From Intercalation to Alloying Chemistry: Structural Design of Silicon Anodes for the Next Generation of Lithium-ion Batteries

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ABSTRACT Lithium-ion batteries, first commercialized in 1991, have been thriving for the past 30 years and become an important basis for portable electronics and electric vehicles. However, this first generation of lithium-ion batteries built on the intercalation materials has limited energy density and can not meet the increased demand of various applications. Thus, a transition from intercalation to alloying chemistry for anodes is on call. Silicon, as the most attractive alloying anode material, has been on the research focus for next-generation high-energy density battery. Alloying mechanism benefits silicon a large capacity while brings silicon the challenge of volume expansion. This article discusses the structure design strategies to address the issues of large volume change and interface instability.

Keywords: silicon anode, alloying chemistry, structural design, lithium-ion battery.

1 INTRODUCTION

Since its appearance on the market in 1991, the lithium-ion battery (LIB) has been the major power source driving the rapid digitalization of our daily life[1-3]. Three scientists, John B. Goodenough, M. Stanley Whittingham and Akira Yoshino, won the 2019 Nobel Prize in chemistry for their outstanding contributions on lithium-ion batteries (LIBs). Established on their studies[5-7], the first generation of LIBs composed of graphite anodes and Li transition-metal oxide cathodes has been well developed over the past 30 years and dominates the current battery markets. However, these first-generation electrodes are all classified as intercalation materials, which can only provide limited space for the intercalation reaction of lithium ions and further limit the energy density below ~300 Wh/kg in practical use[8, 9]. To sustain the energy density demand significantly beyond 300 Wh/kg for electric vehicles[10, 11], the next generation of LIBs call for a paradigm shift from intercalation chemistry to alloying chemistry[12].

2 PROGRESS

Silicon, as an alloying material with lithium, is among the most prominent anode materials for next-generation batteries. With Li ions alloying with silicon atoms, one silicon atom can host up to 4.4 Li-ions by alloying chemistry compared to each carbon just hosting 1/6 Li ions in graphite anodes by intercalation chemistry (Fig. 1a, 1b)[13-15]. This results in ultra-high theoretical capacity of silicon anode (4200

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mAh·g^{-1}), over 10 times higher than that of graphite anode (375 mAh·g^{-1})[13-17]. However, the increased capacity in alloying chemistry is accompanied with the substantial volumetric change. With > 300% volume expansion during lithiation, silicon anode experiences cracks and even pulveriza-tion during cycling, leading to repeated SEI formation and loss of electronic contact with both conductive materials and current collectors[17, 18]. Over the past decade, there have been significant efforts on Si material design to improve its cyclability.

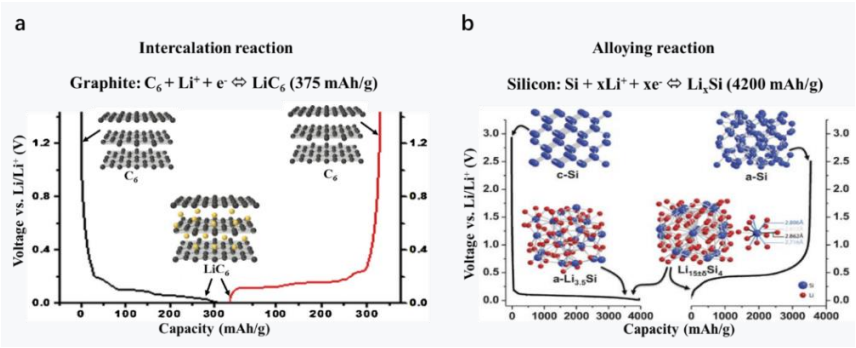

Fig. 1. Schemes of the intercalation chemistry and alloying chemistry. The structural transformations and voltage profiles of intercalation graphite (a) and alloying silicon (b)[15]

Currently, three classes of solutions focusing on the structural designs have been explored to address the cyclability issue of silicon anode: 1. Designs of nanostructured silicon anodes; 2. Development of advanced binders for silicon anodes; 3. Prelithiation of silicon anode to compensate the initial lithium loss. Our group alone has had 12 generations of nano-structure designs of silicon anodes[13, 19, 20]. Starting from shrinking silicon to nano-scale, pulverization of Si is avoided to be benefited from particle size below critical fracture size (Fig. 2a)[16, 21]. Then, nano-scale Si is encapsulated by a series of mechanical strong layers to stabilize the Si interface and reduce SEI repeating formation (Fig. 2b), moving from insulated SiO_2[22] to conductive amorphous carbon[23], and graphene cage[24]. Meanwhile, internal void space is designed into the Si nanostructure to accommodate the volume change and further avoid SEI breaking at the interface (Fig. 2c)[25, 26]. Besides the nanos-tructure design, advanced binders are also developed to strongly bind Si particles together rather than relying on the weak van der Waals forces provided by the conventional poly-(vinylidene fluoride) binder (Fig. 2d, 2e), including conducting hydrogel frame-work[27] and self-healing coating[28]. Prelithiation, aimed at compensating the lithium loss in the first cycle caused by SEI formation, is important for the development of Si anodes (Fig. 2f, 2g). Two preli-thiation approaches of electrochemical shorting[29, 30] and Li_xX prelithiation reagents[31, 32] are developed and successfully improve the 1st cycle CE from con-ventional 70～80% to 100%.

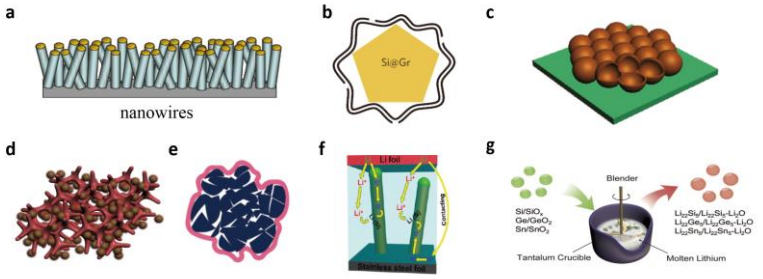

Fig. 2. Designs of nanostructured silicon: silicon size reduced to nano-scale (a)[16], silicon particle encapsulation (b)[24], and internal void space in designed structures (c)[25]. Advanced binders: hydrogel framework (d)[27] and self-healing coating (e)[28]. Prelithiation approaches: electrochemical method (f)[29] and Li_xX prelithiation reagents (g)[32]

3 CONCLUSION

In summary, to overcome the energy density limit of intercalation chemistries, silicon anodes, with ultra-high theoretical capacity benefited from alloy-ing mechanism, show outstanding potential to impel LIBs from intercalation to alloying chemistry. Though silicon anodes suffer from poor cyclability due to drastic volume expansion, tremendous efforts have been devoted to the issue and three classes of structure designs have been explored to com-prehensively improve the cyclability from different aspects. With cycle performance improvement to hundreds or even a thousand stable cycles, silicon opens up a bright future of next-generation high-energy density batteries and more future efforts are expected in low-cost and environmentally friendly large-scale production.

REFERENCES

(1) Armand, M.; Tarascon, J. M. Building better batteries. *Nature* **2008**, 451, 652.

(2) Evarts, E. E. To the limits of lithium. *Nature* **2015**, 526, S93.

(3) Xu, K. Electrolytes and interphasial chemistry in Li ion devices. *Energies* **2010**, 3, 135–154.

(4) Whittingham, M. S.; Panella, J. A. Formation of stoichiometric titanium disulfide. *Mater. Res. Bull.* **1981**, 16, 37–45.

(5) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. Li_xCoO_2 ($0<x<1$): a new cathode material for batteries of high energy density. *Mater. Res. Bull.* **1980**, 15, 783–789.

(6) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* **1997**, 144, 1188–1194.

(7) Yoshino, A.; Sanechika, K.; Nakajima, T. U. S. Patent No. 4,668,595. Washington, DC: U.S. Patent and Trademark Office. **1987**.

(8) Goodenough, J. B.; Kim, Y. Challenges for rechargeable Li batteries. *Chem. Mater.* **2009**, 22, 587–603.

(9) Whittingham, M. S. Ultimate limits to intercalation reactions for lithium batteries. *Chem. Rev*. **2014**, 114, 11414–11443.

(10) Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Amine, K. Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries. *Nat. Nanotech.* **2018**, 13, 715.

(11) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Meng, Y. S. Pathways for practical high-energy long-cycling lithium metal batteries. *Nat. Energy* **2019**, 4, 180–186.

(12) Yoo, H. D.; Markevich, E.; Salitra, G.; Sharon, D.; Aurbach, D. On the challenge of developing advanced technologies for electrochemical energy storage and conversion. *Mater. Today* **2014**, 17, 110–121.

(13) Liu, Y.; Zhou, G.; Liu, K.; Cui, Y. Design of complex nanomaterials for energy storage: past success and future opportunity. *Acc. Chem. Res.* **2017**, 50, 2895–2905.

(14) Ma, D.; Cao, Z.; Hu, A. Si-based anode materials for Li-ion batteries: a mini review. *Nano-Micro. Lett.* **2014**, 6, 347–358.

(15) Zamfir, M. R.; Nguyen, H. T.; Moyen, E.; Lee, Y. H.; Pribat, D. Silicon nanowires for Li-based battery anodes: a review. *J. Mater. Chem. A* **2013**, 1, 9566–9586.

(16) Chan, C. K.; Peng, H.; Liu, G.; McIlwrath, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y. High-performance lithium battery anodes using silicon nanowires. *Nat. Nanotech.* **2008**, 3, 31.

(17) Wu, H.; Cui, Y. Designing nanostructured Si anodes for high energy lithium ion batteries. *Nano Today* **2012**, 7, 414–429.

(18) Su, X.; Wu, Q.; Li, J.; Xiao, X.; Lott, A.; Lu, W.; Wu, J. Silicon-based nanomaterials for lithium-ion batteries: a review. *Adv. Energy Mater.* **2014**, 4, 1300882.

(19) Wang, J.; Liao, L.; Li, Y.; Zhao, J.; Shi, F.; Yan, K.; Cui, Y. Shell-protective secondary silicon nanostructures as pressure-resistant high-volumetric-capacity anodes for lithium-ion batteries. *Nano Lett.* **2018**, 18, 7060–7065.

(20) Wang, J.; Liao, L.; Lee, H. R.; Shi, F.; Huang, W.; Zhao, J.; Cui, Y. Surface-engineered mesoporous silicon microparticles as high-Coulombic-efficiency anodes for lithium-ion batteries. *Nano Energy* **2019**, 61, 404–410.

(21) Cui, L. F.; Ruffo, R.; Chan, C. K.; Peng, H.; Cui, Y. Crystalline-amorphous core-shell silicon nanowires for high capacity and high current battery electrodes. *Nano Lett.* **2008**, 9, 491–495.

(22) Wu, H.; Chan, G.; Choi, J. W.; Ryu, I.; Yao, Y.; McDowell, M. T.; Cui, Y. Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nature Nanotech.* **2012**, 7, 310.

(23) Liu, N.; Wu, H.; McDowell, M. T.; Yao, Y.; Wang, C.; Cui, Y. A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes. *Nano Lett.* **2012**, 12, 3315–3321.

(24) Li, Y.; Yan, K.; Lee, H. W.; Lu, Z.; Liu, N.; Cui, Y. Growth of conformal graphene cages on micrometre-sized silicon particles as stable battery anodes. *Nat. Energy* **2016**, 1, 15029.

(25) Yao, Y.; McDowell, M. T.; Ryu, I.; Wu, H.; Liu, N.; Hu, L.; Cui, Y. Interconnected silicon hollow nanospheres for lithium-ion battery anodes with long cycle life. *Nano Lett.* **2011**, 11, 2949–2954.

(26) Lu, Z.; Liu, N.; Lee, H. W.; Zhao, J.; Li, W.; Li, Y.; Cui, Y. Nonfilling carbon coating of porous silicon micrometer-sized particles for high-performance lithium battery anodes. *ACS Nano* **2015**, 9, 2540–2547.

(27) Wu, H.; Yu, G.; Pan, L.; Liu, N.; McDowell, M. T.; Bao, Z.; Cui, Y. Stable Li-ion battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles. *Nat. Commun.* **2013**, 4, 1943.

(28) Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. *Nat. Chem.* **2013**, 5, 1042.

(29) Liu, N.; Hu, L.; McDowell, M. T.; Jackson, A.; Cui, Y. Prelithiated silicon nanowires as an anode for lithium ion batteries. *ACS Nano* **2011**, 5, 6487–6493.

(30) Kim, H. J.; Choi, S.; Lee, S. J.; Seo, M. W.; Lee, J. G.; Deniz, E.; Choi, J. W. Controlled prelithiation of silicon monoxide for high performance lithium-ion rechargeable full cells. *Nano Lett.* **2015**, 16, 282–288.

(31) Zhao, J.; Lu, Z.; Liu, N.; Lee, H. W.; McDowell, M. T.; Cui, Y. Dry-air-stable lithium silicide-lithium oxide core–shell nanoparticles as high-capacity prelithiation reagents. *Nat. Commun.* **2014**, 5, 5088.

(32) Zhao, J.; Sun, J.; Pei, A.; Zhou, G.; Yan, K.; Liu, Y.; Cui, Y. A general prelithiation approach for group IV elements and corresponding oxides. *Energy Storage Mater.* **2018**, 10, 275–281.