Atomic Ordering in Nanophase Lithium Manganese Oxides

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Introduction

Recently, special attention has been paid to lithium manganese oxides as promising cathode materials for rechargeable batteries [1]. However, most crystalline lithium manganates suffer capacity fading during repeated charge-discharge cycling. The capacity fading is due to a structural transition, leading to a gradual loss of crystallinity and the formation of electronically isolated zones. This inspired a search for nanocrystalline phases of lithium manganates as alternative cathode materials. The hope was that these already structurally disordered materials would be more tolerable for the repeated charging-discharging (Li insertion/deinsertion) process.

Methods and Materials

Two nanophase lithium manganates were studied by high-energy x-ray diffraction and atomic pair distribution function (PDF) analysis to reveal the material's atomic-scale structure. The samples were prepared under aqueous (hydrous sample) and nonaqueous conditions (anhydrous sample) by employing the *Chimie Douce* route at room temperature [2]. Two other crystalline samples with spinel and layered-type structures were studied as well. The experiments were carried out at the BESSRC 11-ID-C beamline at the APS with x-rays of energy 120 keV. The use of higher-energy x-rays allowed higher wave vectors, Q, to be reached, which is important for the success of the PDF studies. Also, it helped reduce several unwanted effects, such as sample absorption and multiple scattering.

Results and Discussion

Experimental powder diffraction patterns are shown in Fig. 1, and the corresponding atomic pair distribution functions are shown in Fig. 2. Sharp Bragg peaks are present in the diffraction patterns of the crystalline samples. The corresponding PDFs also feature sharp peaks, reflecting the presence of long-range order in these materials. The lack of long-range atomic order in the nanophase lithium manganates is evidenced by the absence of Bragg peaks in their diffraction patterns (Fig. 1) and by the rapid decay of the corresponding PDFs to zero (Fig. 2). More detailed analysis of the experimental data is underway. The outcomes will be presented elsewhere.

Acknowledgments

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References

[1] M. Thackeray, Prog. Solid State Chem. **25**, 1 (1997).
[2] S.-J. Hwang et al., J. Phys. Chem. B **106**, 4053 (2002).

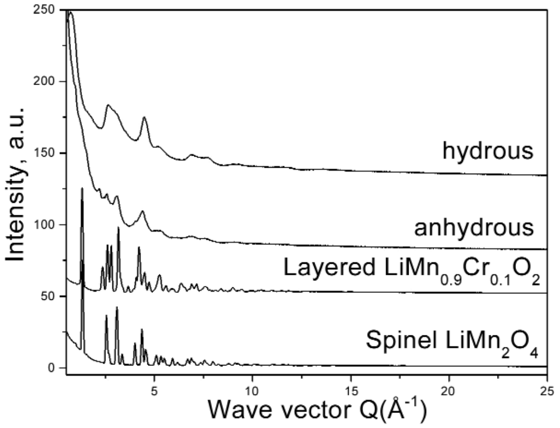

FIG. 1. Powder diffraction spectra of nanocrystalline lithium manganese oxides and two crystalline samples with spinel and llayered-type structures.

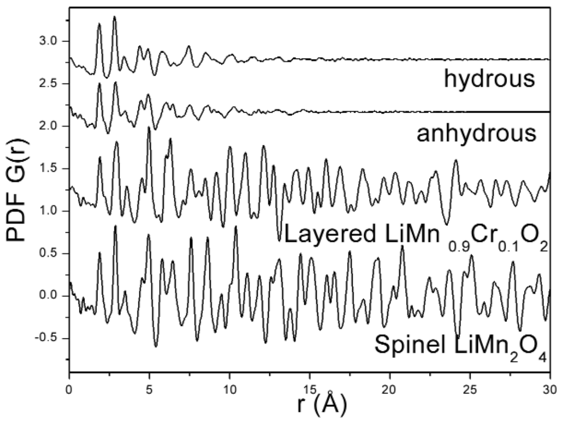

FIG. 2. Experimental PDFs for nanocrystalline lithium manganese oxides and two crystalline samples with spinel and layered-type structures.