

CHARACTERISTICS of LITHIATED TITANIA: Concentration, Morphology, Pressure and Nano Effects

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Abstract

Fast transport of ions in electrode materials is important for electrochemical performance, as fast insertion and de-insertion rates allow efficient cycling of ions in lithium ion battery anodes. Recently, efforts in this area have been devoted for the development of improved nanostructured electrodes, as they lead to reduced diffusion lengths and thus allow fast ionic transport. A fairly general understanding has been established regarding the effect of the nanoscale on the electrochemical efficiency of the electrodes. However, the atomistic details behind the enhanced performance, and the effect of morphology, are still not well understood, and such understanding is crucial for designing materials, which allow better electrochemical performance. This work probes such atomistic details to provide insights into the design of electrode materials with fast ion transport rates. Important factors such as mechanisms and energetics, together with the effects of dynamics, morphology and concentration are discussed for Li ion diffusion in bulk anatase, amorphous and rutile TiO₂. Additionally, such effects will be compared to those for the nanostructures. The structural transitions upon lithiation, and under pressure, will be discussed in detail.

The Li ion diffusion mechanism is found to depend on the morphology of the lattice. Our calculations show that diffusion of Li in anatase is 3D in nature, while that in rutile is 1D. The diffusion in rutile is found to be much faster than that in anatase and amorphous titania. Our simulations indicated that changing the Li ion concentration significantly modifies its diffusivity. However, the changes in diffusivities are found to differ from structure to structure, and are affected by the morphology of the lattice. Our results show that for both anatase and amorphous TiO₂, increasing the concentration increases diffusivities (up to 75% Li loading for anatase, and for all concentrations for amorphous), while the diffusivity decreases for rutile with increasing Li concentration. The reason for the decreasing diffusivity in the latter case is attributed to increasingly blocked diffusion sites, and increasing Li-Li repulsion. The effect of concentration on the diffusivity in amorphous is different than that for the crystalline structures, as the amorphous TiO₂ undergoes structural transitions that lower the barrier for diffusion.

We have identified a structural transition for lithiated amorphous TiO₂ when fully loaded. The new structure is a cubic phase, which provides faster Li diffusion. We find that the configurational energy and entropy of the cubic structure is lower than that of the amorphous titania. We have also examined the stability of the lithiated and the de-lithiated cubic structures by applying pressure at 300K, and find that the lithiated cubic phase is stable under a wide range of pressures, while de-lithiated cubic goes under phase transition to an amorphous. These results will be compared to those for the nanostructures.

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