GGA+*U* description of lithium intercalation into anatase TiO₂

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We have used density-functional theory [generalized gradient approximation (GGA)] to study lithium intercalation at low concentration into anatase TiO₂. To describe the defect states produced by Li doping a Hubbard “+*U*” correction is applied to the Ti *d* states (GGA+*U*). Uncorrected GGA calculations predict Li_{*x*}TiO₂ to be metallic with the excess charge distributed over all Ti sites, whereas GGA+*U* predicts a defect state 0.96 eV below the conduction band, in agreement with experimental photoelectron spectra. This occupied defect state corresponds to charge strongly localized at a single Ti 3*d* site neighboring the intercalated lithium with a magnetization of 1 μB. This polaronic state produces a redshifted optical absorption spectrum, which is compared to those for the native O-vacancy and Ti-interstitial defects. The strong localization of charge at a single Ti center lowers the symmetry of the interstitial geometry relative to that predicted by GGA. The intercalated lithium sits close to the center of the octahedral site, occupying a single potential energy minimum with respect to displacement along the [001] direction. This challenges the previous interpretation of neutron diffraction data that there exist two potential energy minima separated by 1.6 Å along the [001] direction within each octahedron. Nudged elastic band calculations give barriers to interoctahedral diffusion of ~0.6 eV, in good agreement with experimental data. These barrier heights are found to depend only weakly on the position of the donated electron. The intercalation energy is 2.14 eV with GGA and 1.88 eV with GGA+*U*, compared to the experimental value of ~1.9 eV. Li-electron binding energies have also been calculated. The [Li_{*i*}⁺-Ti_{*Ti*}⁺'] complex has a binding energy of 56 meV, and a second electron is predicted to be bound to give [Li_{*i*}⁺-2Ti_{*Ti*}⁺'] with a stabilization energy of 30 meV, indicating that intercalated lithium will weakly trap excess electrons produced during photoillumination or introduced by additional *n*-type doping.

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I. INTRODUCTION

The growing demand for portable and nonpolluting power sources requires the development of new battery technologies with improved charge densities. TiO₂-based materials are being increasingly proposed as promising anodes for lithium-ion batteries, due to their low cost, light weight, and nontoxicity.¹⁻³ A number of polymorphs have been investigated with nanoporous and other nanoscale morphologies often offering improved performance. The use of nanoscale samples results in increased contact areas between electrode and electrolyte, and shortened distances for lithium transport, leading to increased power.⁴⁻⁶ Nanocrystalline samples have also been reported to show a larger range of lithium incorporation than equivalent bulk materials, resulting in greater charge density. This has been attributed to the suppressed formation of interfaces between competing phases as a consequence of the particles' small size.⁷

In all these materials it is important to understand the interplay between the dynamical behavior and spatial distribution of the intercalated lithium and the electronic properties of the system. If the relationship between morphology and these interrelated properties of ionic and electronic charge carriers can be better understood then targeted design of improved battery materials might be possible. Before investigating the effect of morphology, it is necessary to characterize structurally and electronically the intercalation of lithium into bulk systems.

In this paper we model lithium intercalation into anatase TiO₂ at low concentration, using density-functional theory (DFT). Anatase has been proposed as a possible Li-

battery anode material since it can readily incorporate Li atoms at interstitial sites.^{1,2,8,9} Performance of the bulk material is limited by phase separation between a low-lithium-concentration anatase phase and an orthorhombic lithium-titanate phase with a limiting composition of Li_{0.5-0.6}TiO₂.^{10,11} In nanoscale samples it has been reported that this phase separation is suppressed with the two phases coexisting within a single domain. Stoichiometries that are normally unstable in the bulk become accessible, suggesting a synthetic route to achieving increased charge densities,^{12,13} and the electrochemical behavior of lithium insertion into nanotubular anatase has been studied by a number of groups.¹⁴⁻¹⁷ The historical interest in anatase TiO₂ means that lithium intercalation is relatively well characterized experimentally for the bulk system, providing useful reference data for theoretical studies, and making it a prototypical system when considering the properties of more exotic polymorphs and morphologies.

Lithium intercalation into anatase TiO₂ is of interest for technologies in addition to batteries. Electrochemical insertion into thin films is accompanied by a reversible change in coloration from transparent and colorless to dark blue and it has been suggested that this behavior might be exploited in electrochromic devices.^{18,19} Nanocrystalline anatase TiO₂ also finds use in dye-sensitized solar cells (DSSC), where it acts as a transport medium for photogenerated electrons. Adding lithium to the electrolyte allows control of the electron injection yield from the dye to the TiO₂ electrodes²⁰⁻²³ and the rate of interfacial charge recombination,²⁴ as well as increasing both the conductivity of the electrodes,²⁵ and resultant photovoltages.²⁶ Although surface polarization is

likely to play a large role,²⁵ given the ease with which Li intercalates into anatase TiO_2 some interstitial Li is expected to be present. It has been suggested that interstitial lithium modifies the distribution of charge traps within the TiO_2 substrate,^{26–28} with a consequential effect on the dynamics of charge carriers diffusing through the electrode. This interaction between intercalated lithium and electrons resident within the Ti sublattice has theoretical support from interatomic forcefield calculations of Olson *et al.*²⁷ who predicted strong binding between interstitial Li and a neighboring Ti in a +3 oxidation state.

In anatase TiO_2 oxygen atoms form an array of edge-sharing distorted octahedra, giving the octahedra-centers D_{2d} symmetry. In stoichiometric systems, half of these octahedra are occupied by Ti atoms, and the vacant remainder are available as intercalation sites. Electrochemical incorporation of lithium into TiO_2 can be represented as

where x is the mole fraction of lithium. Photoemission spectra for anatase TiO_2 show that as Li is progressively incorporated a feature appears in the band gap with a binding energy of ~ 1.0 eV.¹⁰ This gap state is attributed to occupied Ti 3d states, with core XPS and resonant inelastic soft x-ray scattering also indicating the presence of Ti^{3+} species.^{10,29–31} Similar gap state features attributed to occupied Ti states have been observed experimentally in a number of reduced TiO_2 samples exhibiting both intrinsic and extrinsic n -type defects.^{32,33} In the case of O-deficient TiO_2 , electron paramagnetic resonance data show that the excess electrons are strongly localized at titanium sites near the vacancy,^{34,35} with similar localization reported for fluorine-doped rutile TiO_2 ,³⁶ and this polaronic localization of excess charge in n -type TiO_2 is supported by a number of theoretical studies.^{37–47}

Previous theoretical studies of Li-intercalated TiO_2 have supported the transfer of charge to Ti sites.^{48–57} The distribution of charge and corresponding electronic structure, however, depends strongly on the choice of theoretical method. Stashans *et al.* employed Hartree-Fock to model Li intercalated rutile and anatase TiO_2 , and reported that the electron is transferred to the closest Ti atom to produce Ti^{3+} , which gives rise to a defect peak in the band gap.⁴⁸ Lunell *et al.*⁴⁹ also used Hartree-Fock to model anatase $\text{Li}_{0.5}\text{TiO}_2$, and again reported charge transfer to individual titanium sites, although it should be noted that experimental samples with this stoichiometry adopt the tetragonal lithium titanate structure.^{11,12}

More recently DFT has been used to study Li-intercalated anatase TiO_2 .^{50–57} These studies report the excess electronic charge to be distributed over all the Ti atoms in the calculation, giving a metallic system with partial occupation of the bottom of the conduction band. These predictions of metallic behavior are incompatible with the localized defect state indicated by experimental photoabsorption¹⁰ and disagree qualitatively with previous Hartree-Fock calculations.⁴⁸

Standard DFT functionals (local density or general gradient approximations) often fail to predict correct electronic structures for reduced transition metal oxides,^{58–60} due to the self-interaction error inherent to such functionals,^{61,62} and which is acute for highly localized d and f valence states.

This has been discussed previously for a number of reduced TiO_2 systems.^{37,38,42} By correcting for this self-interaction error it is possible to recover electronic structures in agreement with experimental data, and this has been demonstrated for O deficient and M^{V} doped TiO_2 .^{37–42,46,63} One approach to correcting for the self-interaction error is the addition of a “+ U ” term, which replaces the onsite Coulomb interaction within the chosen functional with a Hubbard term.⁶⁴ This opens a gap between occupied and unoccupied states for the orbitals of interest and gives improved descriptions of polaronic defect states in a number of oxides.^{59–61,65} Richter *et al.*⁶⁶ have previously demonstrated that GGA+ U reproduces the experimental splitting between occupied and unoccupied Ti 3d states in lithium titanate ($\text{Li}_{0.5}\text{TiO}_2$), although the corresponding charge density was not presented, and this method has not yet been applied to the low concentration lithiated-anatase phase.

Here we present GGA and GGA+ U calculations of lithium intercalated into anatase TiO_2 at low concentration [$x(\text{Li})=0.03$]. We find that GGA is unable to even qualitatively describe this system correctly, whereas GGA+ U recovers the gap state seen in experimental photoelectron spectra,¹⁰ as reported previously for the high Li-concentration titanate phase.⁶⁶ This defect state corresponds to the excess electron strongly localized at a single Ti center adjacent to the lithium interstitial with the polaronic nature of this localized electron explaining the electrochromic characteristics of lithiated TiO_2 . The energy of association between the localized electron and the intercalated lithium is found to be favorable but small, providing a possible mechanism for the observed variation in the properties of anatase-based TiO_2 photoelectrodes when lithium ions are present.

II. METHOD

Calculations were performed using the density-functional-theory code VASP,^{67,68} in which valence electrons were described within a plane-wave basis of 500 eV. Valence-core interactions were treated with the projector-augmented wave (PAW) method,⁶⁹ with cores of [Ar] for Ti, [He] for O, and [He] for Li. The gradient-corrected (GGA) exchange-correlation functional of Perdew, Burke, and Ernzerhof was used,⁷⁰ with selected calculations supplemented with a Dudarev + U correction of $U=4.2$ eV applied to the Ti d states (GGA+ U).⁷¹ This U value has been obtained by fitting to experimental data the splitting between occupied and unoccupied Ti d states for oxygen vacancy states at the (110) surface of rutile TiO_2 ,³⁷ and has been used to model oxygen vacancies at other rutile surfaces,⁴³ Nb and Ta substitution,⁴² and O vacancy and Ti interstitial formation in rutile and anatase TiO_2 .⁴⁴ Real space projection was employed for the PAW functions, with projection operators optimized to give an accuracy of $\sim 1 \times 10^{-4}$ eV atom⁻¹, and sufficient G vectors were included in the summation for Fourier transforms between real and reciprocal space that wrap-around errors were avoided. All calculations were performed using a $3 \times 3 \times 1$ anatase supercell (108 atoms), with lattice parameters obtained from optimizing stoichiometric cells at constant volume, and fitting the resultant potential energy versus

FIG. 1. (Color online) Projected EDOS for Li_i calculated with (a) GGA and (b) GGA+*U*. In both cases the energy zero is aligned with the top of the valence band. Occupied states are shaded and vertical dashed lines mark the highest occupied state. Red lines show O *p*, dark blue show Ti *d*, and turquoise shows *d* states for the Ti^{III} for the GGA+*U* calculation. In this energy range contributions from the Li *s* states are negligible. The defect peak states in (b) are multiplied by $\times 5$ for clarity.

volume data to the Murnaghan equation of state. This gave zero-pressure lattice parameters for the stoichiometric system of $a=3.900$ Å and $c=9.760$ Å with GGA, and $a=3.907$ Å and $c=9.724$ Å with GGA+*U*. All calculations were spin polarized, and used a Γ -centered $2 \times 2 \times 2$ Monkhorst-Pack *k*-point mesh, with an additional zero-weighted point at the conduction band minimum to obtain accurate band edge positions. To allow calculation of lithium intercalation energies a reference calculation for $\text{Li}_{(\text{s})}$ was performed for a Li_2 cell, using the same convergence criteria as above and with a $16 \times 16 \times 16$ Monkhorst-Pack grid for *k*-space sampling.

III. RESULTS

A. Electronic structure and magnetism

Figure 1 shows projected electronic densities of states (EDOS) for Li-intercalated anatase TiO_2 for GGA and GGA+*U*; obtained by projecting the full valence density onto atom-centered spherical harmonics. The GGA EDOS [Fig. 1(a)] shows no new features in the band gap, and the excess charge resulting from lithium intercalation occupies the bottom of the conduction band, as in previous calculations and in disagreement with the defect state observed in experimental XPS.^{10,50–57} The projected charge density associated with these occupied conduction band states is distributed over all the Ti atoms in the calculation; Fig. 2(a). This discrepancy between experimental data and the calculated electronic structure is a consequence of the self-interaction error inherent to standard functionals.^{61,62} Using GGA+*U* corrects for this error for the Ti *d* states, and the EDOS is brought into agreement with the experimental data, with a gap state now present in the band gap 0.96 eV below the

FIG. 2. (Color online) (a) Partial charge density corresponding to the excess charge at the bottom of the conduction band in the GGA description. The charge isosurface is shown at $0.01 \text{ e } \text{\AA}^{-3}$. (b) Partial charge density corresponding to the band-gap state in the GGA+*U* description. The charge isosurface is shown at $0.05 \text{ e } \text{\AA}^{-3}$. Titanium atoms are shown in gray, oxygen in red, and lithium in purple.

conduction band minimum; Fig. 1(b). Decomposing the projected charge density into individual atomic contributions shows only a single Ti center neighboring the interstitial site contributes to this defect state; labeled Ti^{III} in Fig. 1(b), and with the associated charge density shown in Fig. 2(b). Integrating over the Ti^{III} gap state feature gives an occupancy of 0.68 e on the Ti center, corresponding well to a +3 oxidation state with the defect complex well characterized formally as $[\text{Li}_i^+ + \text{Ti}_{\text{Ti}}']$. This strong localization of excess charge at a single Ti site is in agreement with previous Hartree-Fock results.⁴⁸ The metallic GGA solution is diamagnetic whereas the GGA+*U* solution is spin polarized with a magnetization of $1 \text{ } \mu\text{B}/\text{Li}$.

B. Optical absorption

Lithium insertion into anatase TiO_2 is accompanied by first blue, then black coloration, which makes it an attractive material for electrochromic applications. It has been proposed that this optical absorption is due to polaronic

trapping of electrons at Ti^{3+} centers and the localized state predicted with GGA+ U calculations supports this model. To characterize the effect of lithium interstitials on the optical absorption of bulk anatase TiO_2 we calculated the absorption spectrum for the optimized Li-intercalated structure. Experimental samples formed under typical growth conditions are intrinsically n -type with oxygen vacancies and titanium interstitials expected to be present.^{44,46} Absorption spectra for these defects were also calculated to allow comparison between intrinsic and lithium-produced spectral features.

The optical absorption spectra were calculated using the transversal approximation and PAW approach.⁷² The optical matrix elements, $\hat{P}_\alpha^{fi}$, are calculated using the method of Adolph *et al.*,⁷³ where

$$\hat{P}_\alpha^{fi} = \langle \Psi_f | \hat{P}_\alpha | \Psi_i \rangle. \quad (2)$$

$\hat{P}_\alpha$ is the momentum operator with polarization α , and Ψ are PAW all-electron wave functions. The imaginary part of the dielectric function is given by

$$\text{Im } \epsilon_{\alpha\beta}(\omega) = \left(\frac{2\pi e}{m\omega} \right)^2 \sum_{if} \hat{P}_\alpha^{if} \hat{P}_\alpha^{fi} \delta[E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega] d(\mathbf{k}) \quad (3)$$

with integration performed using the tetrahedron method⁶⁹ and a fine Γ -centered ($4 \times 4 \times 4$) Monkhorst-Pack k -point mesh. The real part of the dielectric function, $\text{Re } \epsilon_{\alpha\beta}(\omega)$, is obtained from $\text{Im } \epsilon_{\alpha\beta}(\omega)$ using the Kramers-Kronig relations.⁷⁴ The absorption coefficient is then given by

$$\alpha(\omega) = \frac{\sqrt{2[|\epsilon_{\alpha\alpha}(\omega)| - \text{Re } \epsilon_{\alpha\alpha}(\omega)]}}{c}. \quad (4)$$

The absorption spectra are summed over all direct transitions between occupied and unoccupied Kohn-Sham orbitals, and therefore this ignores indirect and intraband absorption.⁷³ Furthermore, this framework of single particle transitions does not allow for electron-hole correlations, which would require treatment by higher order electronic-structure methods.^{75,76}

The calculated optical absorption spectrum for Li_i is shown in the upper panel of Fig. 3, and is repeated in the lower panel alongside the calculated spectra for Ti_i and V_O in anatase TiO_2 , and that of the stoichiometric system. The presence of the Ti^{3+} defect state in the band gap results in the absorption edge moving ~ 1.7 eV below that of the stoichiometric system (at 2.7 eV for the GGA+ U calculations), and supports the hypothesis that polaronic Ti^{3+} centers are responsible for the coloration of experimental samples. The absorption feature appears as two peaks; one broad, or compound feature, at 1.5 eV, and a second smaller peak at 2.1 eV [labeled A and B in Fig. 3(a)].

Although V_O and Ti_i similarly redshift the absorption edge there are differences between these spectra and that of interstitial lithium that are expected to be observable in appropriately treated experimental samples. Li absorption is a maximum around 1.25 eV and falls to zero ~ 0.5 eV below the absorption edge corresponding to the optical band gap of

FIG. 3. (Color online) [(a) and (b)] Calculated optical absorption spectra for the lithium interstitial (red); repeated in (b) alongside the calculated spectra for the oxygen vacancy V_O (blue), titanium interstitial Ti_i (green), and stoichiometric bulk anatase TiO_2 (black) (Ref. 44). In (a), A and B indicate the two features described in the text.

the stoichiometric system. Both V_O and Ti_i show continuous nonzero absorption from the defect induced onset up to the stoichiometric optical band-gap energy. Furthermore the spectrum for V_O shows only very weak absorption below 1.9 eV. For comparison to experimental spectra it should be noted that all the features reported here, including the absorption edge for the stoichiometric system at 2.7 eV, are redshifted with respect to experiment due to the underestimation of the fundamental band gap inherent to these GGA calculations. To a first approximation, correcting the band gap underestimation is expected to rigidly shift both occupied and unoccupied states derived from Ti d states by the same amount, i.e., the d - d splitting is unchanged, and so the relative positions of the calculated spectral features are expected to be accurate.

C. Geometry

Using both GGA and GGA+ U , the optimized structures place the intercalated lithium close to the center of a previously vacant O_6 octahedron. A quantitative analysis of the local coordination environments is presented in Fig. 4. In both cases the tetragonal distortion of the coordination octahedra produces a general [4+2] coordination. In the GGA case, the Li is equidistant from the four equatorial O sites (1.93 Å), and the Li-O distances in the [001] direction are 2.86 and 2.82 Å. In the GGA+ U case the polaronic localization of charge at a single Ti site (indicated as Ti^{III}) bonded to two of the equatorial oxygens produces a small distortion to the coordination geometry. The Ti^{III} ion is larger than the remaining Ti^{IV} ions, resulting in increased Ti^{III} -O distances

FIG. 4. (Color online) Schematic of the interatomic distances that define the octahedral lithium coordination environment for (a) GGA and (b) GGA+*U*. All distances are in Å.

of 2.10 Å, compared with ~ 2.05 Å in the stoichiometric system. This increase is compensated by Ti–O bond lengths shortening to 1.98 Å on the opposite side of the intercalation site.

Wagemaker *et al.*⁷⁷ have reported neutron scattering data that were interpreted as showing that Li intercalated into the anatase structure does not sit at the center of the octahedral interstices but is instead displaced along the *c* direction, occupying one of two equivalent sites separated by 1.61 Å. This preference for an off-center Li position was given support by data from molecular dynamics using the partial charge COMPASS force field.⁷⁸ In contrast, atomistic simulation by Olson *et al.*²⁷ with formal-charge Buckingham poten-

FIG. 5. (Color online) Energy vs relative *z* displacement of Li relative to the center of the intercalation octahedron, for GGA and GGA+*U* calculations. GGA results are shown as open circles (brown) and GGA+*U* results as closed circles (blue). The vertical dashed lines show the positions of off-center minima reported for interatomic potentials by Wagemaker *et al.* (Ref. 77) and Kerisit *et al.* (Ref. 79).

tials found the stable intercalation site to be at the octahedron center. Recent molecular-dynamics simulations performed by Kerisit *et al.*⁷⁹ with a polarizable modification of the partial-charge Matsui-Akaogi potential reported hopping between pairs of intraoctahedral sites separated by 0.8 Å along the *c* direction with a calculated activation energy of 17 meV. While it is clear that the behavior in atomistic models depends on the choice of interaction potential, previous DFT calculations (GGA) have shown no indication of the favored Li position having a large displacement (Δz) along the [001] direction: Tielens *et al.*⁵⁵ reported a Δz of only ~ 0.1 Å. These authors also sought a preferred minimum by performing test calculations with Li initially displaced along *z* and found that geometric optimization resulted in the Li returning to the center of the octahedron.

In agreement with that previous DFT study, the optimized geometries for both GGA and GGA+*U* give Li positions close to the point equidistant from the axial O sites. To examine the potential energy surface for Li free to move along the [001] direction, we performed a series of geometry optimizations, holding fixed the *z*-coordinates of the lithium interstitial and the four Ti atoms that occupy equatorial positions around the coordination octahedron. This gives a constrained Li *z* offset from the octahedron center while all other degrees of freedom are able to relax. The resultant variation in energy with the Li offset is shown in Fig. 5 for GGA and GGA+*U*. With both approaches, only a single potential energy minimum is found, corresponding to the center of the coordination octahedron. We also performed calculations with the lithium initially displaced 0.8 Å along the *z* direction (to give a Li–O distance of 2.0 Å) and with full geometric relaxation. This starting structure was found to spontaneously relax to the octahedra-centered coordination described above, as reported previously by Tielens *et al.*⁵⁵

While the GGA/GGA+*U* geometries do not agree with the interpretation of the neutron data provided by Wage-

FIG. 6. (Color online) A slice through a single stoichiometric anatase TiO_2 unit cell, showing contours in the potential energy experienced by a test point charge. The only minima are at the centers of the vacant octahedra.

maker *et al.*, it should be noted that the potential energy surface within stoichiometric anatase TiO_2 is largely defined by deep wells at the center of the vacant coordination octahedra (see Fig. 6) and the optimized geometries presented here are as expected from electrostatics if the Li ion behaves as a point charge.

D. Intercalation voltages

The energetics of Li intercalation at the composition of $x(\text{Li})=0.03$ were calculated according to

The intercalation energy is 2.14 eV with GGA and 1.88 eV with GGA+ U , showing little difference between the two methods. Voltage data for Li intercalation into anatase TiO_2 have been reported by a number of groups, and these give an initial intercalation voltage of ~ 2.5 eV that rapidly falls to a plateau of 1.78 eV by $x(\text{Li}) \approx 0.05$.^{9,80} At $x(\text{Li})=0.03$ the voltage is ~ 1.9 eV, which would suggest the GGA+ U calculation is more accurate, in line with the results of Zhou *et al.*⁸¹ who reported an order of magnitude improvement in lithiation voltages in layered and spinel-like transition metal oxides. Given the uncertainty associated with assigning a precise experimental value within this regime of rapidly varying voltage, however, we interpret the calculated voltages for GGA and GGA+ U as both being in reasonable agreement with the experimental data.

E. Electron-lithium binding energies

Localized electrons in TiO_2 that are trapped as small polarons undergo thermally activated hopping between available sites.^{82,83} This migration of charge plays a critical role in determining the performance of TiO_2 as a photocatalyst or DSSC component. In photocatalysis, electrons (and holes) that diffuse to the surface are available to interact with adsorbed reactant molecules, and in dye-sensitized solar-cells

voltage production requires photoinjected electrons to diffuse to the anode. In both cases recombination events are a competing pathway that reduce the quantum efficiencies of these materials. It is thought that electron motion is controlled by the energy distribution of trap states.⁸⁴ Defects modify the distribution of trap energies and in the case of deep traps are thought to act as recombination centers.²⁷

To calculate the binding energies of electrons interacting with interstitial lithium we performed additional calculations with the Li-intercalated anatase system in +1 and -1 charge states. This was done by changing the number of electrons included in the calculation with a corresponding background charge included so that the Coulomb energy converges with periodic boundary conditions. To calculate the binding energy between a single electron and intercalated Li we consider the process

The associated change in energy is given by

$$\Delta E_{+1/0} = \{E[\text{Li}:\text{TiO}_2]^{+1} + E[\text{TiO}_2]^{-1}\} - \{E[\text{Li}:\text{TiO}_2]^0 + E[\text{TiO}_2]^0\}, \quad (7)$$

where $E[D]^q$ is the energy of defect D in charge state q . Similarly, the energy associated with trapping a second electron at a Li interstitial is

with the change in energy given by

$$\Delta E_{0/-1} = \{E[\text{Li}:\text{TiO}_2]^0 + E[\text{TiO}_2]^{-1}\} - \{E[\text{Li}:\text{TiO}_2]^{-1} + E[\text{TiO}_2]^0\}. \quad (9)$$

Equations (7) and (9) can be expressed in terms of thermodynamic transition levels, $\epsilon_D(q/q')$ (cf. Appendix), to give

$$\Delta E_{+1/0} = \epsilon_{[\text{Li}:\text{TiO}_2]}(+1/0) - \epsilon_{[\text{TiO}_2]}(0/-1). \quad (10)$$

$$\Delta E_{0/-1} = \epsilon_{[\text{Li}:\text{TiO}_2]}(0/-1) - \epsilon_{[\text{TiO}_2]}(0/-1). \quad (11)$$

This gives a binding energy for a single electron ($\Delta E_{+1/0}$) of 56 meV and a trapping energy for a second electron ($\Delta E_{0/-1}$) of -30 meV.

The interactions between interstitial lithium and electrons trapped at Ti centers have previously been studied by Olson *et al.* with atomistic simulations.²⁷ They reported a binding energy of 0.54 eV for a $[\text{Li}_i^\bullet + \text{Ti}_{\text{Ti}}']$ cluster, indicating a strong preference for electrons to trap at sites adjacent to lithium interstitials. The binding between trapped electrons and interstitial lithium in anatase TiO_2 was also recently examined by Kerisit *et al.*⁷⁹ using a modified Matsui-Akaogi potential, which gave a binding energy of 0.28 eV for a lithium ion-electron polaron pair.⁷⁹ The difference in calculated binding energies is most likely due to the choice of ion charges for each study. Olson *et al.*⁸⁵ used a modified potential due to Grimes *et al.* which used formal charges ($\text{Ti}_{\text{Ti}}^\times:4.0$; $\text{Ti}_{\text{Ti}}':3.0$; $\text{O}_\text{O}^\times:-2.0$), whereas Kerisit *et al.*⁸⁶ used a modified form of the Matsui-Akaogi potential with non-formal charges ($\text{Ti}_{\text{Ti}}^\times:2.2$; $\text{Ti}_{\text{Ti}}':1.6$; $\text{O}_\text{O}^\times:-1.6$) leading to a reduced electrostatic attraction between $\text{Li}_i^\bullet$ and Ti_{Ti}' . The

FIG. 7. (Color online) Schematic showing a four edge-sharing O_6 octahedra and the lithium intercalation sites at their centers; (A–D). The lithium diffusion pathways considered in Fig. 8 are shown as dotted lines. Due to electron localization at a single Ti^{3+} (indicated) the octahedron centers are inequivalent within GGA+*U*. The distortion of the octahedra to D_{2d} symmetry is not shown. Oxygen atoms are red and titanium atoms are gray.

results presented here are in qualitative agreement with the previous theoretical data, as all show a favorable interaction between intercalated lithium and a neighboring localized Ti^{3+} center. The GGA+*U* binding energies are, however, an order of magnitude smaller than predicted by the previous atomistic potential calculations. This is probably due to the inability of simple forcefields to fully account for the very strong screening of electrostatic interactions in TiO_2 .

F. Lithium diffusion and the effect of the Li^+-e^- interaction

When considering anatase TiO_2 as an anode material for lithium ion batteries a critical parameter is the rate of diffu-

sion of intercalated lithium ions since this determines power output and battery charging times. The polaronic localization of the Ti^{3+} state lowers the symmetry of the lithium intercalation site and it is therefore possible that the diffusion behavior of Li ions is itself asymmetric. We performed a series of nudged elastic band calculations,⁸⁷ with three inequivalent diffusion pathways considered, which are illustrated in Fig. 7. For each of the pathways; $A \rightarrow B$, $A \rightarrow C$, and $C \rightarrow D$; the excess electron was localized at the same Ti^{3+} center. For comparison we also calculated the diffusion profile using GGA+*U* with all points considered in the +1 charge state. This removes the localized defect state, and approximates diffusion if the electron is far from the lithium, for example trapped at a competing defect site. Calculation of the diffusion profile was also performed using GGA.

The calculated diffusion profiles are shown in Fig. 8. For the GGA and GGA+*U*[$q=1$] pathways all the Ti centers, and hence all the Li interstitial sites, are equivalent, and the diffusion end points are labeled X and X'. With GGA+*U* the position of the Ti^{3+} center affects both the relative energies of the Li intercalation sites and the barriers for diffusion between them. Site A is the most favorable for Li intercalation, and corresponds to the Ti^{3+} being coordinated to two of the equatorial oxygen atoms of the interstitial octahedron, as shown above in Fig. 4. Site B is in a neighboring octahedron where two coordinating oxygens are also bonded to the Ti^{3+} center; here though one such oxygen is equatorial and one apical around the intercalation center. For intercalation sites where the Li is separated from the Ti^{3+} the intercalation energy increases; by 49 meV at C, and 53 meV at D. The difference between A and D of 53 meV compares well with the energy of 56 meV calculated by considering different charge states and taken as the energy change for infinite separation, i.e., the binding energy between the interstitial

FIG. 8. (Color online) Energy profiles for lithium diffusion between adjacent octahedra. Three sets of calculations are shown corresponding to (a) GGA+*U* (red), (b) GGA+*U* (green), with all points calculated in the +1 charge state, equivalent to the electron being far from the interstitial site, and (c) GGA (blue). For (a) the reaction coordinate labels are shown in Fig. 7. For (b) and (c) all the Ti sites, and hence all interstitial sites (X and X'), are equivalent.

lithium and an electron localized at a polaronic Ti^{3+} center.

The heights of the diffusion barriers also increase as the Li moves away from the Ti^{3+} . For diffusion between the two interstitial sites coordinated to the Ti^{3+} ; $\text{A} \rightarrow \text{B}$; the barrier is 0.588 eV. Moving the Li away from the Ti^{3+} center along $\text{A} \rightarrow \text{C}$ is less favorable with a barrier height of 0.657 eV. This difference in barrier height between $\text{A} \rightarrow \text{B}$ and $\text{A} \rightarrow \text{C}$ is greater than the difference in site energies between B and C, suggesting the distortion of the potential energy surface produced by the localization of the electron at the Ti^{3+} center is greater at the barrier peaks than at the centers of the interstitial octahedra. This difference in stabilization is as expected from electrostatic considerations. The lithium is closest to the Ti^{3+} site at the midpoint of the diffusion pathway and it is at this point that the difference in electrostatic $\text{Li}^+ - \text{Ti}^{3+}$ is most significant. Moving along $\text{C} \rightarrow \text{D}$ the barrier is 0.636 eV with motion back to A along $\text{C} \rightarrow \text{A}$ crossing a barrier of 0.608 eV. The reverse $\text{D} \rightarrow \text{C}$ barrier is 0.632 eV, with the symmetric barrier height for $\text{C} \leftrightarrow \text{D}$ again suggesting that by D the $\text{Li} - \text{Ti}^{3+}$ interaction is close to the limiting case of far separation due to the very strong electrostatic screening in this high-dielectric material. The GGA + $U[q=+1]$ calculated barrier gives a good approximation to the large-separation limit barrier for GGA + U with a barrier height of 0.623 eV. If this behavior transfers to other TiO_2 polymorphs, then similar calculations in +1 charge states will provide a means of estimating the upper limit to the true GGA + U diffusion barrier in more complex structures; e.g., $\text{TiO}_2\text{-B}$,^{88,89} without having to explicitly account for the direct (and asymmetric) $\text{Ti}^{3+} - \text{Li}^+$ interaction that potentially arises from polaronic localization of excess charge. In contrast the GGA calculated barrier (calculated for the GGA-optimized lattice parameters) is much lower at 0.511 eV. This difference is not due to variation in zero-pressure volume between GGA and GGA + U . Repeating the calculation using GGA at the GGA + U optimized lattice parameters gives an even smaller barrier of 0.463 eV.

The calculated GGA + U diffusion barriers of ~ 0.6 eV agree with experimental values due to Lunell *et al.*⁴⁹ who reported a diffusion barrier of 0.6 ± 0.1 eV. The GGA value of 0.511 eV is still compatible with this range, although lies at the limits of the experimental data. The result that the diffusion barrier heights are anisotropic, and depend on the position of the Ti^{3+} center relative to the intercalated lithium, is in qualitative agreement with the findings of Kerisit *et al.* from atomistic simulations.⁷⁹ In that work the diffusion started from the same arrangement as B in this work with the diffusion pathways sampling a total of three jumps away from the B position. This difference means a direct comparison between the two pathways is impossible. Kerisit *et al.* similarly found the largest barrier for the initial separation of Li from the neighboring Ti^{3+} , although a much larger variation of diffusion barrier heights with relative $\text{Li}^+ - \text{Ti}^{3+}$ geometry was predicted: The barrier from B to the neighboring interstitial site was calculated to be 0.53 eV with successive barriers at ~ 0.4 eV (a change of 22%). The difference between barriers for $\text{A} \rightarrow \text{C}$ and $\text{C} \rightarrow \text{D}$ presented here is much smaller at 0.657 and 0.636 eV (a change of only 3%). This difference is most likely due to the much stronger $\text{Li}^+ - \text{Ti}^{3+}$ interaction for the atomistic simulations, mirroring the larger

FIG. 9. (Color online) Lithium positions at the NEB images for the GGA + $U[q=+1]$ calculation, showing the curved diffusion path between adjacent octahedra.

$\text{Li}^+ - \text{Ti}^{3+}$ binding energy also predicted by Kerisit *et al.*⁷⁹

Examining the Li positions for the NEB calculations reveals that rather than lithium moving in a straight line between adjacent octahedra, the preferred diffusion pathway follows a curving s shape; Fig. 9. Curved diffusion paths for Li motions are well documented in a number of other Li-intercalated oxides, for example LiMPO_4 olivine-type materials.⁹⁰

IV. SUMMARY AND DISCUSSION

We have performed periodic density-functional-theory calculations on Li_xTiO_2 anatase at $x=0.03$, which approximates the dilute limit. In experiment, Li intercalation of anatase is accompanied by the formation of a defect state ~ 1.0 eV below the conduction band edge,^{10,29-31} and similar features in other n -type TiO_2 systems have been attributed to localized Ti^{3+} defect states. Standard GGA calculations fail to predict such a defect state, instead delocalizing the excess charge over all the Ti centers in the calculation, and partially occupying the bottom of the conduction band to give a metallic system. This is a consequence of the self-interaction error inherent to standard DFT functionals, and similar behavior has previously been described for a number of defective oxide systems.^{59-61,65}

Using GGA + U to provide an approximate correction for this error predicts a defect state 0.96 eV below the conduction band edge, in good agreement with the Li-produced state seen in valence XPS. This state is strongly localized at a single Ti center as a small polaron, with a local magnetic moment of 1 μB , and is well described formally as Ti_{Ti}' or Ti^{3+} . This occupied defect state in the band gap produces a new absorption peak that is redshifted relative to the fundamental absorption edge, which explains the progressive coloration of TiO_2 that accompanies Li intercalation. The localization of charge also breaks the crystalline symmetry with the coordination geometry around the Li intercalation site distorting to accommodate the larger ionic radius of the Ti^{3+} .

Because standard GGA fails to even qualitatively describe the electronic structure for Li intercalated anatase TiO_2 , care should be taken, in general, in modeling Li-intercalation into TiO_2 -based materials, particularly where the description of the electronic structure is critical to understanding the phe-

nomena of interest. For example, a number of TiO_2 systems doped with transition-metal ions have been proposed as dilute magnetic semiconductors. Park *et al.*^{52,91} have suggested that additional intercalation of lithium can be used to control the magnetic properties of these materials since the accompanying transfer of electrons to the Ti sublattice will modify carrier concentrations, and possibly even the preferred charge states and magnetic moments of the TM-dopants. The qualitative difference in charge localization and magnetism between GGA and GGA+*U* for lithium intercalated into stoichiometric anatase indicates that the choice of functional is critical for density-functional-theory studies of lithium in TM-doped TiO_2 and that such studies cannot be relied upon to give realistic descriptions if the self-interaction error is not taken into account. This qualitative failure of standard DFT functionals is also expected to be a problem for descriptions of Li intercalation into other transition metal oxides for which the self-interaction error in standard density functionals is known to be an acute problem for descriptions of *n*-type doping.

Previous neutron-diffraction data for Li-intercalated anatase TiO_2 have been interpreted as the existence of two potential energy minima for Li occupation within each interstitial octahedron.⁷⁷ This dual-basin feature is not reproduced by our calculations, and only a single potential energy minimum exists at the center of the interstitial sites, in agreement with previous *ab initio* studies of this system.⁵⁵

Geometry optimization of different relative $\text{Li}^+ - \text{Ti}^{3+}$ positions shows that the two possible configurations, where the Ti^{3+} is coordinated to two of the oxygen atoms that make up the interstitial cage, are close in energy ($\Delta E = 4$ meV). Occupation of interstitial sites separated from the Ti^{3+} is less favored, with the furthest considered separation 53 meV higher in energy than the most favored configuration. Calculations of charged defect states, used to examine the energy required to separate the Li and electron, predict a binding energy of 56 meV which agrees well with the energy difference obtained from a geometry optimization of the lithium occupying a next-next-nearest interstitial site, and suggests that the Li-electron interaction is short-ranged, being well screened within the high-dielectric TiO_2 lattice. The short-range and weak energy of this interaction suggest that while an electron is expected to preferentially associate with intercalated lithium, under thermal equilibrium a large number of lithium-electron geometries are expected to be thermally accessible where only a small proportion correspond to the associated $\text{Li}^+ - \text{Ti}^{3+}$ defect complex.

Diffusion barriers have been calculated using nudged elastic band methods. These barriers also depend on the relative position of the Li^+ and the Ti^{3+} , in agreement with previous atomistic simulation calculations.⁷⁹ Li motion between sites mutually neighboring the Ti^{3+} has a smaller barrier than motion of the Li away from the Ti^{3+} ; or of motion of the Li^+ in a locally uniform lattice where the Li and Ti^{3+} are well separated.

The favorable $\text{Li}^+ - \text{Ti}^{3+}$ association energy, and the dependence of the barrier height for diffusion on the relative $\text{Li}^+ - \text{Ti}^{3+}$ geometry supports previous suggestions that diffusion occurs via a coupled ambipolar process, where the motion of Li and corresponding electron is correlated to some

degree.^{49,79} The strength of the interaction between the Li^+ and Ti^{3+} is, however, predicted to be much weaker than suggested by previous atomistic simulations,^{27,79} which would indicate the dual Li—electron motion is less strongly correlated than predicted previously. Depending on the strength of the $\text{Li}^+ - \text{Ti}^{3+}$ interaction, and the effect this has on the relative diffusion barriers for a bound $\text{Li}^+ - \text{Ti}^{3+}$ and a well separated Li^+ , it may be possible to probe this difference with suitable experiments. For example, diffusion coefficients may reveal a non-Arrhenius temperature dependence, or it might be possible to manipulate electron trapping by further doping. N doping of TiO_2 is thought to introduce substitutional $\text{N}_\text{O}^\times$ with an empty defect state lying just above the valance band edge.⁹² Although these are likely to be compensated for by native defects such as V_O and Ti_i ,⁴⁶ uncompensated $\text{N}_\text{O}^\times$ can trap the electron introduced by *n*-type defects, forming diamagnetic $\text{N}_\text{O}^\bullet$. The suppression of the UPS feature associated with native *n*-type defects in rutile following N-implantation has been interpreted as demonstrating this process⁹³ and in the case of Li-intercalation similar behavior would prevent the formation of a $\text{Li}^+ - \text{Ti}^{3+}$ associated pair.

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APPENDIX: CHARGE-TRAPPING ENERGETICS

Defect energies are formally defined relative to the stoichiometric system via

$$\Delta H_{\text{D},q}(E_{\text{F}},\mu) = (E_{\text{D},q} - E_{\text{H}}) + qE_{\text{F}} + \sum n_\alpha \mu_\alpha, \quad (\text{A1})$$

where

$$E_{\text{F}} = \Delta E_{\text{F}} + E_{\text{VBM}} + \Delta v_{\text{D}}. \quad (\text{A2})$$

Here E_{H} is the total energy of the stoichiometric host supercell and $E_{\text{D},q}$ is the total energy of the defective cell. μ_α are the chemical potentials of species either added to or removed from the system with respect to some reference reservoir with n_α giving the required change in stoichiometry. ΔE_{F} is the Fermi level relative to the valence band maximum of the stoichiometric host and can range from the valence band maximum ($\Delta E_{\text{F}} = 0$ eV) to the conduction-band minimum ($\Delta E_{\text{F}} = E_{\text{CBM}} - E_{\text{VBM}}$), and Δv_{D} is a core-level alignment between the stoichiometric and defect cells, obtained by taking the difference of O 1s core-level energies for an oxygen atom well removed from the defect position.

The thermodynamic (adiabatic) transition levels of a given defect, $\epsilon_{\text{D}}(q/q')$ are given by the Fermi energy at which charge states q and q' have equal energy

$$\epsilon_D(q/q') = \frac{E_{D,q} - E_{D,q'}}{q' - q}. \quad (\text{A3})$$

For a given Fermi energy relative to the valence-band maximum, ΔE_F , the difference in energy between two charge states is

$$\Delta E_D(q/q') = (q' - q)[\epsilon_D(q/q') - \Delta E_F]. \quad (\text{A4})$$

Hence, thermodynamic tendency for charge to transfer from one defect type to another is

$$\Delta E[D_\alpha(q_\alpha/q'_\alpha):D_\beta(q_\beta/q'_\beta)] = \Delta E_{D_\alpha}(q_\alpha/q'_\alpha) + \Delta E_{D_\beta}(q_\beta/q'_\beta), \quad (\text{A5})$$

$$= (q'_\alpha - q_\alpha)[\epsilon_{D_\alpha}(q_\alpha/q'_\alpha) - \Delta E_F] + (q'_\beta - q_\beta)[\epsilon_{D_\beta}(q_\beta/q'_\beta) - \Delta E_F]. \quad (\text{A6})$$

Under the constraint of conservation of charge ($q'_\alpha - q_\alpha + q'_\beta - q_\beta = 0$), and the driving force per unit charge transferred simplifies to

$$\epsilon_{D_\alpha}(q_\alpha/q'_\alpha) - \epsilon_{D_\beta}(q_\beta/q'_\beta), \quad (\text{A7})$$

i.e., is given by the difference in energy between the respective transition levels for different defects.

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