

Combining the Pair Distribution Function and Computational Methods To Understand Lithium Insertion in Brookite (TiO₂)

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Supporting Information

ABSTRACT: X-ray pair distribution function (PDF) methods and first-principles calculations have been combined to probe the structure of electrochemically lithiated TiO₂ Brookite. Traditional powder diffraction studies suggest that Brookite amorphizes upon lithium insertion, with the Bragg reflections disappearing. However, PDF analysis indicates that the TiO₂ framework connectivity is maintained throughout lithium intercalation, with expansions along the *a* and *b* axes. The Li⁺ ions within the framework are poorly observed in the X-ray PDF, which is dominated by contributions from the more strongly scattering Ti and O atoms. First-principles calculations were used to identify energetically favorable Li⁺ sites within the Brookite lattice and to develop a complete structural model of the lithiated material. This model replicates the local structure and decreased intermediate range order observed in the PDF data. The analysis suggests that local structural distortions of the TiO₂ lattice accommodate lithium in five-coordinate sites. This structural model is consistent with the observed electrochemical behavior.

Titanium oxides are promising novel electrode materials because of their high electrochemical potential, which confers enhanced device safety and stability. A key question with this class of materials is the response of the structure to lithium intercalation and the resulting impact on the electrochemical performance. Among known TiO₂ polymorphs, anatase (*I4₁/amd*), rutile (*P4₂/mnm*), and the TiO₂-B (*C2/m*) phases have been extensively studied, probing structural changes that occur upon lithiation and the impact that nanoscale particles have on lithium insertion.¹ In contrast, relatively little is known about the structural changes that occur in the Brookite form of TiO₂ during lithiation, which is challenging to prepare as a single phase.² This naturally occurring form of TiO₂ (*Pbca*; *a* ~ 9.187 Å, *b* ~ 5.447 Å, *c* ~ 5.145 Å)³ consists of edge- and corner-sharing TiO₆ octahedra, which form channels along the *c* axis (Figure 1). The dimensions of the channels are suitable to accommodate lithium ions (~0.76 Å). As for rutile and anatase, the particle size has been found to strongly impact lithium insertion into Brookite, with nanoscale particles capable of accommodating up to 0.9 lithium per formula unit during the first discharge.^{4,5} X-ray diffraction studies of samples recovered from different stages in lithium insertion and deinsertion reactions suggest that the Brookite

framework amorphized during discharge, with a partial recovery of the crystallinity upon (re)charging.⁵ This apparent amorphization, along with the smooth potential–composition relationship, indirectly suggests that Brookite exhibits solid–solution behavior upon insertion. However, the observed amorphization at high levels of lithiation impedes reliable structural analysis (e.g., lattice expansions and interatomic distances) using conventional Bragg crystallography and, as such, the structure of the lithiated material is not fully understood.

The pair distribution function (PDF), $G(r)$, which is obtained from total scattering data by Fourier transformation of the structure function, $S(Q)$, includes information from both the Bragg and diffuse intensities. In contrast to conventional Bragg analysis, this method does not require that the sample be crystalline and provides local and long-range structural information as a distribution of all of the atom–atom distances.⁶ This structural information extends beyond the first few coordination shells, probed in X-ray absorption spectroscopy studies, to provide additional insight to the framework connectivity. The magnitude of the contribution to the intensity of the correlations in the PDF is dependent on the scattering intensity of the atoms with the pair. With X-rays, this scales with the number of electrons in the atoms. As such, direct insight into the coordination environment of weakly scattering Li atoms can be challenging (although the global framework structure can be well-defined). Accordingly, it is important to combine different complementary approaches to gain a complete understanding of the structure of these materials. For example, *ab initio* simulations have been widely used, enabling a more detailed atomic-scale structure to be obtained.⁷ Here, we have combined the synergies of X-ray PDF analysis and first-principles calculations to understand the structure of lithiated TiO₂ Brookite.

In the present study, a chemical composition of Li_{0.75}TiO₂ was obtained by electrochemical lithiation of high-surface-area TiO₂ Brookite. For both compounds, high-energy X-ray scattering data were collected at the beamline 11-ID-B at the Advance Photon Source located at Argonne National Laboratory. Details about material preparation, synchrotron data reduction, and simulations can be found in the Supporting Information. The PDFs obtained for TiO₂ and Li_{0.75}TiO₂ are shown in Figure 2.

Refinement of a model based on the known Brookite structure, against the data obtained for the pristine material, confirmed the

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phase purity of the prepared TiO₂ Brookite.³ Upon lithium insertion, features in the PDF shifted to higher r , indicating a general framework expansion, as expected upon reduction. Additionally, a

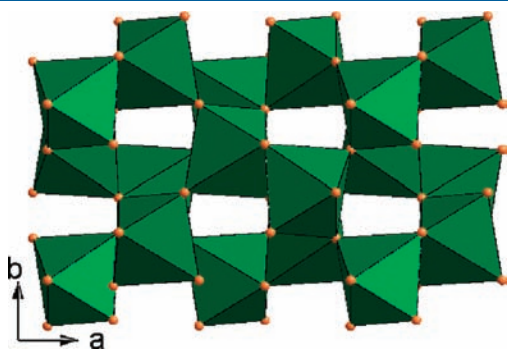


Figure 1. Polyhedral representation of the structure of TiO₂ Brookite.

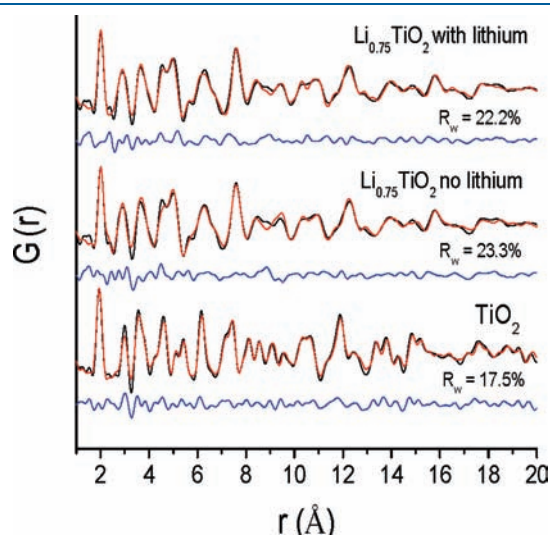


Figure 2. PDFs (black) of the pristine and lithiated phase Li_{0.75}TiO₂, refined profiles (red), and residual to the fit (blue). The residuals are relatively even and featureless.

broadening of the peaks is evident upon lithiation, as consistent with reduced sample crystallinity.⁵ Apparent changes in intensity of certain features in the PDF are associated with a changing overlap of unresolved peaks corresponding to individual correlations rather than a change in coordination number of these individual correlations. The first peak in the PDF, corresponds to Ti–O bond within the TiO₆ octahedra. Fits of Gaussian functions to this peak indicates that the average Ti–O distance increases from 1.954 to 2.018 Å upon lithiation. The latter is within the range typical of Ti³⁺–O²⁻ bonds, indicating a partial reduction of Ti⁴⁺ to Ti³⁺ upon lithium insertion. Fitting the PDF data for Li_{0.75}TiO₂ using the Brookite structural model, indicates a general increase in lattice volume, with expansions along the a - and b -directions by 2.9% and 4.2%, respectively, and a slight contraction along the c -direction (0.6%). Structural refinement without adding Li sites, provides an acceptable fit to the data ($R_w \sim 23.3\%$), confirming the retention of the Brookite framework at this level of lithiation and the relatively weak contributions of Li correlations to the PDF. However, refinement of the Ti and O positions within this model, resulted in unacceptably long Ti–O distances (Table 1). This could be alleviated through the application of anisotropic atomic displacement parameters for the O atoms, although it is difficult to physically justify such a refinement strategy.

The addition of partially occupied Li sites, fixed at positions within the Brookite channels suggested by our earlier modeling studies, 8c (0.403, 0.345, 0.449),⁸ led to an improved fit to the data ($R_w \sim 22.2\%$). In this case, the refined structural model showed chemically reasonable bond lengths and distances. A comparison of the refined structural parameters for the pristine and lithiated phases is shown in Table 1. The origin of the changes in the PDF can be identified by considering the partial pair contributions to the PDFs (Supporting Information).

Although the addition of lithium within the refined model led to a more chemically reasonable structure, the weak scattering of lithium prevented the direct refinement of the coordinates. Analysis of first-principles calculations was used to provide more insight into the structure of the lithiated phase and, specifically, the lithium environment within the Brookite framework. These calculations optimized a $1 \times 2 \times 1$ supercell model containing 16 TiO₂ units [(Li_{0.75}TiO₂)₁₆] with Li atoms added to the framework channels.⁸ To permit local structure distortions, not

Table 1. Structural Parameters from PDF Refinements

	TiO ₂ ^a	Li _{0.75} TiO ₂ , ^a no lithium modeled	Li _{0.75} TiO ₂ , ^{a,b} lithium modeled
a (Å)	9.19(1)	9.47(1)	9.47(1)
b (Å)	5.438(7)	5.69(1)	5.68(1)
c (Å)	5.143(5)	5.09(1)	5.13(1)
V (Å ³)	257.0(5)	274.2(7)	275.9(8)
Ti(x,y,z)	0.1296(6), 0.103(1), 0.862(1)	0.1242(9), 0.1222(2), 0.893(3)	0.126(1), 0.121(3), 0.897(2)
O1(x,y,z)	0.009(2), 0.152(5), 0.183(4)	0.980(2), 0.134(7), 0.252(4)	0.0135(2), 0.11(1), 0.221(4)
O2(x,y,z)	0.226(2), 0.120(4), 0.540(4)	0.237(2), 0.123(6), 0.563(5)	0.240(2), 0.12(1), 0.560(5)
$d_{\text{Ti-O1}}$ (Å)	1.897(2)	1.909(34)	1.958(41)
	1.962(2)	2.075(31)	1.975(20)
	2.006(2)	2.282(24)	2.070(45)
$d_{\text{Ti-O2}}$ (Å)	1.880(2)	1.991(28)	2.007(46)
	1.973(2)	1.998(30)	2.038(26)
	2.017(2)	2.103(29)	2.045(43)
$d_{\text{Ti-O average}}$ (Å)	1.955	2.059	2.015

^a Space group: $Pbca$, $Z = 8$. ^b The lithium atomic coordinates were fixed as 8c (0.403, 0.345, 0.449), the occupancy was set to 0.75, and the atomic displacement parameter was set at 0.01 \AA^2 .

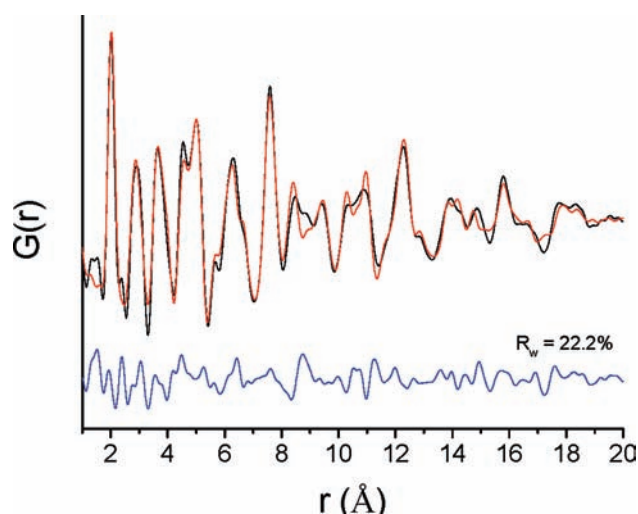


Figure 3. PDF (black) of $\text{Li}_{0.75}\text{TiO}_2$, refined (red) using the $(\text{Li}_{0.75}\text{TiO}_2)_{16}$ supercell model predicted by ab initio calculations. Difference between the calculated and experimental data (blue).

confined to the symmetry of the parent structure, an ab initio energy minimization of this model was undertaken in P1, that is, without any symmetry operators.

The computationally derived supercell model $(\text{Li}_{0.75}\text{TiO}_2)_{16}$ was validated against the PDF data measured for the lithiated material. The PDF calculated for this model, allowing relaxation of the lattice parameters, atomic displacement parameters, and instrument parameters, provided an improved fit of the data ($R_w \sim 22.2\%$; Figure 3), particularly at short distances. As such, the supercell model replicates the local structure and decreased intermediate range order observed in the PDF data. The unit cell parameters and atomic coordinates of the refined supercell $(\text{Li}_{0.75}\text{TiO}_2)_{16}$ are provided in the Supporting Information. Partial PDFs based in this supercell model (see Supporting Information) demonstrate the relatively weak contribution from the correlations involving lithium, which are largely overlapped with other correlations within the material. This underlies the difficulty in directly determining the structure of the lithiated system from the PDF analysis alone and clearly emphasizes the value of combining different approaches in order to gain insight into lithium-based intercalation compounds.

The Li site within the model is surrounded by six O atoms in a distorted octahedral geometry (Figure 4). One of the Li–O bonds is particularly long ($\sim 2.5 \text{ \AA}$), such that the Li ion can be considered to be five-coordinate, with an average Li–O distance of 2.0 \AA .

In summary, PDF analysis gave direct evidence on the stability of the Brookite network upon lithium intercalation. Insights from ab initio calculations were used as a complementary tool to locate lithium positions within the TiO_2 framework. The calculated model finds a five-fold coordination environment for the Li ion. From the combined PDF and computation approach, it is clear that the TiO_2 connectivity within the Brookite framework remains intact. The flexibility of the framework, which, in part, allows it to accommodate the Li ions, is also responsible for the broadening of the Bragg reflections and apparent amorphization evident in earlier studies. The observation that the framework remains intact is ultimately linked to the property of the material to retain its capacity over many cycles (see Supporting Information). Typically, the observation of amorphization is correlated with the assumption of changes in connectivity. Here the use of methods that probe the local and

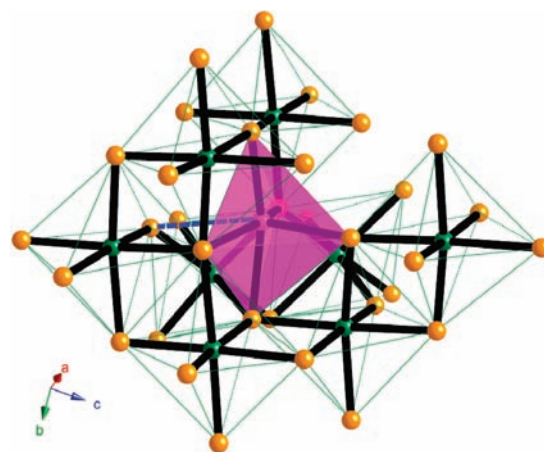


Figure 4. Lithium environment (pink) within the Brookite framework. The dashed blue line indicates the elongated Li–O distance.

intermediate atomic structures shows that the process of amorphization is not necessarily linked to changes in atomic connectivity. We envision that this approach will find wider use in the study of the structure function properties of battery materials.

■ ASSOCIATED CONTENT

S Supporting Information. Details of sample preparation, PDF analysis, and simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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