Evaluation of the local structure in a material for Li-ion battery by RMC method

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The spinel LiMn2O4 (LMO) is one of the most promising candidates for a cathode material because of its thermal stability, non-toxicity, and low cost. LMO has a structural phase transition with a hysteresis between the heating and cooling process in a previous study on the single-crystal structural analysis and the differential scanning calorimetry measurement [1, 2]. However, the cathode materials in Li-ion batteries are in a polycrystalline state, there has been little research on the local structure in powder form. Therefore, to evaluate the local structure of spinel-LMO in a polycrystalline state, we applied the reverse Monte Carlo (RMC) method to the total scattering profile.

To estimate the local structure in a crystalline material, we proposed the new approach for RMC modelling as follows:

\[
S_{\text{RMC}}(Q) = \int_0^{r_{\text{max}}} 4\pi r^2 \rho_0 (g_{\text{RMC}}(r) - 1) \sin Qr \frac{dr}{Qr} + \int_{r_{\text{max}}}^{\infty} 4\pi r^2 \rho_0 (g_{\text{obs}}(r) - 1) \sin Qr \frac{dr}{Qr} + 1
\]

where \(F_{\text{Local}}(Q)\) and \(F_{\text{Periodic}}(Q)\) is the local structure term and a long-range periodic structure term, respectively. \(F_{\text{Local}}(Q)\) is calculated from atomic coordination in the calculation box. On the other hand, \(F_{\text{Periodic}}(Q)\) is calculated from the experimental pair distribution function due to the limitation of the calculation box size. RMC trials are performed to decrease R-factor \(R_p\) defined in Eq.2 by changing the atomic configuration in the simulation box until \(R_p\) becomes almost constant,

\[
R_p = \sqrt{\frac{\sum (S_{\text{obs}}(Q_i) - S_{\text{calc}}(Q_i))^2}{\sum S_{\text{obs}}^2(Q_i)}}
\]

Figure 1 shows the experimental and RMC results for spinel-LMO and the corresponding R-factor \(R_p\) value denotes \(R_p = 1.01\%\). To characterize the valence of each simulated MnO6 octahedra, the valence of all Mn atoms was evaluated using the Bond Valence Sum BVS method (\(BVS = \sum_{\text{val}} \exp((r_0 - r)/B)\)), whose parameters are \(r_0 = 1.75\ \text{Å}\) and \(B = 0.374\ \text{Å}\) for the Mn-O bond [3]. Furthermore, we calculated the average distortion parameter \(\Delta_{\text{val}} = 1/\nu_{\text{val}} \sum_{j=1}^{\nu_{\text{val}}} \Delta_j\) of MnO6 octahedra for each Mn valence, where \(\nu_{\text{val}}\) is the number of each valence Mn atom categorized by the BVS analysis and \(\Delta_j\) is the distortion parameter for each MnO6 octahedra [3]. The number of Mn\(^{3+}\) sites is larger than that of Mn\(^{4+}\) in the low-temperature LMO. The Mn\(^{3+}\)O6 octahedra are more distorted and show 3.1 times larger \(\Delta_{\text{val}}\) than that of Mn\(^{4+}\)O6 octahedra. These results indicated that the present RMC procedure for disordered crystal materials is very useful to evaluate small structural changes. We will also discuss the local structure of each Mn valence using the partial pair distribution function and the angular histogram [4].

![Figure 1](image_url)

Figure 1. The observed (black solid line) and the calculated (red broken line) structure factor, the corresponding residual curve (green solid line) of spinel-LMO.