Supporting Information

Improving the Performance of Silicon Monoxide Anode via Tuning a Multiple Pre-doping System: A First-Principles Study

Wei Xie,*[,‡,a] Chunlei Pang, [‡,a] Peng He, [a] Chengmao Xiao, [a] Michihisa Koyama,*[,b] Jiantao Wang, [c] Xiaopeng Qi, [c] Jianguo Ren, *[,a] and Xueqin He[a]

a. BTR NEW MATERIAL GROUP CO. LTD. Xitian High-tech Industrial Park, Guangming New District, Shenzhen 518106, China.

b. Global Research Centre for Environment and Energy Based on Nanomaterials Science, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

c. China Automotive Battery Research Institute Co., Ltd., No.11 Xingke Dong Street, Huairou District, Beijing, 101407, China.

‡. These authors contributed equally to this work.

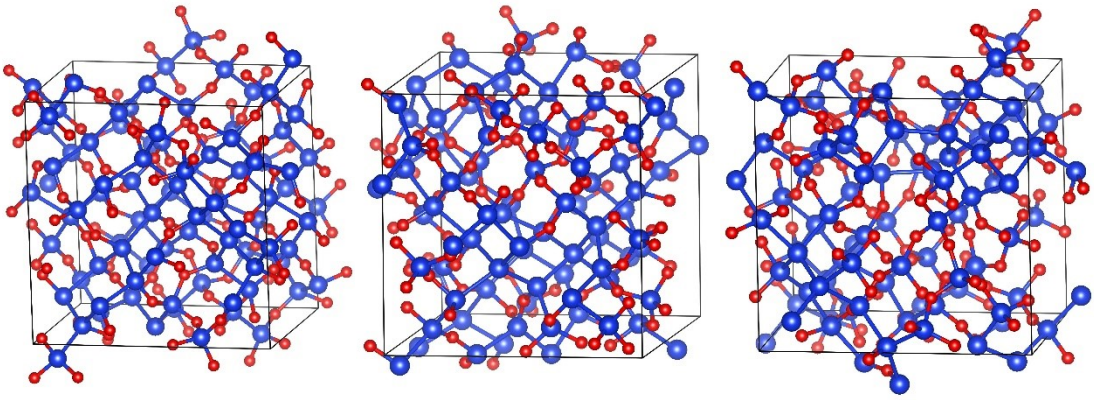
All the structures used in our simulation are from random initial configurations, and these structures are not unique. To make sure the results based on those structures are repeatable and accurate, we constructed three amorphous SiO from the different initial structures.

Figure S1 exhibits three optimized amorphous structures of SiO from three different initial configurations, which were modeled by randomly removing 64 oxygen atoms from a 2 × 2 × 2 cristobalite SiO_2 supercell. The volumes of these three final structures are 1835.72Å^3, 1860.56Å^3, and 1889.59Å^3, the densities are 2.55g/cm^3, 2.51g/cm^3, 2.48g/cm^3, which are in the acceptable error range. In geometry from Figure S2, three final SiO have the highly consistent g(r) curves. According to their respective first g(r) peaks, they have the similar average bonds length of Si-Si and Si-O, with the values of 2.36Å and 1.65Å, 2.37Å and 1.65Å, 2.40Å and 1.65 Å, respectively. The coordinate number of Si-O (CN_{Si-O}) for three models are the same with the value of 4.03, 4.00, 4.00, respectively, as well as CN_{Si-Si} with the value of 3.02, 3.06, 3.09. All of the three structures exhibit the typical, geometrical features of disordered SiO. In energic, the free different SiO structures also have the similar free energies (-7.20eV/atoms, -7.22eV/atoms, -7.23eV/atoms), which means the formation energy based on their system energies are accurate and repeatable with very small deviation. In addition, we also calculated the average free energy of these structures by using the energies in last 100fs steps during AIMD process as a supplement, the values are 7.01eV/atoms, 7.00eV/atoms, 6.98eV/atoms, respectively.

We also investigated their density of states to evaluate their differences in electronic structures. Three DOS curves shown in Figure S3 exhibit the same tendency, their main DOS peaks locate at the same position, which suggests all of them may have the similar electronic structures. Further investigation in detail, we found some differences. Figure S4 exhibits the total DOS features near fermi level, we found that the band gaps are 1.75eV, 1.98eV, 2.04eV. This difference is caused by the Si agglomeration in smaller-scale space, a very few active Si could greatly change DOS shape near fermi level, moves the band top and bottom, shortens the band gaps, and heightens the fermi energy (the values of fermi energy are 4.42eV, 4.35eV, 4.26eV, respectively). The same situation in band center analysis, Figure S5 shows the local DOS curves of Si. For the results as whole, the curves have the same tendency as total DOS, but their band centers (s, p band of Si) are different, with the value of 3.25eV, 3.26eV, and 2.99eV.

In summary, the results from different initial structures are accurate and repeatable, which will

lead to a same conclusion. The deviations in band gaps and band centers are due to the natures of amorphous structures.



SiO-1 SiO-2 SiO-3

Figure S1. Three final SiO configurations after AIMD and DFT process based on the different initial structures

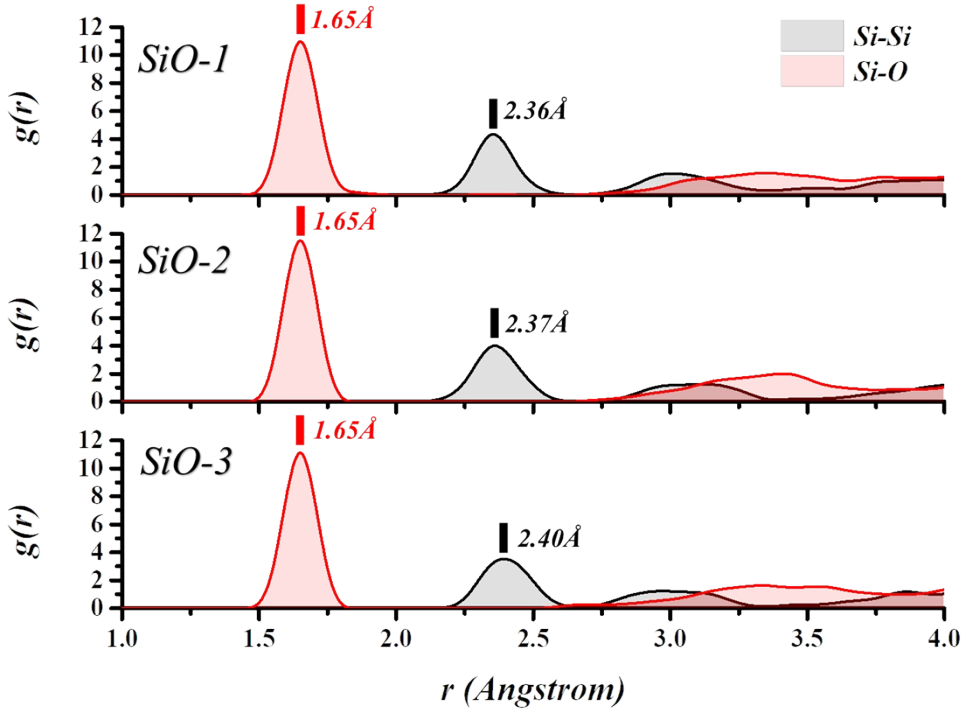


Figure S2 Radial Distribution Functions (RDF) of Si-Si, Si-O in SiO-1, SiO-2, and SiO-3

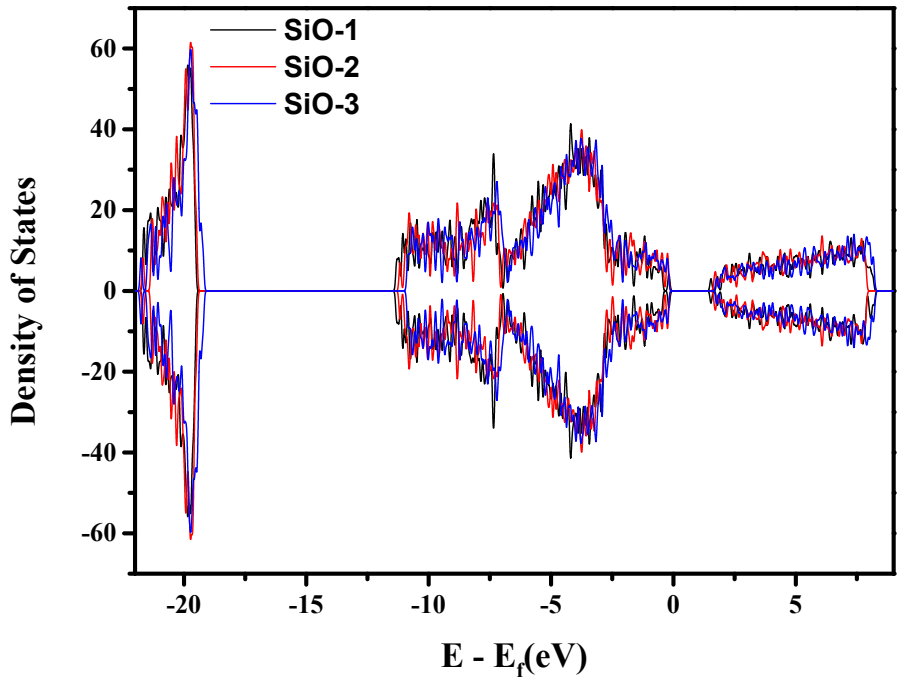


Figure S3. Total density of States of SiO-1, SiO-2, and SiO-2. Three of DOS curves all have the similar tendency with some differences in details.

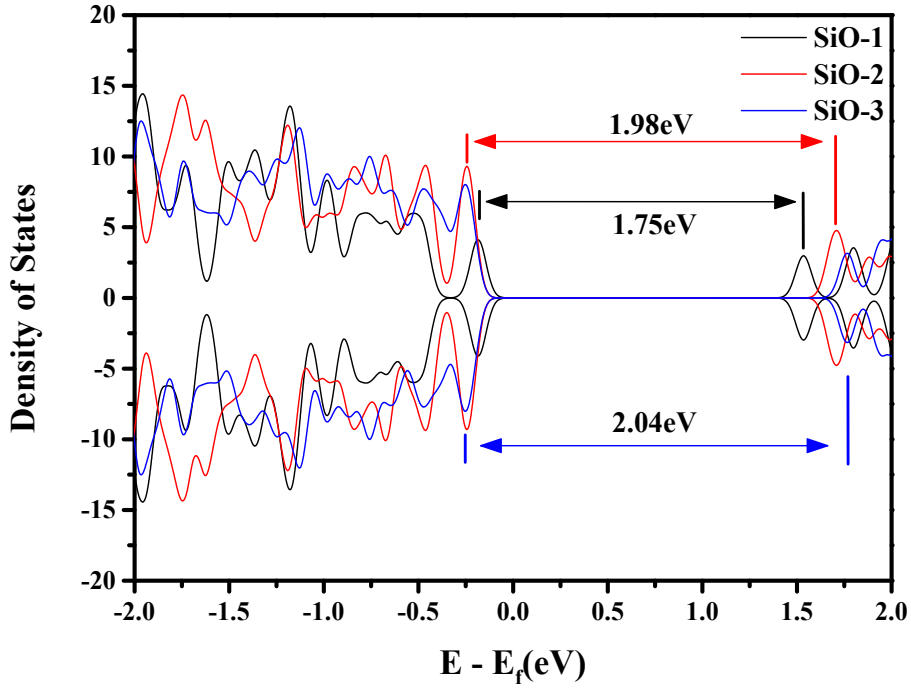


Figure S4 The total Density of States near Fermi level (from -2.0 eV to 2.0eV). The band gaps of the three SiO models are 1.75eV, 1.98eV, 2.04eV, respectively.

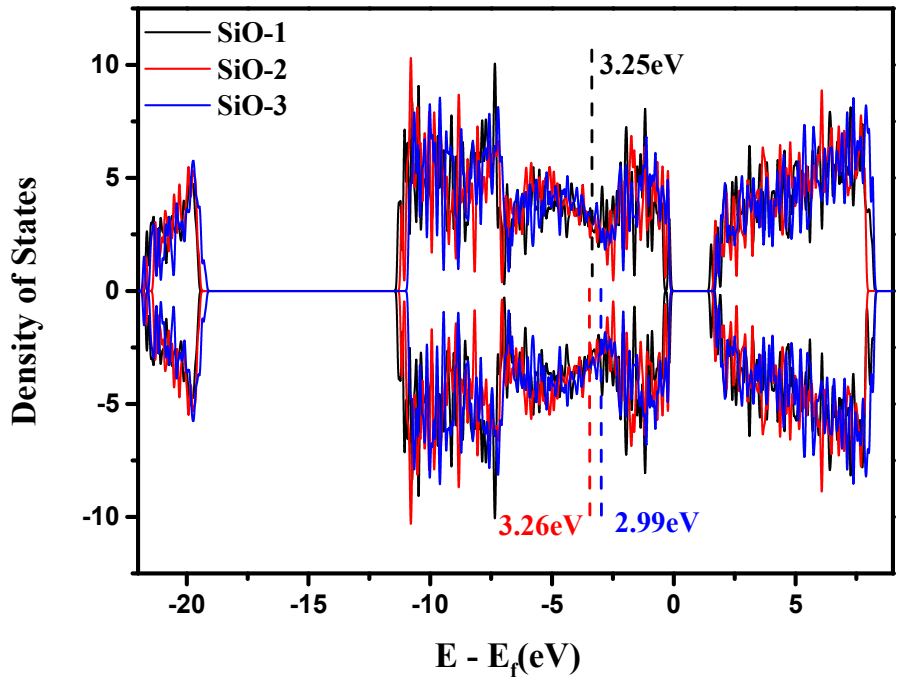


Figure S5 The local density of States for Si. The band centers are 3.25eV, 3.26eV, 2.99eV, respectively.

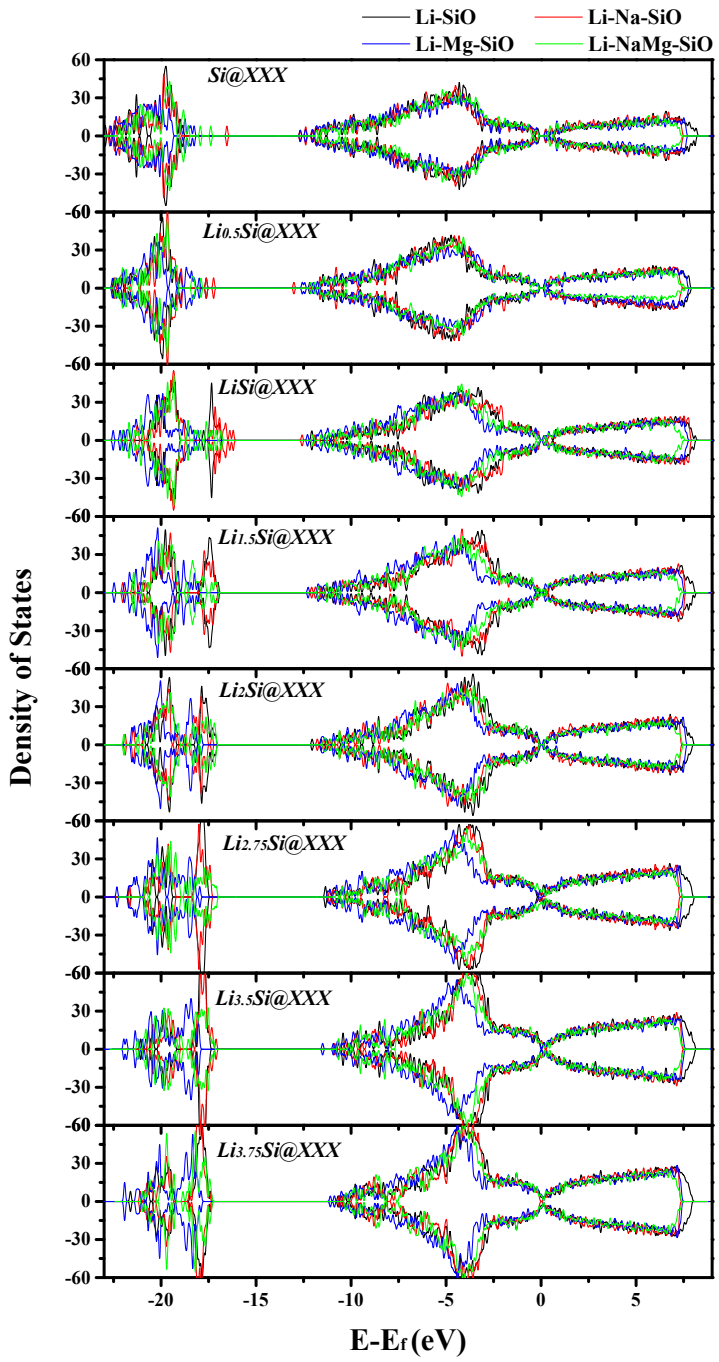


Figure S6 Total density of States with different x in $Li_XSi@Li_4SiO_4$, $Li_XSi@Na_4SiO_4$, $Li_XSi@Mg_2SiO_4$, and $Li_XSi@Li_4SiO_4$

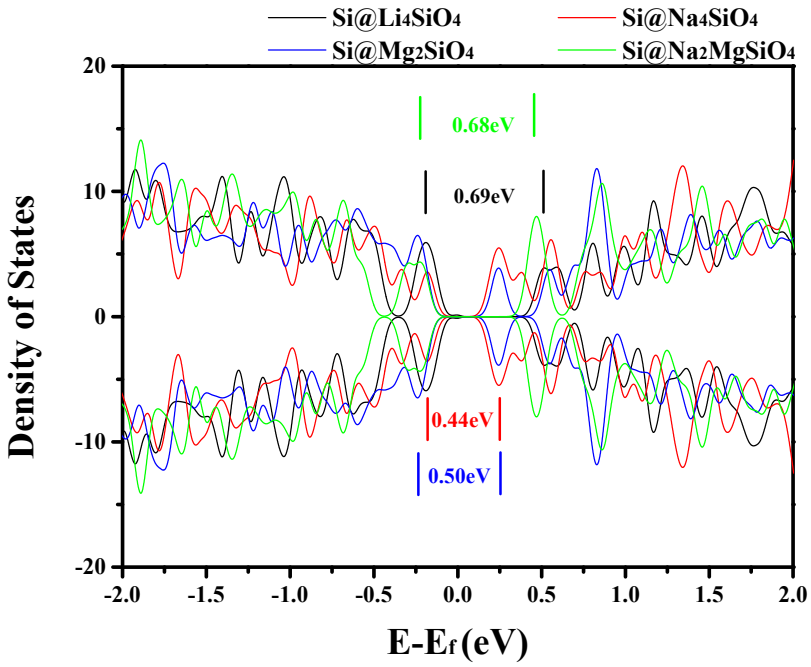


Figure S7 Total density of States of $Si@Li_4SiO_4$, $Si@Na_4SiO_4$, $Si@Mg_2SiO_4$, and $Si@Li_4SiO_4$ near fermi level