New Sn-Cu/C composite anode materials with high cyclic stability for Lithium ion battery

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Abstract. Sn-Cu/C anode material with core-shell structure was obtained, in which the crystallization of Sn-Cu alloy was weakened. The results show that the weakening of the crystallization decreases the binding force on the interstitial sites and is benefit for the inserting and escaping of the lithium ions. And “Core-shell” structure design can effectively disperse the Sn-Cu alloy particles and leave room for the volume expansion of Sn-Cu alloy. Furthermore, the volume change is controlled within the “core-shell” structure. Through these methods, Sn-Cu/C composite anode material with high cyclic stability was obtained, whose reversible capacity was 450 mAh g⁻¹, without any capacity loss till the 200th cycle. The volume change and irreversible capacity loss of Sn-based anode materials can be partly solved by the weakening of the crystallization and “core-shell” structure design.

Keywords: Lithium ion battery, anode, Sn-Cu/C composite, modification

1. Introduction
Because of the high-speed development of electronic products and electric vehicle (EV) [1], high energy density and long cycle life are required for new generation lithium ion battery. And current commercial anode material (graphite) is considered as one of the bottlenecks in the development of lithium ion battery for low theoretical capacity [2]. Sn-based alloy materials are one of the most popular fields as the substitution anode material. But for the considerable volume change, Sn-based anode materials exhibit poor cyclic stability [3-5].

To buffer the volume change, synthesizing Sn-M (active-active/inactive) systems is considered as a useful way in improving the cyclic stability [6-12]. But adding another component(active or inactive) will only decrease the volume expansion ratio of Sn, which can’t completely solve the volume change. To make the Sn-M alloys become commercial anode materials, more modifications are required [13-14].

In this paper, the Sn-Cu alloy is modified by the weakening of the crystallization. And the cyclic stability is further improved by “core-shell” structure design. The crystallization degree is weakened by ball milling, to decrease the binding force from the crystal on the interstitial sites and benefit for the lithium intercalation/deintercalation. And through “core-shell” structure design, room is left for the possible volume change of Sn-Cu alloy and the volume change will be controlled within the core layer. Through these modifications, we obtain a new Sn-based anode material with high cyclic stability.
2. Experimental
Sn-Cu alloy sample synthesis: Sn-Cu alloy was synthesized by solution chemical reduction method. SnCl₂ and chlorides of Cu was reduced by NaBH₄, in which Sn:Cu=15:85 (atomic ratio). And NaOH was added (till pH>12) to slow the speed of the reactions. The samples were washed by de-ionized water and vacuum dried at 70 °C for 24 h.

Weakening of the crystallization: The Sn-Cu alloy sample was ball-milled in ethanol with ball material ratio of 20:1, and sampled at 5 h, 10 h, 15 h and 20 h.

“Core-shell” structure design: The Sn-Cu alloy (20 h ball-milled) sample was ball-milled again with graphite for 5 h, in which citric acid was added. Then the sample was dried by spray drying and heated under 460 °C for 4 h and under 600 °C for 6 h. The preparation process is shown in figure 1.

![Figure 1. Diagrammatic sketch of the “core-shell” structure design process.](image)

3. Result and Analysis

3.1. Weakening of the crystallization

![Figure 2. XRD patterns of the Sn-Cu samples after ball-milling.](image)

Figure 2 shows the XRD patterns of the Sn-Cu alloy samples after ball-milling. According to the results, the sites of the characteristic peaks are the same among the samples. Therefore, the components of the Sn-Cu samples haven’t changed after ball-milling. For the Sn-Cu (10H) sample, the characteristic peaks (double peaks) at 2θ=42° become single peak, also for the characteristic peaks at 2θ=51°. According to the intensity of the characteristic peaks, as the increasing of ball-milling, the crystallization degree of the sample become weaker and weaker. After ball-milled for 20 h, the Sn-Cu sample become non-crystallization.
Figure 3 shows the morphology of the Sn-Cu samples before and after ball-milling. According to figure 3(a), the Sn-Cu sample is nano-scale and reunion into particles of 2 µm. Figure 3(b) shows that after 10 h of ball-milling, the Sn-Cu sample become smaller single-particle size and more serious reunion. However, as the increasing of ball-milling, the particle size of the Sn-Cu sample decrease quickly. As shown in figure 3(c), after 15 h of ball-milling, small part of flocculent morphology even occur. And after 20 h of ball-milling, the sample all become flocculent.

Figure 4 shows the charge and discharge capacity curve of the Sn-Cu alloy samples after ball milling. According to the results, after 10 h of ball-milling, the charge and discharge specific capacity of the Sn-Cu sample decrease more than 100 mAh·g⁻¹, without any improvement of the cyclic stability. However, as the increasing of ball milling, the cyclic stability is gradually improved. And the best cyclic performance is obtained after 20 h of ball-milling.
Figure 4. Discharge (a) and charge capacity (b) curves of the Sn-Cu samples after ball milling.

According to the morphology of the Sn-Cu samples, 10 h of ball-milling can only decrease the size of the particles and lead to more serious reunion. As a result, the increasing of reunion is not conducive to the infiltration of the electrolyte and lead to more irreversible capacity loss. This is the reason why 10 h of ball-milling can’t improve the cyclic performance and lead to higher capacity loss. According to the XRD patterns and the morphology, the crystallization degree of the sample become weaker and weaker as the increasing of ball-milling. And flocculent morphology occur after 15 h of ball-milling. It should be interpreted that the flocculent morphology provide room for the volume change of Sn-Cu alloy and benefit for inserting and escaping of lithium ions.

To study the relationship between the crystallization degree and lithium intercalation potential, cyclic voltammogram tests are carried out on the Sn-Cu samples. The test results are showed in figure 5. According to figure 5 (a) and (b), the characteristic peaks higher than 1.5V disappear after ball-milling. Meanwhile, several lithium intercalation peaks occur below 1.0V. It can be interpreted that after the weakening of the crystallization, the binding force on the interstitial sizes decrease, resulting in the decrease of the lithium intercalation formation energy, which present as lower lithium intercalation potential. As shown at figure 5(c), the reversible capacity below 1.0V is activated as the increasing of the cycle number. It should be interpreted that the increasing of reunion is not conducive to the infiltration of the electrolyte and the electrolyte continuously infiltrate with the increasing of the cycle number. According to figure 5(e), after 20h of ball-milling, although the capacity below 0.5V still show trend of increasing, the values difference among the cycles is small and the cyclic voltammogram curves nearly coincide with each other. The Sn-Cu sample after 20 h of ball-milling show the best cyclic stability.
3.2. “core-shell” structure design

Figure 6 shows the surface and profile morphology of the sample after “core-shell” structure design. According to figure 6(a) and (b), the shape of the sample is spherical with diameter of less than 10µm. According to figure 6(c), the Sn-Cu alloy particles stay at the surface of the graphite, which is nano-scale. And shells formed by the citric acid cover the whole particle. The structure of the sample accords with that of the target product model. The effective dispersion of Sn-Cu alloy particles will leave room for the
volume expansion of the Sn-Cu alloy. And the shell will control the expansion within the “core-shell” structure.

Figure 7. Charge and discharge capacity curve of the Sn-Cu samples with “core-shell” structure.

Figure 7 shows the charge and discharge capacity curve of the Sn-Cu samples with “core-shell” structure. According to the cyclic efficiency curve, although the sample still show large initial irreversible capacity (the initial cyclic efficiency is only 68%), the sample exhibit high cyclic stability. The charge capacity stay at 450 mAh g$^{-1}$ from the 38th cycle and without any capacity loss till the 200th cycle.

After weakening of the crystallization and “core-shell” structure design, the Sn-Cu/C composite anode material exhibit high cyclic stability. The results shown in figure 7 prove that the volume change and irreversible capacity loss of Sn-based anode materials can be partly solved by the weakening of the crystallization and “core-shell” structure design. And the preparation method is simple and low cost.

4. Conclusions
In this paper, by the ways of weakening of the crystallization and “core-shell” structure design, Sn-Cu/C composite with high cyclic stability was obtained. Conclusions are showed as following.

The weakening of the crystallization will decrease the binding force on the interstitial sites and benefit for the inserting and escaping of the lithium ions, which is presented as the decrease of lithium intercalation potential.

“Core-shell” structure design can effectively disperse the Sn-Cu alloy particles and leave room for the volume expansion of Sn-Cu alloy. Furthermore, the volume change is controlled within the “core-shell” structure. Therefore, the way of “core-shell” structure design can dramatically improve the cyclic stability of Sn-Cu alloy anode material.

In this paper, Sn-Cu/C composite anode material with high cyclic stability is obtained, whose reversible capacity was 450 mAh g$^{-1}$, without any capacity loss till the 200th cycle.

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References
[1] Fotouhi A, Auger D J, Propp K, Longo S and Wild M 2016 Renewable & Sustainable Energy Reviews 56 1008–1021
[2] Bai X, Yu Y, Kung H H, Wang B and Jiang J 2016 Journal of Power Sources 306 42–48
[3] Huang Y G, Pan Q C, Wang H Q, Yan Z X, Yang G H and Chen Y H 2015 Ceramics International 42(3) 4586–4593
[4] Yan Y, Ben L B, Zhan Y and Huang X 2016 *Electrochimica Acta* **187** 186–192
[5] Agubra V A, Zuniga L, Garza D D L, Gallegos L, Pokhrel M and Alcoutlabi M 2016 *Solid State Ionics* **286** 72–82
[6] Wei L, Zhang K, Tao Z and Chen J 2015 *Journal of Alloys & Compounds* **644** 742–749
[7] Uysal M, Cetinkaya T, Alp A and Akbulut H 2015 *Journal of Alloys & Compounds* **645(2)** 235–242
[8] Wu X, Zhang S, Qi T, Fang H, Liu G and Xing Y 2016 *Journal of Power Sources* **307** 753–761
[9] Yui Y, Hayashi M, Hayashi K and Nakamura J 2016 *Solid State Ionics* **288** 219–223
[10] Schmuelling G, Oehl N, Fromm O, Knipper M, Kolny-Olesiak J and Plaggenborg T 2016 *Electrochimica Acta* **196** 597–602
[11] Liu C J, Xue F H, Huang H, Yu X H, Xie C J and Shi M S 2014 *Electrochimica Acta* **129(10)** 93–99
[12] Guo W, Li F, Duan X and Ma J 2016 *Materials Letters* **166** 210–214
[13] Cui C, Liu X, Wu N and Sun Y 2015 *Materials Letters* **143** 35–37
[14] Zhang J, Ma Z, Jiang W, Zou Y, Wang Y and Lu C 2016 *Journal of Electroanalytical Chemistry* **767** 49–55