Understanding the Structure of $LiMn_2O_4$ by Aberration-Corrected HAADF STEM and Differential Phase Contrast

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Abstract: The rising need for portable energy storage has led to the creation of a formidable Li-ion battery industry, which is poised to grow strongly in the near future. Of the many cathode chemistries for Li-ion batteries, Li[Mn2]O4(LMO) stands out as a particularly appealing cathode due to its moderate capacity, use of environmentally-friendly and cost-effective Mn, and high rate capabilities associated with its cubic spinel framework, which allows three dimensional Li+diffusion. Yet, this material has shown capacity loss, attributed to the dissolution of Mn to the electrolyte. In this work we show by HAADF STEM that a restructured surface is formed in this material, where a stable surface layer of Mn3O4, followed by Li1+xMn2O4 subsurface with retention of bulk LiMn2O4 is formed. In addition, recent advances in STEM allow us to observe not only the structure of the materials at atomic level, but also to obtain images proportional to the projected potential, the projected electric field and the projected charge distribution, by using differential phase contrast technique (DPC). Thus, in this work we also use DPC to determine the Li, Mn and O atomic positions, thus providing a novel insight into the structure of LiMn2O4. Our results clearly show local regions depleted in Li and the existence of manganese atoms in tetrahedral sites occupying a typical Li atom position, or occupying a free octahedral site in the same column, in agreement with the Mn disproportionation reaction reported for such compound. These findings contribute to a better understanding of the mechanisms of lithium and manganese exchange in LiMn2O4 spinel structures.

REFERENCES

[1] S. Calderon, R. Ribeiro. P.J. Ferreira, “Manganese Migration in Li1-xMn2O4 Cathode Materials”, Ultramicroscopy, Vol. 225, pp. 113285 (2021)
[2] Charles Amos, Manuel Roldan, Maria Varela, John Goodenough, Paulo Ferreira, “Revealing the Reconstructed Surface of Li[Mn2]O4”, Nanoletters, Vol. 16, pp 2899–2906 (2016).

FIGURES

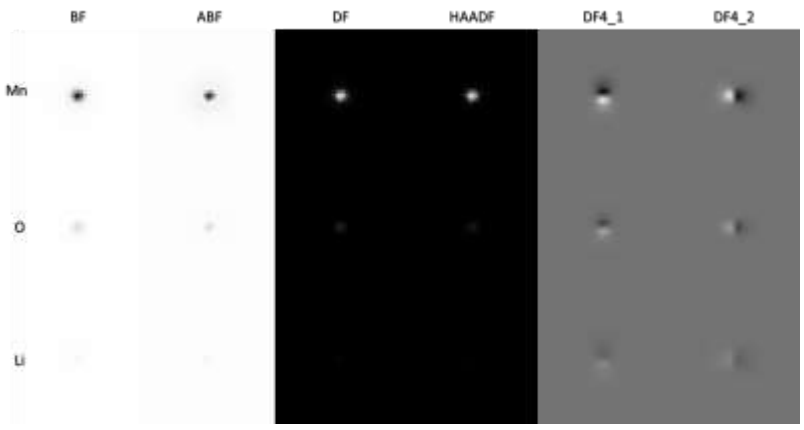

Figure 1: BF, ABF, DF, HAADF and DPC signals for manganese, oxygen and lithium.