

Structural characterization of the delithiated noncrystalline phase in a Li-rich $\text{Li}_2\text{VO}_2\text{F}$ cathode material

Lithium-ion batteries (LIBs) have been widely used in various portable products as energy storage devices. The properties of LIBs, including energy density, power density, and rate performance, are mostly determined by the cathode material and its crystal structure. Currently, the most widespread cathode materials are those in which Li ions are extracted and inserted by topochemical reactions, such as spinel-structure layered rock salt. The energy density of these cathode materials is limited by the presence of their well-ordered framework, although they have superior rate performance. Further improvements of LIBs for practical applications will require the development of alternatives to layered rock salt and spinel structures as cathode materials.

A disordered rock-salt (DRS, space group $Fm\bar{3}m$) cathode material, $\text{Li}_2\text{VO}_2\text{F}$ (LVOF), was reported by Chen *et al.* [1]. The estimated theoretical capacity of 462 mA h/g is higher than that of current commercial cathodes. Moreover, there is little volume expansion of the LVOF lattice upon cycling, which reduces stress on the device. Unfortunately, the LVOF materials suffer from rapid capacity decay and increased polarization in applications. Very recently, Baur *et al.* have carried out *operando* X-ray powder diffraction measurements for LVOF and reported the amorphization of the DRS crystal upon delithiation [2]. Hence, the DRS structure of LVOF collapses owing to a decrease in Li ion concentration because the framework is not strongly fixed in the system. Because the local structure around V ions changes upon charging, it is likely that the amorphous structure is related to cycling performance. The structural analysis of both the crystalline and noncrystalline phases is important for understanding the origin of the properties of cathode materials.

The structural analysis of disordered materials, such as amorphous materials lacking a long-period structure, is challenging because no Bragg peaks are observed in X-ray powder diffraction measurements. Atomic pair distribution function (PDF) analysis is a powerful method that provides insights into the structure of disordered materials. The PDF corresponds to the correlation strength between atomic pairs, which provides structural information in a short-range region. However, PDF analysis for a mixture of crystalline and noncrystalline phases such as an LVOF sample in the charged state cannot be quantitatively evaluated by a conventional technique. If the PDF

of mixed material could be evaluated quantitatively, we would be able to characterize the noncrystalline phase.

For the structural characterization of the noncrystalline phase in delithiated LVOF, the PDF analysis method proposed by Hiroi *et al.* was applied [3]. This method precisely evaluates the scattering intensity from the crystal structure and refines the structural parameters based on the experimental PDF. It is suitable to analyze the PDF measured under the nonideal optical condition because structural parameters that depend on the momentum transfer, such as the instrumental resolution function, can also be treated correctly. When structural parameters of the crystalline phase in a mixture are precisely optimized by the method, the partial PDF of the noncrystalline phase can be extracted from the experimental PDF by subtraction [4]. To obtain the quantitative PDF under several cycling conditions, X-ray total scattering measurements for LVOF materials were performed at a high-energy X-ray diffraction beamline, SPing-8 BL04B2. Figure 1(a,b) shows the experimental scattering intensity and the partial component including the crystalline and noncrystalline phases. The partial scattering intensity from the noncrystalline phase shown in the grey area was markedly enhanced by the lithiation of the LVOF sample. This supports the idea that the noncrystalline phase forms from the broken DRS crystal via delithiation. Figure 1(c,d) shows experimental and

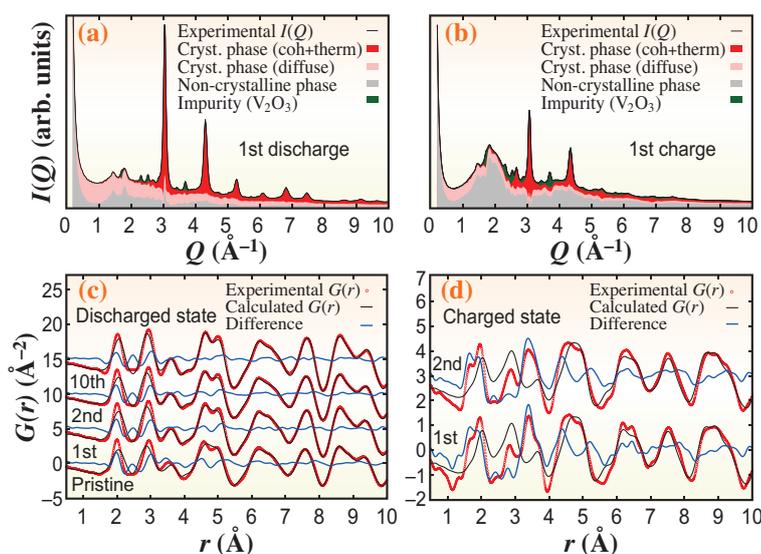


Fig. 1. Partial scattering components of crystalline, noncrystalline, and impurity phases in the (a) discharged and (b) charged states. Experimental and calculated atomic PDFs in the (c) discharged and (d) charged states.

calculated PDFs under several conditions in the range of $r < 10 \text{ \AA}$. A noteworthy change in PDF by delithiation in this range was observed. A shoulder of the first peak at the short-range side and a correlation at 3.4 \AA were derived from the noncrystalline phase. These peaks are ascribed to a V–O bond (1.7 \AA) and a V–V pair (3.4 \AA), respectively. It is suggested that delithiation of the crystalline phase leads to the formation of an amorphous structure through local structural changes that increase the V–V distance. Inversely, the noncrystalline phase returned to the DRS crystal in the discharged state. However, the difference between the experimental and calculated PDFs, shown as blue curves in Fig. 1(c), decreased with an increase in the number of cycles. This reveals that the crystallinity of the DRS crystal in the discharged state was irreversibly improved by cycling.

To analyze the structure of the noncrystalline phase in the charged state, the partial PDF was extracted by the subtraction of the contribution from the crystalline phase. The extracted partial PDF is drawn as red points in Fig. 2(a). Notably, although the PDF of the crystalline phase had a strong atomic correlation at around 2.8 \AA , weak contributions were

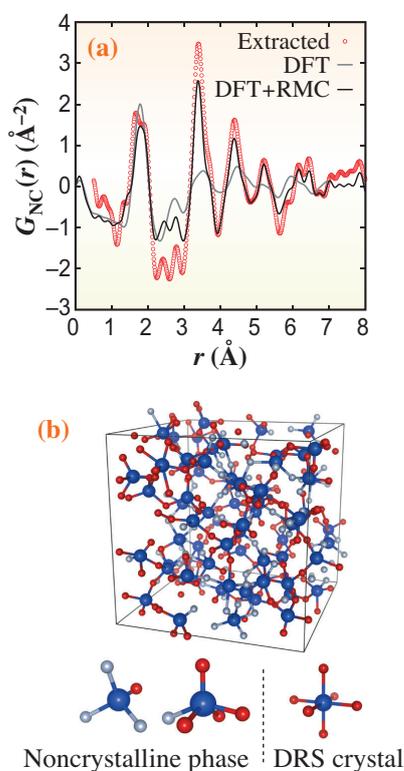


Fig. 2. (a) Extracted atomic PDFs of the noncrystalline phase in the charged state and calculated by RMC and DFT modelling. (b) Atomic structural model obtained by the DFT and RMC model (blue: V, red: O, gray: F). Extracted tetrahedral and pyramidal units from the model and an octahedral structure in the DRS crystal are also shown here.

found here in the extracted PDF. This indicates that the noncrystalline phase consists of not the $\text{V}(\text{O,F})_6$ octahedral structure but the other polyhedrons. We performed reverse Monte Carlo [5] (RMC) and density functional theory (DFT) atomic configurational modelling using the extracted PDF to elucidate the local structure in the noncrystalline phase. Figure 2(b) shows the three-dimensional structural model obtained from RMC and DFT. The local atomic configuration in the noncrystalline phase is characterized by a network of tetrahedral and pyramidal units consisting of V ions and anions. During the charging process, delithiation creates many defects at cation sites in the DRS crystal. A rotation of octahedra in the DRS crystal would be allowed because these defects generate the free volume. The octahedral structure will change to the tetrahedral structure involving the oxidation of V ions at the same time as the delithiation. Figure 3 shows a schematic diagram of the structural transformation of the LVOF crystalline phase upon cycling. With every repetition of V-ion recovery on the cation site upon lithiation, the local disorder may be relaxed owing to the acceleration of the uniform random distribution of V ions. Simultaneously, the short-range order on the anion site near V ion is also likely to change upon cycling.

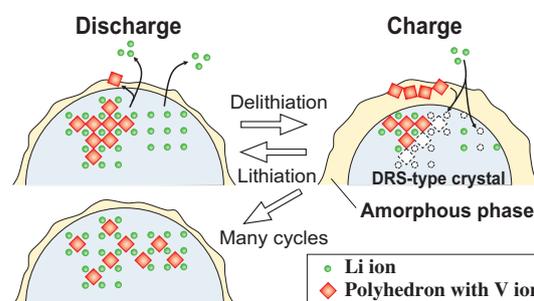


Fig. 3. Schematic diagram of the structural transformation of the LVOF crystalline phase upon cycling.

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