Electronic Supplementary Information for

Modeling of Li diffusion in nanocrystalline Li-Si anode material

F.W. Tang, X.Y. Song*, C. Hou, X.M. Liu, H.B. Wang and Z. R. Nie

College of Materials Science and Engineering, Key Laboratory of Advanced Functional Materials, Education Ministry of China, Beijing University of Technology, Beijing 100124, China

* To whom correspondence should be addressed. E-mail: xysong@bjut.edu.cn

1. Parameters and figure concerning equation (2)

$$\Delta V = \frac{d^3-(d-h)^3}{d^3} / (A + B \cdot d^C) \qquad (2)$$

In equation (2), ($A + B \cdot d^c$) equates to ρ_b/ρ_i, where ρ_b and ρ_i are the spatial distribution densities of atoms in the nanograin interior and at the nanograin boundary, respectively. It is used to describe the relative atomic density at the grain boundaries. The thickness of the grain boundary *h* may vary from 0.5 to 2 nm in the nanocrystalline alloys, here we define the thickness of the grain boundary in the Li-Si nanocrystalline as 0.8 nm in the present work. The relationship between the excess volume and nanograin size is demonstrated in Fig. S1, with the relative atomic density at the grain boundaries, ρ_b/ρ_i, as a function of grain size.

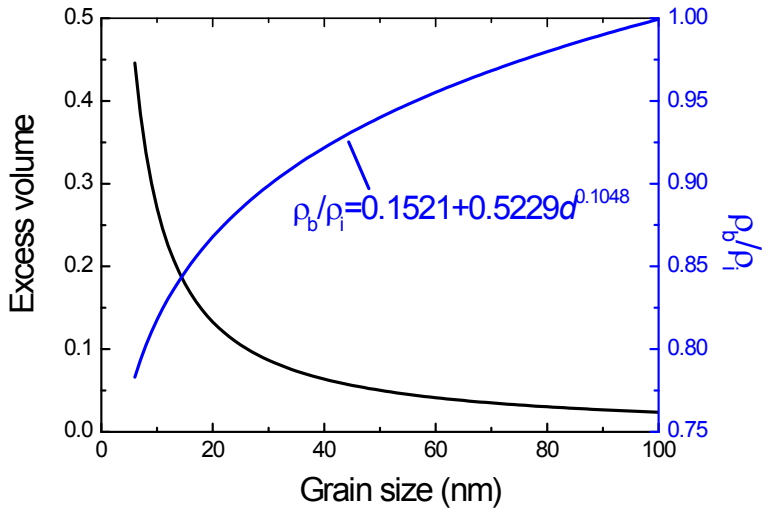


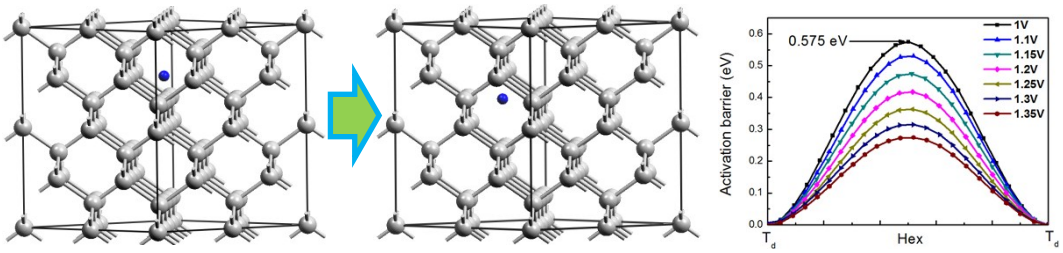
Fig. S1. The relationship between the excess volume and nanograin size for the nanocrystalline Li-

Si alloy, with the relative distribution density of atoms at the nanograin boundary ρ_b/ρ_i as a function of the grain size.

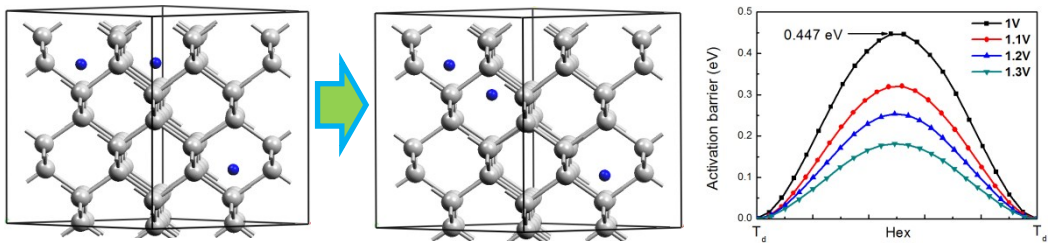
2. Calculation details for Figure 2

The data for the jump distance and activation barrier in Fig. 2 were obtained from our DFT calculations. For each Li concentration in Fig. 2, a number of initial geometrical configurations were considered and fully relaxed to the stable structures. We selected those corresponding to the lowest energy for calculations of the activation barrier and jump distance and also the expanded unit cells with different volumes (the lattice parameters were fixed and the internal atomic coordinates could be relaxed) using the NEB method. The schematic diagrams and the related details in Fig. 2 are shown as below.

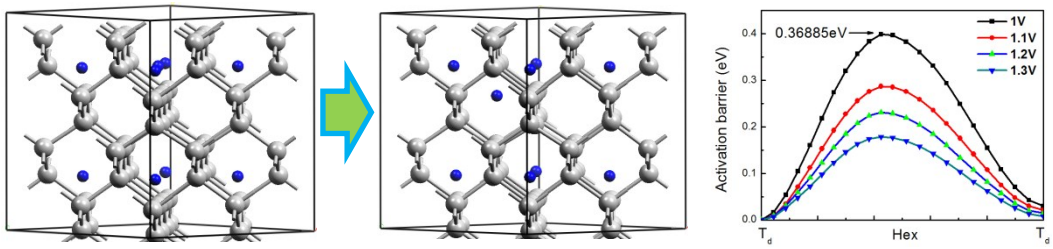
Li concentration: 0



Li concentration: 0.031



Li concentration: 0.125



Li concentration: 0.188

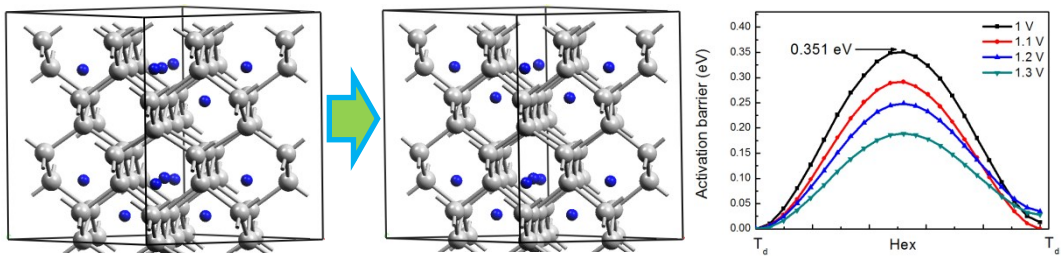


Fig. S2. The schematic diagrams and details for the calculation results in Fig. 2 (the large and small balls represent the Si and Li atoms, respectively).

The activation barrier for Li diffusion at different concentrations and expanded unit cells can be obtained directly from Fig. S2. The jump distance for Li diffusion can be obtained by measuring the distance between the initial and final states of Li in the optimized structures. Moreover, the results show that the activation barriers at different Li concentrations are mainly symmetric.