What is the maximum electrochemical Li insertion capacity in anatase? Insights from Density Functional Theory

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ABSTRACT

We present a detailed analysis of stability and voltages of Li insertion in anatase using screened-exchange hybrid DFT calculations. Li insertion is studied for a range of compositions in Li_xTiO_2 with $0 \leqslant x \leqslant 1$. Our calculations indicate that while tetragonal $LiTiO_2$ exhibits a smaller binding energy than the orthorhombic symmetry, both are actually stable compositions with respect to pure Li metal and anatase. We show that although the orthorhombic symmetry can be maintained to achieve the theoretical maximum capacity of $LiTiO_2$, in this situation, the electrode will undergo a large volume expansion that will affect the cycling performance of the electrode. On the other hand, if the tetragonal symmetry is maintained in the experiment, only capacities of about $x = 0.5$ will be achieved.

1. Introduction

TiO_2 has been widely studied for a variety of applications [1–3]. The first experimental works considering different structures of TiO_2 for battery applications appeared as early as in the late 70s with active research on the subject still underway [4–8]. Ohzuku et al. reported a change in structure upon lithiation through XRD experiments that indicated a transition from the tetragonal structure to a cubic structure [4]. Later, Mackiln and Neat presented the charge-discharge voltage profiles for TiO_2 in the rutile and anatase forms against Li metal [6]. In that work, it is shown that for the first charge, the voltage rapidly decreases from about 2.4 V to a first plateau at 1.78 V that is sustained until a stoichiometry of about $Li_{0.6}TiO_2$ is reached. These authors had been able to further insert Li and a second plateau was observed at about 1.55 V, leading to a final composition close to the maximum theoretical capacity of 335 mAh/g corresponding to a stoichiometry of $LiTiO_2$. However, cyclability is shown to be extremely poor with a dramatic drop in capacity of 50% for the second cycle. Moreover, only the first plateau is observed from the second to subsequent cycles with capacity retention only becoming worse upon further cycling. The work of Wagemeker et al. [9] presents the synthesis of Li_xTiO_2 nanoparticles prepared by chemical insertion of vacuum oven-dried TiO_2 powder with *n*-butyllithium with varying sizes, followed by neutron diffraction experiments. These experiments show that the Li-rich titanate phase is followed by a recovery of the tetragonal phase for a composition of $LiTiO_2$. However, as explained by Yang et al. in their recent review, [8] a number of studies indicate that bulk anatase can only accommodate Li up to a stoichiometry of $Li_{0.5}TiO_2$ in electrochemical experiments. To

overcome diffusion problems that are thought to be the main cause of capacity fading and to improve the electrode reactivity towards Li, researchers have studied nanoparticles of titania with shorter diffusion lengths, as well as doping [9–15].

Computational works based on Density Functional Theory (DFT) as well as DFT + U have been instrumental in elucidating the physical processes taking place in TiO_2 upon Li insertion [16–19]. At low Li concentrations, it is found that the tetragonal structure is retained and the electron donated by Li produces a well localized state in the middle of the gap [18]. Dawson and Robinson presented a study that showed superior results obtained with a screened exchange functional compared to a more standard generalized gradient density functional [16]. Most of these studies concentrate in dilute Li regimes that maintain the original tetragonal symmetry and at voltages where the first experimental plateau of 1.78 V [6] is not yet reached. A direct comparison of calculated voltage profiles with experiments has not yet been presented. In this work, we utilize the screened-exchange hybrid functional of Heyd, Scuseria, and Ernzerhof, HSE [20,21], to obtain structural parameters, energetics, and voltage profiles of Li_xTiO_2 with $0 < x \leqslant 1$.

2. Computational details

All calculations presented here have been carried out using periodic boundary-conditions (PBC) as implemented in GAUSSIAN [22]. Three-dimensional, self-consistent, spin-polarized Kohn-Sham calculations were performed on all systems using atom-centered Gaussian basis sets. These basis sets are modified to remove Gaussians with small exponents that are usually present in optimized basis sets for accuracy in modeling
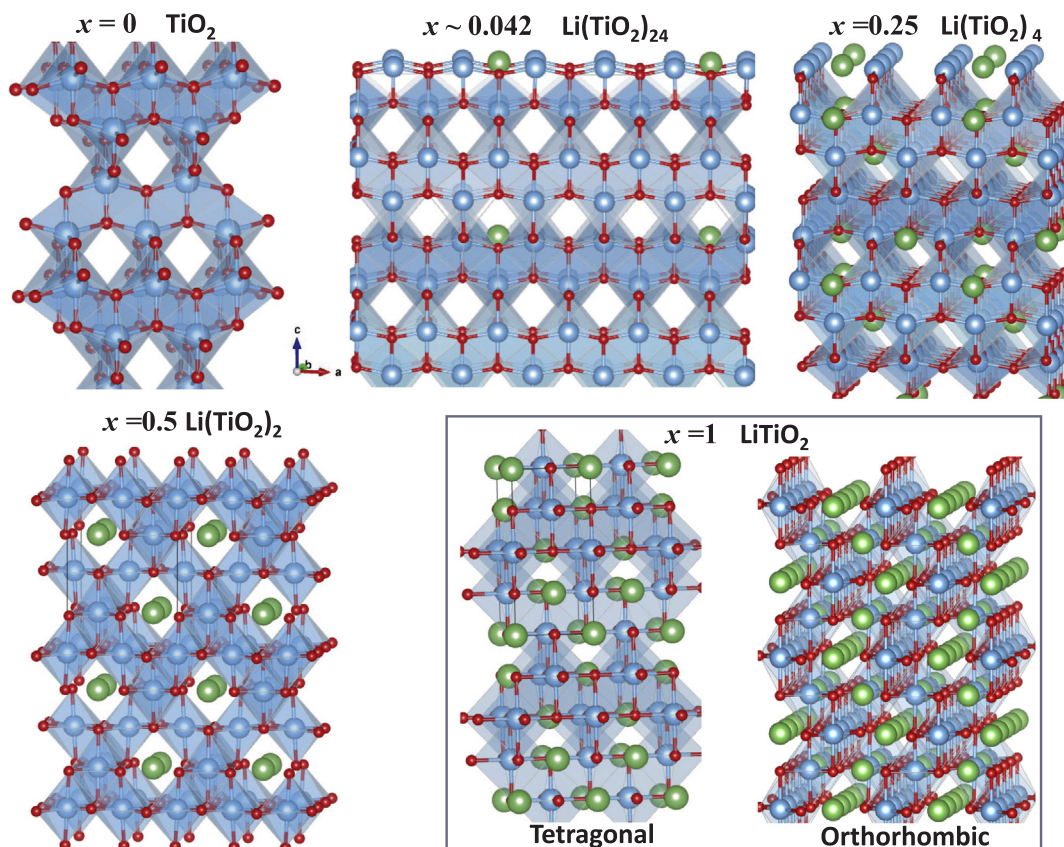
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Fig. 1. Geometric structures of anatase and Li intercalated anatase for several Li insertion compositions. Titanium atoms are shown in blue, oxygen in red, and lithium atoms in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Relative energies (meV/TiO$_2$ unit), a, b, and c cell parameters (Å), and volumes (Å^3), for anatase and the tetragonal and orthorhombic LiTi$_4$O$_8$ and LiTiO$_2$ structures after relaxation with the HSE functional.

		Relative Energy	a	b	c	Volume
TiO$_2$	Anatase	–	3.765	3.765	9.498	134.6
LiTi$_4$O$_8$	Tetragonal	47.7	3.866	3.866	9.199	137.5
	Orthorhombic	0.00	3.826	3.916	9.064	135.8
LiTiO$_2$	Tetragonal	0.00	4.026	4.026	8.379	135.8
	Orthorhombic	46.44	5.781	5.765	8.253	275.1

the tails of the wavefunctions in atomic and molecular systems. These tails, however, are not present in compact 3D systems. Moreover, the presence of the diffuse functions negatively affects PBC calculations in solids and can potentially generate numerical problems [23]. Therefore, in this work, functions with exponents smaller than 0.1 are removed from the basis contraction. With these modifications, it becomes necessary to assess the quality of the resulting basis set. Our assessment, shown in supplementary materials, indicates that the use of the modified 6-31G* basis can accurately reproduce lattice parameters in TiO$_2$ in the anatase, rutile, and TiO$_2$(B) structures as well as in and Li$_{0.5}$TiO$_2$ and LiTiO$_2$. Therefore, we adopt this basis set for all the calculations presented in this work. The screened exchange HSE functional is used throughout the work since it has been shown to accurately reproduce the properties of bulk systems [20,23,24]. In all calculations the requested convergence of the total energy per cell of the self-consistent field procedure is 10^{-6} Hartree. Geometry optimizations without symmetry constraints were carried out throughout this work until maximum forces and displacements were smaller than 4.5 × 10^{-4} Hartree/

Bohr and 1.8 × 10^{-4} Bohr, respectively. The k-space meshes utilized varied depending on the size of the unit cell. For instance, in the case of anatase and tetragonal LiTiO$_2$, a mesh of 10 × 10 × 6 k-points was used.

Li binding energies per TiO$_2$ unit are calculated with respect to Li metal and anatase according to the relation

$$E_b = -\frac{E_{Li_x TiO_2} - E_{TiO_2} - xE_{Li}}{x},\tag{1}$$

where x is the fraction of Li per TiO$_2$ unit, $E_{Li_x TiO_2}$ represents the total energy of the lithiated system per TiO$_2$ unit, E_{TiO_2} is the total energy of anatase per TiO$_2$ unit, and E_{Li} is the energy per Li atom in Li metal. With this definition, positive binding energies represent stable configurations. In experiments, x varies in a smooth fashion as more and more Li is inserted into the electrode. In calculations at a temperature of 0 K, however, an average constant voltage can be obtained from the total energies of two discrete compositions, x_1 and x_2, according to the relation [25].

$$V_{av}(x) = -\frac{E_{Li_{x_2} TiO_2} - E_{Li_{x_1} TiO_2} - (x_2 - x_1)E_{Li}}{nF},\tag{2}$$

where n is the charge of the electron, F is the Faraday constant, E_{Li} is the energy per atom of Li metal, and the composition x is such that the voltage remains constant for $x_1 \leqslant x \leqslant x_2$. Positive voltages indicate the formation of the given composition x while negative voltages indicate that instead of insertion, Li plating should proceed in the experiment. In this work, we have chosen the intervals $(x_1, x_2)_i$ in Eq. (2) such that they produce a more dense mesh at low Li concentrations where the voltage varies more rapidly and a sparser mesh for $x > 0.25$ where the voltage remains more stable.