Chemical Structures of Specific Sodium Ion Battery Components Determined by Operando Pair Distribution Function and X-ray Diffraction Computed Tomography

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Abstract: To improve lithium and sodium ion battery technology, it is imperative to understand how the properties of the different components are controlled by their chemical structures. Operando structural studies give us some of the most useful information for understanding how batteries work, but it remains difficult to separate out the contributions of the various components of a battery stack (e.g., electrodes, current collectors, electrolyte, and binders) and examine specific materials. We have used operando X-ray diffraction computed tomography (XRD-CT) to study specific components of an essentially unmodified working cell and extract detailed, space-resolved structural information on both crystalline and amorphous phases that are present during cycling by Rietveld and pair distribution function (PDF) methods. We illustrate this method with the first detailed structural examination of the cycling of sodium in a phosphorus anode, revealing surprisingly different mechanisms for sodiation and desodiation in this promising, high-capacity anode system.

One of the biggest problems in studying battery structures in general, and in particular when using total X-ray scattering methods, is the contribution to the data from parts of the battery other than those in which we are interested. This is less significant for conventional X-ray diffraction studies of crystalline materials where it is usually possible to mask the background features and concentrate on the Bragg peaks from the component of interest. Unfortunately, many of the most interesting battery materials are amorphous at some stages of cycling. Studying amorphous materials with X-ray scattering requires us to use the total scattering of the sample to calculate the pair distribution function (PDF). To do this, the non-sample contributions must be removed. Allan and co-workers and Chapman et al. have addressed this by using background subtraction methods and adapting their batteries significantly for total scattering experiments. Herein, we propose an alternative and much more informative method based on the PDF-CT approach first reported by Jacques and co-workers. Although operando tomographic imaging has recently revealed significant information on the macrostructure of batteries and has been combined with scanning X-ray diffraction (XRD), the tomographic technique has not been applied for atomic structural data. Jensen and co-workers have studied commercial lithium ion and nickel metal hydride batteries with XRD-CT methods, mapping the distribution of LiCoO₂ from the intensity of a single peak and obtaining information on its orientation from the 2D diffraction patterns. By reconstructing the entire battery system with XRD-CT and carrying out Rietveld and PDF analysis of the data as a function of the charge state, we have 1) obtained data focusing specifically on the phosphorus anode of a basically unmodified (i.e., not significantly different from a normal coin cell; this may be compared to the highly adapted electrode particles studied with absorption CT by Ebner et al.) working sodium ion battery (SIB) and 2) removed all contributions from the other components of the cell and sample container, giving the best quality data on the anode for Rietveld and PDF analysis. As we have shown elsewhere, the use of full structural methods allows data to be extracted from tomograms that would have been considered useless if analyzed with conventional phase contrast and absorption tomography techniques.

Phosphorus is one of the most promising alloying anodes for SIBs owing to its high capacity (theoretical capacity 2596 mAh g⁻¹, reversible capacity up to 1890 mAh g⁻¹ as a composite with carbon) and considerable cycling stability. Its structure has previously not been studied under working conditions and is amorphous except when fully sodiated to form crystalline Na₃P. Combining operando XRD and PDF-CT reveals with full clarity the different mechanisms of sodiation and desodiation of phosphorus (despite its low X-ray scattering factor and location inside an electrochemical cell), in good agreement with cycling data and density functional theory (DFT) calculations. The technique described here was also combined with operando X-ray absorption tomographic imaging to provide additional information on the macrostructure of the battery (e.g., volume changes, dendrite formation). This allowed us to identify...
potential problems, such as movement and expansion of the battery components, that are particularly relevant for alloying anodes such as phosphorus that can undergo volume changes of as much as 400% during cycling (see the Supporting Information, Movie S1).

Initial analysis of the reconstructed XRD-CT data for the anode region using “surface” Rietveld methods (with the crystalline Na$_3$P$_2$ structure) showed limited structural variations within the individual tomographic slices (Figure 1), but confirmed the stability of the methods and the location of the anode material at this stage. Slices 4 and 5 of the tomogram contain significant amounts of glass fiber separating material, with slice 5 containing virtually no anode material despite the volume expansion. The resolution of the tomograms in XRD-CT is limited by the size of the beam (see the Supporting Information) and was also optimized to give enough tomograms during battery cycling to see the structure at different points in the charge/discharge curve. Improvements in both beam line optics and detector technology (in place at ID15 since January 2017) will improve the space and time resolution of the method, and may allow extraction of structural data from individual particles in the future. Variations in the parameters between the layers are probably due principally to the changes in charge state during the 7 min acquisition time per slice. Electrochemical cycling curves showing the points at which each tomographic slice was acquired are shown in the Figure S19.

Further analysis focused on the central voxels of the slices. Reconstructed diffractograms of the voxel at position (15,15) in slice 3 for the first desodiation and the second sodiation are shown in Figure 2. The Bragg peaks from the Na$_3$P$_2$ phase are clearly visible when the anode is fully sodiated, and a broad feature in the diffraction patterns at 2θ ≈ 4° appears during sodiation but not during desodiation. The broad peak at about 2.5° is due to phosphorus nanoparticles.

Rietveld analysis of voxel (15,15) in tomographic slices 2 and 3 showed the appearance of the crystalline Na$_3$P$_2$ phase during sodiation and its disappearance during desodiation. Trends in the crystallite size, unit cell axes, and occupancy of the Na atom sites of the layered Na$_3$P$_2$ structure are shown in Figure 3 along with the voltage profiles. A clear decline in crystallite size is observed during desodiation with a corresponding growth in the crystallite size during sodiation when the phase reappears. The two Na sites are seen to depopulate during desodiation and gradually repopulate as the Na$_3$P$_2$ phase reappears during sodiation. This suggests that Na mobility in the phase, in agreement with the findings of Qian and co-workers.[11,12] High Na mobility was also observed in Na$_3$Sb.[13] In addition, the occupancies of the Na sites never reached 100%, suggesting that stoichiometric Na$_3$P$_2$ is not formed. The lattice parameter data show small variations in the a-axis while the c-axis is extended significantly during the first desodiation and contracts slightly during the second sodiation.

The fitted PDFs ($G(r)$) are shown in Figures S3–S15, with the fit agreement factors in Table S1. Despite the high noise levels in the $G(r)$ functions during the amorphous stages of cycling, our models explain the key features of the PDFs. From the extent of the peaks in the PDF, we extracted crystallite/cluster sizes at each charge state. The simplest possible cluster models were used in fitting to avoid fitting noise at high $G(r)$ in the amorphous materials. Scale factors for the fitted phases are plotted in Figure 4 with the voltage curves above. The crystallite size from the Rietveld refinement is plotted on the same axes for comparison. For full...
desodiation, the $G(r)$ has only one peak at approximately 2.25 Å (the approximate length of a P–P bond), indicating a cluster of a few phosphorus atoms with no order beyond the first shell of P–P bonds. We fitted this using a model cluster of four P atoms (Figure 5).

The PDF analysis shows clearly that NaP (with a cluster size of less than 10 Å) is formed during sodiation but not during desodiation while Na₃P is present for longer during desodiation. Compared to the Rietveld analysis of Na₃P, we observed the phase later during desodiation and earlier during sodiation in the PDF data, suggesting that amorphous Na₃P exists before the crystalline form.

DFT calculations were used to construct a convex energy hull diagram for the Na/P system (Figure 6), which is in agreement with that reported by Mayo and co-workers.[13] The hull shows the thermodynamically most favorable route between P and Na₃P. In agreement with our PDF results, the lowest-energy route to Na₃P passes through the rather stable NaP helical P-chain structure (Figure 1b). This acts as an intermediate in a two-phase-type mechanism, easing the transition to layered Na₃P. We have thus far found no evidence for the presence of any of the other stable Na/P phases lying on or close to the energy hull at any stage of cycling, though this cannot be entirely ruled out. It is possible that they may be observed with better time/space resolution and that the tiny clusters may exhibit varying stoichiometry. These phases would further ease the transition from very small P clusters to the layered structure of Na₃P (see the

![Figure 3](image3.png)

**Figure 3.** Voltage profiles for desodiation and sodiation (a) and data from Rietveld refinements of Na₃P in the voxel at position (15,15) of tomographic slice 3: crystallite size (b), lattice parameters (c), and Na site occupancy (d). Lattice parameters and site occupancy results from diffractograms collected at charge states where crystalline Na₃P is not present are not shown.

![Figure 4](image4.png)

**Figure 4.** Voltage profiles for desodiation and sodiation (a) and plots of the PDF scale factor for all phases (b). The crystallite size obtained from the Rietveld refinement of Na₃P is plotted for comparison.

![Figure 5](image5.png)

**Figure 5.** Models used in the PDF analysis: a) amorphous P nanocluster, b) amorphous NaP nanocluster, and c) crystalline Na₃P.

![Figure 6](image6.png)

**Figure 6.** DFT energy hull diagram showing the lowest-energy phases in the P–Na phase diagram and formation enthalpies for Na-deficient NaₓP structures (magenta). The black line indicates the lowest-energy route while the blue and red dotted lines show the observed routes of desodiation and sodiation, respectively.
Energy hull does not help us to understand why the thermodynamic route is not followed on desodiation. We therefore carried out further calculations on the deintercalation of Na from Na$_3$P, maintaining the layered structure as observed in the operando tomographic experiment. We found that several stable phases exist, suggesting that a smooth transition from Na$_3$P through Na$_{1.3}$P to P should be favored by kinetics over the nucleation of NaP, that is, in the case of high Na mobility as is the case here, NaP should not form. Na$_{2.3}$P and Na$_{2.39}$P are the possible stable Na-deficient structures in the Na$_3$P matrix and are included as points in Figure 6 (the red dotted line indicates the kinetically favored path from Na$_3$P to P). Furthermore, we calculated that Na$_3$P, which might serve as an intermediate on the path to Na$_3$P during desodiation, is highly unstable (this phase is also shown, well above the convex hull, in Figure 6). We believe that the small plateau observed at about 0.7 V during desodiation for phosphorene/graphene anodes is a sign that the thermodynamic mechanism (Na$_3$P→NaP→P) co-exists with the kinetic deintercalation mechanism to some degree at lower rates of desodiation. Similar kinetic mechanism was observed during desodiation of the Na/Sb system. These mechanisms are supported by the lattice parameters presented in Figure 3c. The large extension and small contraction of the c-axis during desodiation and the second sodiation, respectively, indicate that the structure is retained for longer during desodiation, and that increasing levels of Na probably serve to hold the layered structure together.

The reasons for the different mechanisms of sodiation and desodiation of the Group 15 elements are still unclear, though size effects may be significant. P (0.44 Å) and Sb (0.90 Å) have sodiation routes different from those of their desodiation, which include significant amorphous components. The somewhat larger Bi (1.03 Å) follows the same route on sodiation and desodiation and retains crystallinity at all stages, with the crystal structure of Na$_3$Bi depending on the crystallite size. In addition, the size of Bi is similar to that of Na$^+$ (1.02 Å effective ionic radius) while P and Sb are smaller. No experimental data on the Na/as system are available, although gallium arsenide has recently been studied as an anode for LIBs. The rate of deintercalation of Na from crystalline Na$_3$P is probably too high for the formation of intermediates except at very low rates of desodiation. Na$_3$Sb is similar, with the deintercalation leading to other clearly identifiable amorphous intermediates, but not Na$_3$Sb. The $^{29}$Na NMR results reported by Allan and co-workers show high Na mobility (which they relate to the excellent high rate performance of Sb anodes) in crystalline Na$_3$Sb, which supports the idea that fast Na deintercalation is connected to the differences between sodiation and desodiation routes in P and Sb anodes. The thermodynamic sodiation route, from P nanoclusters to NaP chains to layered Na$_3$P, involves the breaking and forming of many bonds and should be significantly slower than deintercalation. A similar scheme with kinetic and thermodynamic routes for charge and discharge, respectively, has been described for the Na/Co$_3$O$_4$ system.

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