanic reaction, and subsequently, the Ag-deposited Si was chemically etched to make 3D porous Si particles. Lower: a SEM image of Ag-deposited Si. b SEM image of chemically etched Si. c Magnified SEM image of samples seen in (b) [37]
efficiency of 94.4%, and stable cycling retention (Fig. 9) [37].

2.2 Si/M Composites (M: Active/inactive Conductive Materials)

In comparison with bulk Si materials, the pristine nanostructures of Si have shown improved capacity retention. However, the nano-sized Si anode materials are still plagued with the intrinsic low electrical conductivity of Si. Liu et al. have shown that increasing the conducting additive content played an important role in improving battery performance of the electrodes [38].

Several groups have paid attention to some intermetallic compounds containing Si as anode materials, such as Mg$_2$Si, CaSi$_2$, NiSi, FeSi, CoSi$_2$, FeSi$_2$, and NiSi$_2$ [12, 39–44]. For example, the first discharge capacity of NiSi is shown to be 1,180 mAh g$^{-1}$, which corresponds to the insertion of 3.82 mol Li, and the initial coulombic efficiency was 80%. Here, Ni is expected to act as a buffering and conductive matrix for the formation of Li$_x$Si in the subsequent cycles. Nano-Si/polypyrrole (PPy) composites are prepared by HEMM and chemical polymerization, respectively [45]. It is found that the PPy conducting polymer matrix is effectively acting to increase the electrical conductivity and buffer the volume change.

Recently, some works on Si–C composites have been reported. When graphite and pyrolyzed carbon are used as matrices, some promising results have been obtained in terms of initial coulombic efficiency, high reversible...
capacity, and cycling stability. Carbon is expected to play an important role in electrode reliability owing to its relative softness, small volume change during Li insertion, and good electronic conductivity. Graphene is a good candidate to host active nanoparticles among the various carbon materials because of its high surface area, superior electrical conductivity, and excellent mechanical flexibility [46–49]. In general, graphene sheets in the as-obtained hybrid materials can function as supports of active materials and provide conductive channels for electrons through the electrodes. Chou et al. prepared Si/graphene composite by sample mixing of nano-sized Si and graphene [50]. The improved cycling stability is attributed to the good mechanical properties and conductivity provided by graphene. Zhao et al. reported Si/graphene composite constructed with a graphitic scaffold with in-plane carbon vacancy defects [51]. Figure 10 shows the schematic drawing. They demonstrated the beneficial effects of nanometer-sized in-plane vacancies on ion transport for use in a 3D graphitic scaffold that can be fabricated into hybrid materials with a combination of power capability and storage capacity for battery electrode applications. Zhou et al. used a self-assembly approach to encapsulate Si nanoparticles in graphene via electrostatic force (Fig. 11) [52]. A good cycling performance of the composite had been observed. The capacity reached 1,205 mAh g\(^{-1}\) after 150 cycles.

### 2.3 Hollow and Yolk–Shell Structure Composites

Pioneering works have shown that decreasing the feature size to the nanoscale allows for the material to withstand the large (de) lithiation strains without fracture. However, the cycle life of nano-sized silicon is still limited due to the unstable SEI on the surface. Recently, hollow and yolk–shell structures of Si composites, coated with conductive materials, have been shown to be an efficient way to solve the problem [53–58].

Cui et al. demonstrated a novel secondary structure for Si anodes [59], as shown in Fig. 12. Such a design has multiple advantages: (1) the nano-sized primary particle and the well-defined internal void space allow the silicon to expand; (2) the carbon framework functions as an electrical highway so that all nanoparticles are electrochemically active; (3) carbon completely encapsulates the entire secondary particle, limiting the SEI film formation to the outer surface, which not only limits the amount of SEI, but also...
Recent studies have also shown that many important battery characteristics, including stability and irreversible capacity losses, are critically dependent on the binder’s properties [61–64]. It is found that polymers containing carboxy groups, such as polyacrylic acid (PAA) and carboxymethyl cellulose (CMC), demonstrate promising characteristics as binders for Si-based anodes [65, 66]. The polar hydrogen bonds between the carboxy groups of the binder and the SiO2 on the Si surface are proposed to exhibit a self-healing effect and reform if locally broken.

Kovalenko et al. used alginate as the binder of nano-Si electrode, which yielded a remarkably stable battery anode [67]. As shown in Fig. 15, charge–discharge cycling performance with Li insertion capacity limited to 1,200 mAh g\(^{-1}\) shows stable anode performance for more than 1,300 cycles. At a current density of 4,200 mA g\(^{-1}\), the reversible Li extraction specific capacity of an alginate-based Si anode ranges from 1,700 to 2,000 mAh g\(^{-1}\) (Fig. 15b). At a smaller current density of 140 mA g\(^{-1}\) (Fig. 3c), the specific capacity of the Si anode reaches 3,040 mAh g\(^{-1}\). The good battery performance can be contributed to several reasons. First, a very weak binder–electrolyte interaction prevents access of the solvent molecules to the Si–binder boundary. Second, the alginate can provide access of Li ions to the Si surface because it is an ion conductor. Third, it also can assist in building a deformable and stable SEI on the Si surface.

2.4 Effect of Binder

retains the internal void space for silicon expansion; and (4) the dilemmas of high surface area and low tap density, which are introduced when using nano-sized primary features, are partially solved. As shown in Fig. 13a, its reversible capacity reaches 2,350 mAh g\(^{-1}\) at a rate of C/20, and after 1,000 cycles, over 1,160 mAh g\(^{-1}\) capacity can be reached. The average coulombic efficiency from the 500th to 1000th cycles of the Si pomegranate is as high as 99.87 %, indicating that SEI is very stable.

Chen et al. reported a facile approach to fabricate monodisperse hollow porous Si (HPSi) nanoparticles (ca. 120 nm) by the magnesiothermic reduction of hollow porous SiO\(_2\) (HPSiO\(_2\)) nanoparticles [60]. This step was followed by Ag coating the nanoparticle for conductivity enhancement (Fig. 14). The HPSi anode showed a high specific reversible capacity (3,762 mAh g\(^{-1}\)), good cycle stability (over 93 % capacity retention after 99 cycles), and high rate performance (over 2,000 mAh g\(^{-1}\) at a current density 4,000 mA g\(^{-1}\)).

Fig. 14 Scheme of preparing hollow porous Si nanoparticles [60]
3 Summary and Outlook

To sum up, we have briefly reviewed the recent advances in the studies on the Si anode materials. Although Si has an extremely high theoretical capacity, the bulk Si powders have demonstrated very poor electrochemical performance, due to the large volume variation during the charge and discharge processes, resulting in pulverization and delamination from the current collectors. Reducing the materials size to nanoscale is an effective method to solve this problem. For example, diverse nanostructured Si (0D, 1D, 2D, and 3D), Si/metal nanocomposites, and Si/C nanocomposites show improved battery performance. However, these methods cannot form stable SEI on the surface of Si, which is another important reason for the failure of Si anode. Experimental results show that surface modification is a practical method to control the formation of SEI. For example, hollow and yolk–shell structures of Si composites, coated with conductive materials, show excellent battery performance.

Although considerable advances have been achieved in the last decade to design and synthesize Si-based anode materials, for the practical application composite, several fundamental issues remain to be solved. First, nanomaterials have the genuine potential to make a significant impact on the performance of LIBs. However, they are certainly not a panacea. For example, coulombic efficiency of nanopowder is very low, because the high electrolyte/electrode surface area leads to more significant side reactions. Further, the density of nanopowder is generally less than the same material formed from micrometer-sized particles, which would reduce the volumetric energy density of battery. The problem mentioned above should be solved in the subsequent researches. Possible strategies include the following: (1) fabricating hierarchical nano/micrometer-sized structures to improve the tap density of electrode materials and building ultrathick electrodes to enhance the overall volumetric capacity [68–70]; (2) adopting surface coating to avoid unnecessary side reactions [71, 72]; and (3) using advanced manufacturing methods, such as 3D printing, to fabricate electrodes with 3D battery architecture by optimizing the structures of both anodes and cathodes [73, 74].
In addition, the electrolyte offers a promising field for more extensive research efforts. It is found that the electrolyte containing VC or FEC has been recognized to favor the formation of more stable SEI film. Furthermore, the fabrication cost of nano-structured Si remains high and needs to be reduced for its practical applications.

**Acknowledgments** This work is partially supported by Beijing High-level Oversea Talent Project and the strategic research grant “Laser interference process of silver nanostructures for surface enhanced Raman spectroscopy and environment application” (KZ2021410005001) of Beijing Nature Science Foundation, the P. R. China.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

**References**

1. B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices. Science 334(6058), 928–935 (2011). doi:10.1126/science.1212741
2. K. Kang, Y.S. Meng, J. Bréger, C.P. Grey, G. Ceder, Electrodes with high power and high capacity for rechargeable lithium batteries. Science 311(5763), 977–980 (2006). doi:10.1126/science.1122152
3. C.M. Park, J.H. Kim, H. Kim, H.J. Sohn, Li-alloy based anode materials for Li secondary batteries. Chem. Soc. Rev. 39(8), 3115–3141 (2010). doi:10.1039/b919877f
4. N.S. Choi, Z. Chen, S.A. Freunberger, X. Ji, Y.K. Sun, K. Amine, G. Yushin, L.F. Nazar, J. Cho, P.G. Bruce, Challenges facing lithium batteries and electrical double-layer capacitors. Angew. Chem. Int. Ed. 51(40), 9994–10024 (2012). doi:10.1002/anie.201204129
5. L. Wang, X. He, J. Li, W. Sun, J. Gao, J. Guo, C. Jiang, Nanostructured phosphorus composite as high-capacity anode materials for lithium batteries. Angew. Chem. Int. Ed. 51(36), 9034–9037 (2012). doi:10.1002/anie.201204591
6. A.N. Dey, Electrochemical alloying of lithium in organic electrolytes. J. Electrochem. Soc. 118(10), 1547–1549 (1971). doi:10.1149/1.1407783
7. X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B.W. Sheldon, J. Wu, Silicon-based nanomaterials for lithium-ion batteries: A review. Adv. Energy Mater. 4(1), 1–23 (2014). doi:10.1002/aenm.201300882
8. Y.X. Yin, L.J. Wan, Y.G. Guo, Silicon-based nanomaterials for lithium-ion batteries. Chin. Sci. Bull. 57(32), 4104–4110 (2012). doi:10.1007/s11434-012-0517-2
9. B. Gao, S. Sinha, L. Fleming, O. Zhou, Alloy formation in nanostructured silicon. Adv. Mater. 13(11), 816–819 (2001). doi:10.1002/1521-4095(200106)13:11<816::AID-ADMA816>3.0.CO;2-P
10. H. Li, X. Huang, L. Chen, G. Zhou, Z. Zhang, D. Ya, Y.J. Mo, N. Pei, The crystal structural evolution of nano-Si anode caused by lithium insertion and extraction at room temperature. Solid State Ionics 135(1–4), 181–191 (2000). doi:10.1016/S0167-2738(00)00362-3
11. P. Limthongkul, Y.I. Jang, N.J. Dudney, Y.M. Chiang, Electrochemically-driven solid-state amorphization in lithium-silicon alloys and implications for lithium storage. Acta Mater. 51(4), 1103–1113 (2003). doi:10.1016/S1359-6454(02)00514-1
12. A. Netz, R.A. Huggins, W. Weppner, The formation and properties of amorphous silicon as negative electrode reactant in lithium systems. J. Power Sources 119–121, 95–100 (2003). doi:10.1016/S0378-7753(03)00132-0
13. M.N. Obrovac, L. Christensen, Structural changes in silicon anodes during lithium insertion/extraction. Electrochem. Solid-State Lett. 7(5), A93–A96 (2004). doi:10.1149/1.1652421
14. T.D. Hatcher, J.R. Dahn, In-situ XRD and electrochemical study of the reaction of lithium with amorphous silicon. J. Electrochem. Soc. 151(6), A838–A842 (2004). doi:10.1149/1.1739217
15. J. Li, J.R. Dahn, An in situ X-ray diffraction study of the reaction of Li with crystalline Si. J. Electrochem. Soc. 154(3), A156–A161 (2007). doi:10.1149/1.2409862
16. J.H. Ryu, J.W. Kim, Y.E. Sung, S.M. Oh, Failure Modes of silicon powder negative electrode in lithium secondary batteries. Electrochem. Solid-State Lett. 7(10), A306–A309 (2004). doi:10.1149/1.1792242
17. C.J. Wen, R.A. Huggins, Chemical diffusion in intermediate phases in the lithium-silicon system. J. Solid-State Chem. 37(3), 271–278 (1981). doi:10.1016/0022-4596(81)90487-4
18. J.H. Kim, PhD Dissertation, Seoul National University, 2006
19. Y. Oumellal, N. Delpuech, D. Mazouzi, N. Dupré, J. Gaubicher, P. Moreau, P. Soudan, B. Lestriez, D. Guyomard, The failure mechanism of nano-sized Si-based negative electrodes for lithium ion batteries. J. Mater. Chem. 21(17), 6201–6208 (2011). doi:10.1039/c1jm10213c
20. C.K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, High-performance lithium battery anodes using silicon nanowires. Nat. Nanotechnol. 3(1), 31–35 (2008). doi:10.1038/nnano.2007.411
21. H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L. Hu, Y. Cui, Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. Nat. Nanotechnol. 7(5), 310–315 (2012). doi:10.1038/nnano.2012.35
22. P.G. Bruce, B. Scrosati, J.M. Tarascon, Nanomaterials for rechargeable lithium batteries. Angew. Chem. Int. Ed. 47(16), 2930–2946 (2008). doi:10.1002/anie.200702505
23. H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, A high capacity nano Si composite anode material for lithium rechargeable batteries. Electrochem. Solid-State Lett. 2(11), 547–549 (1999). doi:10.1149/1.1390899
24. H. Kim, M. Seo, M.-H. Park, J. Cho, A critical size of silicon nano-anodes for lithium rechargeable batteries. Angew. Chem. Int. Ed. 49(12), 2146–2149 (2010). doi:10.1002/anie.200906287
25. T. Song, J. Xia, J.H. Lee, D.H. Lee, M.S. Kwon, J.M. Choi, J. Wu, S.K. Doo, H. Chang, W. Park, D.S. Zang, H. Kim, Y.G. Huang, K.C. Hwang, J.A. Rogers, U. Paik, Arrays of sealed silicon nanotubes as anodes for Lithium ion batteries. Nano Lett. 10(5), 1710–1716 (2010). doi:10.1021/nl100086e
26. S. Ohara, J. Suzuki, K. Sekine, T. Takahara, A thin film silicon anode for Li-ion batteries having a very large specific capacity and long cycle life. J. Power Sources 136(2), 303–306 (2004). doi:10.1016/j.jpowsour.2004.03.014
27. K.L. Lee, J.Y. Jung, S.W. Lee, H.S. Moon, J.W. Park, Electrochemical characteristics of a-Si thin film anode for Li-ion rechargeable batteries. J. Power Sources 129(2), 270–274 (2004). doi:10.1016/j.jpowsour.2003.10.013
28. M.S. Park, G.X. Wang, H.K. Liu, S.W. Dou, Electrochemical properties of Si thin film prepared by pulsed laser deposition for lithium ion micro-batteries. Electrochim. Acta 51(25), 5246–5249 (2006). doi:10.1016/j.electacta.2006.01.045
29. J.P. Maranchi, A.F. Hepp, P.N. Kumta, High capacity, reversible silicon thin-film anodes for lithium-ion batteries. Electrochem.
61. J.S. Bridel, T. Azaïs, M. Morcrette, J.M. Tarascon, D. Larcher, Key parameters governing the reversibility of Si/Carbon/CMC electrodes for Li-ion batteries. Chem. Mater. 22(3), 1229–1233 (2010). doi:10.1021/cm902688w

62. L. Fransson, T. Eriksson, K. Edström, T. Gustafsson, J.O. Thomas, Influence of carbon black and binder on Li-ion batteries. J. Power Sources 101(1), 1–9 (2001). doi: 10.1016/S0378-7753(01)00481-5

63. S.S. Zhang, T.R. Jow, Study of poly (acrylonitrile-methyl methacrylate) as binder for graphite anode and LiMn$_2$O$_4$ cathode of Li-ion batteries. J. Power Sources 109(2), 422–426 (2002). doi:10.1016/S0378-7753(02)00107-6

64. D. Guy, B. Lestriez, D. Guyomard, New composite electrode architecture and improved battery performance from the smart use of polymers and their properties. Adv. Mater. 16(6), 553–557 (2004). doi:10.1002/adma.200306075

65. D. Mazouzi, B. Lestriez, L. Roue, D. Guyomard, Silicon composite electrode with high capacity and long cycle life. Electrochem. Solid-State Lett. 12(11), A215–A218 (2009). doi:10.1149/1.3212894

66. A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C.F. Huebner, T.F. Fuller, I. Luzinov, G. Yushin, Toward efficient binders for Li-ion battery Si-based anodes: polyacrylic acid. ACS Appl. Mater. Inter. 2(11), 3004–3010 (2010). doi:10.1021/am100871y

67. I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, A major constituent of brown algae for use in high-capacity Li-ion batteries. Science 334(6052), 75–79 (2011). doi:10.1126/science.1209150

68. M.Y. Wu, J.E.C. Sahisch, X.Y. Song, A.M. Minor, V.S. Battaglia, G. Liu, In situ formed Si nanoparticle network with micronsized Si particles for lithium-ion battery anodes. Nano Lett. 13(11), 5397–5402 (2013). doi:10.1021/nl402953h

69. P.J. Zhang, L.B. Wang, J. Xie, L.W. Su, C.A. Ma, Micro/nano-complex-structure SiOx-PANI-Ag composites with homogeneously-embedded Si nanocrystals and nanopores as high-performance anodes for lithium ion batteries. J. Mater. Chem. A 2(11), 3776–3782 (2014). doi:10.1039/c3ta14498d

70. H.L. Zhang, Y. Zhang, X.G. Zhang, F. Li, C. Liu, J. Tan, H.M. Cheng, Urchin-like nano/micro hybrid anode materials for lithium ion battery. Carbon 44(13), 2778–2784 (2006). doi:10.1016/j.carbon.2006.03.029

71. M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, Carbon-coated Si as a lithium-ion battery anode material. J. Electrochem. Soc. 149(12), A1598–A1603 (2002). doi:10.1149/1.1518988

72. H.Y. Lee, S.M. Lee, Carbon-coated nano-Si dispersed oxides/graphite composites as anode material for lithium ion batteries. Electrochem. Commun. 6(5), 465–469 (2004). doi:10.1016/j.elecom.2004.03.005

73. A.J. Lopes, E. MacDonald, R.B. Wicker, Integrating stereolithography and direct print technologies for 3D structural electronics fabrication. Rapid Prototyping J. 18(2), 129–143 (2012). doi:10.1108/13552541211212113

74. L.T. Le, M.H. Ervin, H. Qu, B.E. Fuchs, W.Y. Lee, Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide. Electrochem. Commun. 13(4), 355–358 (2011). doi:10.1016/j.elecom.2011.01.023