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Structural and Electrochemical Properties of Na_2FeSiO_4 Polymorphs for Sodium-Ion Batteries

Lin Zhu[1)*], Ya-Ru Zeng[1)], Jing Wen[1)], Lin Li[1)*], Tai-Min Cheng[2)]

1) College of Sciences, Northeastern University, Shenyang 110819, China

2) Department of Mathematics and Physics, Shenyang University of Chemical Technology, Shenyang 110142, China

* Corresponding author:

Ph.D.; E-mail: zhulin@mail.neu.edu.cn (L. Zhu); Prof., Ph.D.; E-mail: ririn@sohu.com (L. Li)

Abstract

The advance of battery technology in electric vehicle and large-scale energy storage applications drives the development of new battery materials, such as sodium iron silicate Na_2FeSiO_4. In this work, structural characteristics, deintercalation voltages, ionic conductivities, and mechanical properties of Na_2FeSiO_4 polymorphs are investigated by using potential-based lattice dynamics and density functional theory methods. To simulate the polymorphism of Na_2FeSiO_4, a total of 14 structural models are constructed from the structure types ABC_2X_4 of Na- and Li-based silicates. Free energies are calculated within the quasi-harmonic approximation to evaluate the relative stabilities of 13 dynamically stable structures under temperature and pressure conditions. The energetically favored structures reveal that Na_2FeSiO_4 polymorphs tend to form the structures with three-dimensional (3D) framework of FeO_4 and SiO_4 tetrahedra. In comparison with Li-equivalent, Na_2FeSiO_4 is predicted to have the characteristics of smaller volume change, lower deintercalation voltage, 3D or quasi-3D ionic mobility, and better mechanical property, which may deliver a prospect of higher electrochemical performance. The mechanism of substitution Na for Li on the effects of structural and electrochemical properties is also discussed. Helpful information is expected to provide for the preparation of high-performance cathode materials of Na-ion batteries and the fundamental understanding of Na-intercalation chemistry.