

Optimal design of hollow core–shell structural active materials for lithium ion batteries



Wenjuan Jiang^a, Tingting Li^a, Zengsheng Ma^{a,*}, Jianguo Lin^{a,*}, Chunsheng Lu^b

^aKey Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, and School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, Hunan, China

^bDepartment of Mechanical Engineering, Curtin University, Perth, WA 6845, Australia

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ABSTRACT

To mitigate mechanical and chemical degradation of active materials, hollow core–shell structures have been applied in lithium ion batteries. Without embedding of lithium ions, the rigid coating shell can constrain the inward volume deformation. In this paper, optimal conditions for the full use of inner hollow space are identified in terms of the critical ratio of shell thickness and inner size and the state of charge. It is shown that the critical ratios are 0.10 and 0.15 for Si particle and tube (0.12 and 0.18 for Sn particle and tube), and above which there is lack of space for further lithiation.

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1. Introduction

Lithium ion batteries (LIBs) with the highest energy densities among all rechargeable batteries have been widely used in portable electronic devices such as cell phones, digital cameras, laptops, and tablet E-book readers [1]. To further improve their energy densities, cycle lives and rate capabilities are nowadays the primary requirements for LIBs to be suitable for advanced applications [2–5]. Interestingly, all the relevant research works are more or less related to the lithium ion diffusion-induced stress evolution in electrode materials during electrochemical cycling [6,7].

Stress arising in electrode materials is mainly due to changes of the lattice dimension, crystal structure, and phase transformation in crystalline and amorphous phases accompanying insertion/removal reactions [8,9]. These can induce a large volume deformation of active materials, against the constraining effects of inactive regions of electrodes or other parts of the cell and mismatches between regions with different Li⁺ concentrations [10,11]. There is mounting evidence that the deformation and stress evolution are the bottleneck toward enlarging the capacity of active materials. Though these anode materials (e.g., Si, Sn and Al) have high theoretical specific capacities (3 to 10 times more than the presently used graphitic materials), their recyclability is poor because of large volume deformation (up to ~400%) in the lithiation process [12,13].

Extensive investigations have been carried out toward modeling the stress evolution with lithium ion diffusion [14–17]. For example, Liu et al. calculated the hoop stress curve with center distance of hollow core–shell nanoparticle using finite element analysis and found out that the center region of a hollow nanoparticle is in tension while the interface layer is in compression [18]. Golmon et al. established a mechanical–chemical coupling model based on the elastic theory, where axisymmetric spherical particles are assumed to be isotropous and deformation during lithiation is elastic without consideration of surface stress [19]. However, to take into account of plastic deformation of electrode materials that occurs during lithiation, Brassart and Suo divided the deformation of electrode materials during imbedding in/taking out lithium-ions into the elastic and inelastic strains, and then suggested a mechanical–chemical coupling model [17]. Recently, based on a theoretical model, we calculated the critical sizes of nano thin films, nanoparticles and nanowires, below which there are no cracks in these nanomaterials [20,21].

Here, a key issue is that how much of the inner space is optimal for hollow core–shell structures. In this paper, we work out such a relationship between the critical space of hollow core–shell structures and the charge state, which can provide guidance for structural design of active materials.

2. Theoretical framework

A hollow core–shell sphere/tube with a shell thickness of D and an inner radius of h is taken as a reference model, as shown

* Corresponding authors. Tel./fax: +86 731 58293577.

E-mail addresses: zsma@xtu.edu.cn (Z. Ma), lin_j_g@xtu.edu.cn (J. Lin).

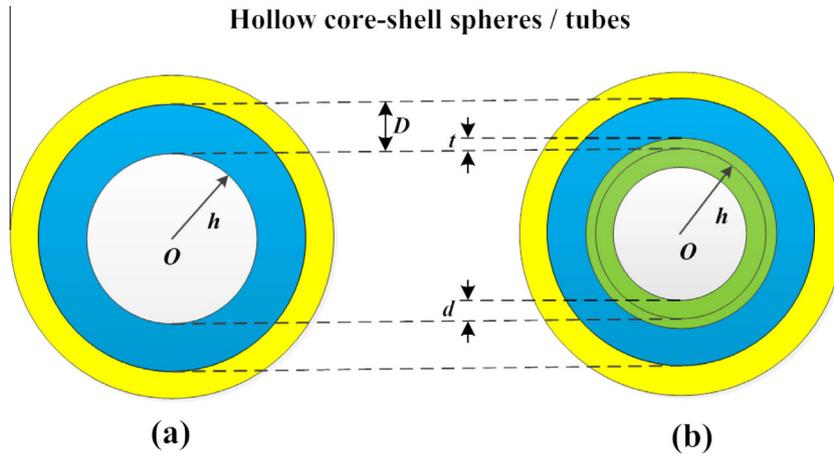


Fig. 1. Illustration of (a) the reference state, where the hollow core-shell material is lithium-free; and (b) the current state, where the hollow material is partially lithiated.

in Fig. 1(a). For simplification of analysis, the outer shell is assumed to be rigid, which can promote active materials to expand inwards. In the case of uniform lithiation, the reaction interface remains to be spherical. As shown in Fig. 1(b), a two-layer structure appears during lithiation in active materials with rich and free Li⁺ states. At a given time, the thickness of lithiation layer is defined as $d + t$, and then the volumetric swelling ratio β can be written as

$$\beta = \frac{(h + t)^\chi - (h - d)^\chi}{(h + t)^\chi - h^\chi}, \quad (1)$$

where χ is the Euclidean dimension with the values of 3 and 2 for sphere and tube, respectively.

As for the charge of state (SOC), it is obvious that 0 and 1 represent the lithium-free and fully lithiated states. Here, SOC can be derived according to $SOC = Q'/Q$, with Q' and Q being the charges for a given charge stage and the full charge stage, respectively. For a given state during the partially uniform lithiation of active materials, the Li ion concentration C is a constant. Hence, SOC can be determined by the volume ratio before and after being fully charged in a specimen, that is, $SOC = CV'/CV = V'/V$, where V' and V are the consumed volumes of active materials for the given and full charge stages, respectively. Then, SOC can be represented as

$$SOC = \frac{(h + t)^\chi - h^\chi}{(h + D)^\chi - h^\chi}. \quad (2)$$

As lithiation of materials goes on, the hollow parts are constantly filled with Li-alloy until the thickness of lithiation layer reaches the inner radius (i.e., $d = h$), and Eq. (1) becomes

$$\beta = \frac{(h + t)^\chi}{(h + t)^\chi - h^\chi}. \quad (3)$$

Similarly, the relationship between SOC and the ratio of $\frac{D}{h}$ can be obtained by combining Eqs. (2) and (3), that is

$$\frac{D}{h} = \left(\frac{1}{(\beta - 1)SOC} + 1 \right)^{\frac{1}{\chi}} - 1. \quad (4)$$

It is obvious that the ratio D/h is related to the SOC and volumetric swelling ratio β . Let us use Si and Sn to discuss their critical inner space curves.

3. Results and discussion

It is known that in Si materials, a Si atom can adsorb 4 Li ions (i.e., the volumetric expansion ratio $\beta = 4$) [16], and Eq. (4) can be rewritten as

$$\frac{D}{h} = \left(\frac{1}{3SOC} + 1 \right)^{\frac{1}{3}} - 1. \quad (5)$$

For Sn materials, $\beta = 3.5$ [22] and Eq. (4) becomes

$$\frac{D}{h} = \left(\frac{1}{2.5SOC} + 1 \right)^{\frac{1}{2}} - 1. \quad (6)$$

As shown in Fig. 2, the full lithiation in Si materials occurs when the inner space is completely filled, where the critical ratio D/h is equal to 0.10 and 0.15 for sphere and tube structures, respectively. That is, the critical curve can be considered as a criterion for hollow

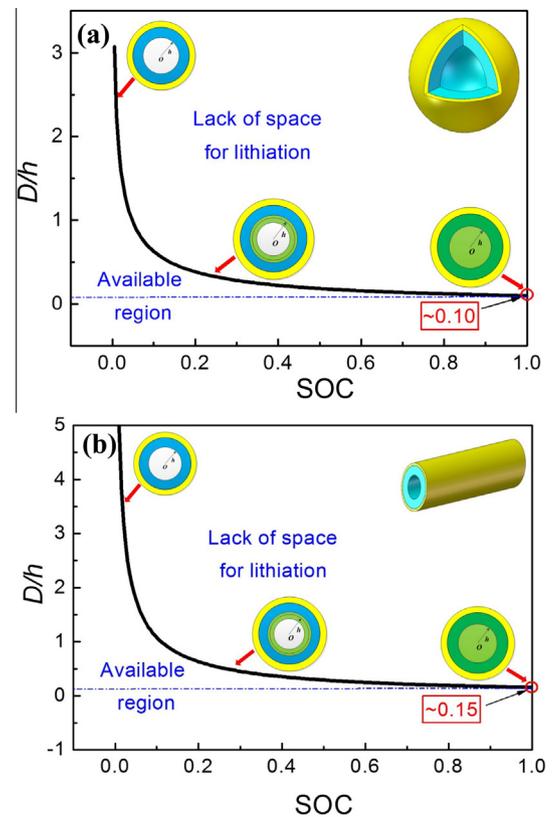


Fig. 2. The critical ratio D/h for Si materials with a structure of (a) sphere and (b) tube.

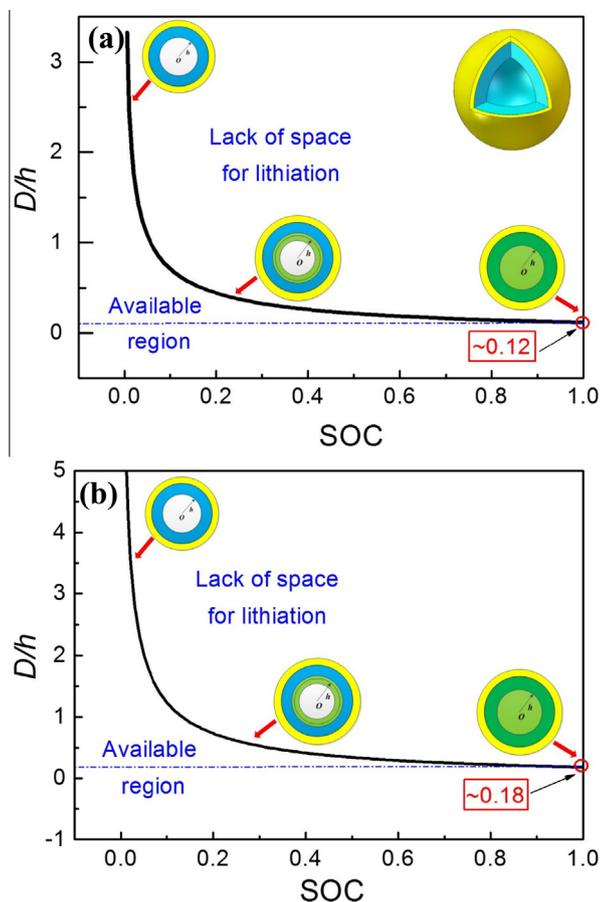


Fig. 3. The critical ratio D/h for Sn materials with a structure of (a) sphere and (b) tube.

core-shell structural materials, below which the inner space is still available after full-lithiation and above which there is lack of space for lithiation.

As shown in Fig. 3, the critical ratio D/h for Sn hollow core-shell sphere/tube is 0.12 and 0.18 for sphere and tube structures, respectively. Therefore, if the ratio D/h is more than the critical value, the inner space is filled before full-lithiation; and in contrast, the inner space cannot be effectively utilized in the case of a smaller ratio D/h that is below the critical value.

4. Conclusions

In summary, a theoretical model has been proposed to investigate hollow core-shell sphere/tube structures in LIBs. It is shown that the critical ratio (D/h) depends on the charge state and volume expansion. For Si sphere and tube, the critical ratios are 0.10 and 0.15, and for Sn sphere and tube, the critical ratios are 0.12 and 0.18. It is expected that this work provides a general approach to optimal design of hollow core-shell structures for LIBs.

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