



Short communication

Effect of particle size on the phase behavior of Li-intercalated TiO₂-rutile

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ARTICLE INFO

Article history:

Received 5 October 2010

Received in revised form

15 December 2010

Accepted 17 December 2010

Available online 8 January 2011

Keywords:

Anodes

Nanomaterials

Li-batteries

Computer simulations

ABSTRACT

With the aid of *ab initio* calculations, we compare the phase behavior upon lithiation of rutile particles of different sizes and morphologies. A rationale for the differences in their structural behavior is provided by combining concepts from Crystal Field Theory and semi-empirical concepts, such as bond length variation, minimal volume expansion, with accounts for the effects of diffusion and the anisotropy of the Li-distribution. It is shown that the phase behavior of spaghetti-like nano-particles differs from bulk rutile as a result of an extended single phase insertion domain and increased disorder of Li-ions. As Li-ions strive to minimize their repulsions by increasing their mutual separation a regular network of Li-ions is formed, being a precursor to the transformation of the rutile host lattice into spinel.

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1. Introduction

For decades rutile structured titanium dioxide has been disregarded for applications as an anode since at normal conditions Li-uptake by polycrystalline rutile is insignificant [1]. An exception was the report of Li-insertion to high concentration at elevated temperatures [2]. Interest in this material has been sparked recently, when a high Li-uptake was observed at normal conditions for nanostructured rutile [3–8].

The striking temperature dependence of intercalation behavior of bulk rutile has been rationalized in terms of limitations imposed by diffusion of Li-ions on the observed thermodynamics of Li-insertion [9]. Using *ab initio* simulations, it was shown that the limiting step is associated with restricted access to stable Li-sites upon single phase insertion up to Li-concentrations $x = [\text{Li}]/[\text{Ti}] \sim 0.2$ due to a highly anisotropic Li-diffusion [9,10]. At elevated temperature and in small particles Li-diffusion is activated enabling access to the stable sites and intercalation occurs to much higher Li-concentrations. It appeared that diffusion controlled Li-insertion is not specific for TiO₂ rutile, but occurs in a wider range of transition metal oxides, including TiO₂-brookite [11,12], TiO₂-B (at elevated Li-concentrations [13,14]) as well as some other rutiles (MnO₂ [15], VO₂ [16]).

More recently it has been found that the phase behavior of lithiated rutile may be influenced by the shape of nano-particles [3,4,7]. While Li-intercalation into nanostructured rutile follows the bulk

behavior at elevated temperature [3], the phase transformations upon lithiation of specially tailored (spaghetti-like) nano-particles are different [4–7]. In both cases, initial insertion is a single phase reaction, to $x \sim 0.2$ [2,3] and ~ 0.4 – 0.5 [4,7], respectively, which, however, is followed by a different sequence of phase transformations. While in the former case a monoclinically distorted rutile (Li_{0.75}TiO₂) and a layered hexagonal LiTiO₂ phase [2,3,17] are formed, spaghetti-like nano-particles transform to a spinel structured titanate (Li_{0.5}TiO₂) and a rock-salt LiTiO₂ [7]. The reasons for these different structural behaviors are at present not understood. Here, with the aid of *ab initio* simulations, we aim to rationalize the phase behavior of intercalated rutile and to get insights into the underlying mechanisms.

2. Details of calculation

All calculations were performed within the framework of density functional theory as implemented in the CASTEP software, within the pseudopotential plane-wave formalism [18]. Electron exchange and correlation effects are treated within the spin polarized generalized gradient approximation [19] with ultrasoft pseudopotentials [20] used to replace the Ti (1s, 2s, 2p), O (1s), and Li (1s) core orbitals. This set-up results in calculated cell parameters within 1% from the experimental values for undoped rutile. The calculations were performed on supercells containing up to 16 formula units of TiO₂, which was found to be of sufficient size to predict the intercalation behavior of various titanate structures [10,21,22]. All degrees of freedom, including internal ionic positions and the size and shape of the computational unit were fully optimized in simulations. In order to quantify the distribution of electron den-

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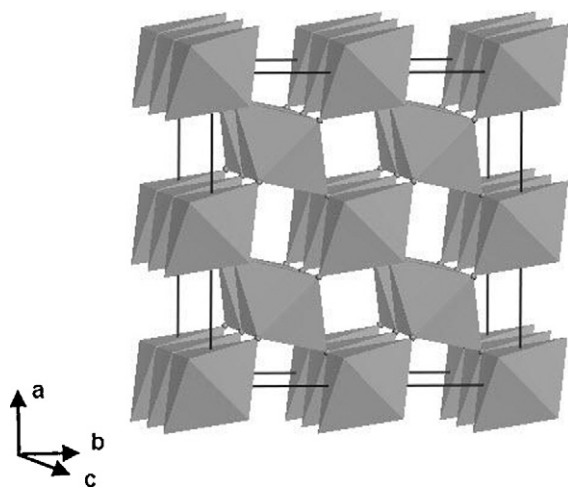


Fig. 1. Polyhedral representation of the structure of rutile.

sity donated to the host lattice upon intercalation and to monitor the changes in ionic charges, Mulliken population analysis was performed. The spatial orientation of the charge donated to the Ti-ions was monitored by visualizing the distribution of the charge density in t_{2g} -orbitals as described in Refs. [10,23].

3. Results and discussion

3.1. Li-intercalation into bulk rutile

Rutile is built from pillars of TiO_6 octahedra, in which each octahedron shares two opposite edges. The pillars are joined by corners to form a tetragonal structure with straight channels along the tetragonal axes (the c -direction) (Fig. 1), where intercalated lithiums can be accommodated in vacant interstitial sites. In polycrystalline rutile Li-ions are inserted along the c -direction and have a high mobility along c -channels [9,10,24,25]. The ordering of Li-ions in bulk rutile has been studied by Koudriachova et al. [9,10]. It was shown that deformations of the local structure of the host, induced by intercalation, cause Li-ions to order themselves in the ab -planes rather than adopt configurations maximizing their separations under electrostatic repulsions [26]. A very slow diffusion of Li-ions in the ab -planes in bulk rutile restricts access to stable configurations, and thus limits the insertion concentration [9].

Detailed analysis of the fully relaxed configurations of lithiated structures performed here suggests that the ordering pattern of the Li-ions in the bulk, which plays such important role in intercalation behavior of rutile, is a direct consequence of insufficient separation between the inserted Li^+ -ion and the neighboring Ti^{4+} -ions. Strong Coulomb repulsions with the inserted Li-ions pushes neighboring Ti-ions away from their crystallographic positions into the c -channels, increasing the Ti–Ti separation in the occupied site (from 4.6 Å in undoped rutile to 5.14–5.17 Å), but reducing the available space in the neighboring vacant sites. The resultant local deformations affect the ability of the vacant sites to insert Li-ions upon further intercalation. Here we use Ti–Ti distances across the insertion site to characterize this ability: the vacant sites with the reduced separations compared to the bulk are less favorable for Li-insertion, while more spacious vacant sites become more favorable. As an example, a fully relaxed configuration at $[\text{Li}]/[\text{Ti}] = 0.0625$ is shown in Fig. 2, where the Li-ion adopts an asymmetric position at (0.25a, 0, 0.134c), which locally breaks the tetragonal symmetry. The sites with the largest Ti–Ti separations (4.92–4.95 Å) are labeled as B and C, the sites with a modest expansion as D and E (4.78 Å), while sites labeled A, which neighbor the occupied site

in the a - or b -direction are closed in, to 4.18 Å (4.23 Å). Therefore, at $[\text{Li}]/[\text{Ti}] = 0.125$ occupation of the most “open”, B and C, sites is preferred, as it is confirmed by direct calculations. However, the displacements of Ti-ions affect transport of inserted Li-ions to these sites along the c -channels, in addition to limited accessibility due to slow diffusion in the ab -planes [9]. Li-migration through the “closed” sites hinders the accessibility of the B-, E- and, in particular, the C-sites, where the barrier is in excess of 1 eV. In comparison, all Ti–Ti distances across the c -channels with D-sites are larger than in bulk rutile (4.62–4.75 Å). As a result, population of the less favorable, but more accessible D-site at higher Li-concentrations is more likely.

At higher concentrations ($[\text{Li}]/[\text{Ti}] = 0.125\text{--}0.75$) the most stable configurations are formed upon occupation of both B and D sites [10] and the accessibility of the B-sites is improved at higher Li-concentrations, after a collective lattice expansion in the b -direction. Geometric considerations suggest that the C-sites would be occupied if superstructures with maximum Li-separation are formed at $x > 0.25$. Therefore, slow diffusion of Li-ions along the “closed” c -channels makes formation of such superstructures in bulk rutile infeasible.

A direct consequence of the edge sharing motif of rutile is that electronic charge transferred to the host upon intercalation is accommodated in localized $R\text{-}d_{yz}$ -orbitals (in the notation from Ref. [23]) of the Ti-ions, causing locally an elongation of the Ti–O bonds along the z -direction (apical bond) of the local frame of reference (i.e. in the ab -planes) and an overall volume expansion [23]. The deformations of the TiO_6 octahedra associated with the displacements of the Ti-ions reshape these orbitals as shown in Fig. 2A. In the “deformed” octahedra only one apical Ti–O bond is elongated to the $\text{Ti}^{3+}\text{-O}^{2-}$ value (by 10–12%) and tilted to the local equatorial (xy -)plane, while the second apical Ti–O bond is contracted (by approximately 10%). As the overall volume expansion at $x \sim 0.0625$ and 0.125 is predicted to be much smaller (1–2%), such deformations clearly minimize the volume expansion as the charge donated to the host lattice is accommodated and, therefore, will be favorable under the volume relaxation constraints. Since reduction of Ti-ions to their 3^+ -state and elongation of all six bonds to the $\text{Ti}^{3+}\text{-O}^{2-}$ values occurs upon accommodation of one donated electron, elongation of one bond, as shown in Fig. 2A is expected at $1/6 |e|$. *Ab initio* calculations show that Li-ions donate $-0.82 |e|$ to the lattice, hence this electron charge will be donated at Li-concentration of ~ 0.2 $[\text{Li}]/[\text{Ti}]$, which is an estimate for the upper boundary of single phase insertion in bulk rutile, in excellent agreement with that observed experimentally [2] and predicted earlier using *ab initio* simulations [10]. The above simple considerations represent an “averaged” picture of the charge distribution. The exact distribution depends of course on the ordering of Li-ions as, through elongation of the particular Ti–O bonds, it supports the structural distortions required for accommodation of the Li-ions. Each Li-ion neighbors six Ti-ions, with two of them being displaced as described above (and receiving $\sim -1/6 |e|$ each). Assuming for the sake of simplicity that the rest of the charge is distributed uniformly among the remaining Ti-ions, it is easy to see that at ~ 0.2 $[\text{Li}]/[\text{Ti}]$ all Ti-ions receive $\sim 1/6 |e|$ each, validating the “averaged” description at these concentrations. The restriction on Li-concentration in the single phase domain under the current scenario is also evident from counting the sites available for intercalation. As each Ti-ion neighbors four insertion sites, reduction of two Ti-ions per inserted Li precludes occupancy of seven sites around them. It is easy to check that in the cell used here for computation ($\text{Li}_x\text{Ti}_{16}\text{O}_{32}$) these considerations yield a maximum occupancy of 3 Li per 16 Ti-ions, i.e. ~ 0.2 $[\text{Li}]/[\text{Ti}]$.

Upon further intercalation, the single phase insertion is followed by a two phase insertion, whereby a tetragonal rutile phase coexists with the monoclinically distorted rutile with an ordering of Li-ions

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