Order-disorder transitions in battery electrodes studied by operando X-ray scattering

Dorthe B. Ravnsbæk*, Christian K. Christensen, Christian L. Jakobsen, Martin A. Karlsen

Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

dbra@sdu.dk

Development of novel electrode materials for intercalation type batteries have in the past focused on highly crystalline materials with the capability to retain long-range order during cycling. However, re-cent years have seen an increased interest for disordered materials, e.g. with the discovery of multiple high capacity electrodes based on disordered rock-salt structures or even completely amorphous materials exhibiting higher capacities than their crystalline counterparts [1,2]. Furthermore, it was recently showed by Ceder and co-workers, that long-range order is not a prerequisite for maintaining percolating intercalation pathways [3]. Still very little is known about the structural mechanisms behind order-disorder transitions induced by ion-intercalation or about ion-storage mechanisms in disordered mate-rials. This is in spite that fact that understanding these processes may also provide enhanced insights about how disorder influences the properties of traditional ordered electrodes.

Using operando synchrotron X-ray total scattering with pair distribution function analysis, we have studied a series of battery electrode materials, which undergo severe disordering during charge or discharge, i.e. during ion-extraction or -intercalation [4]. This allows us to map out the structural evolution during battery charge and discharge at the atomic-scale, and begin to understand the ion-storage mechanisms in such materials. The studied materials cover both Li-, Na and Mg-ion electrode materials composed of transition metal (Tm) oxides and phosphates with both layered and 3D-framework structures, e.g. Na_xTmO_2, Na_xFePO_4, Li_xTiO_2, $Li_xV_2O_5$ etc.[4] Our findings reveal that the order-disorder transition can occur both reversibly and irreversibly, via topotactic or completely reconstructive transitions and entail several disordering phenomena such as cation disorder, nano-crystallization, amorphization etc. This talk will illustrate the large variety in order-disorder phenomena within battery electrodes and highlight our methodology for the operando total scattering studies and pair distribution function analysis.

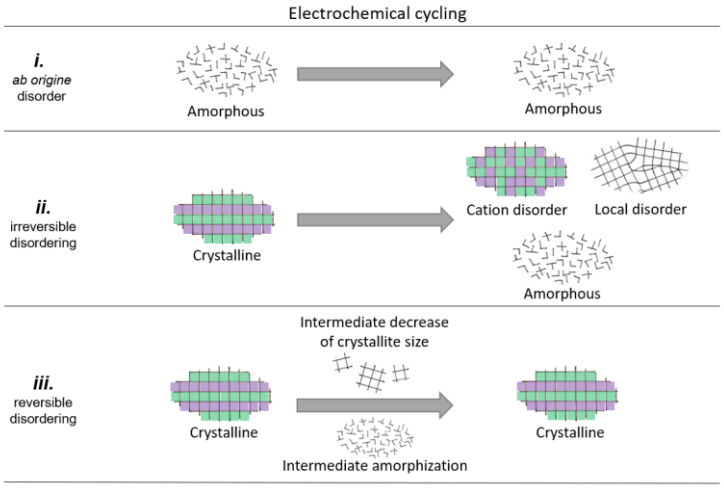

Figure 1. Illustration of the three categories of structural evolution during involving disorder in battery electrodes.

[1] Lee,, J., Kitchaev, D. A., Kwon, D.-H. Lee, J. K,. Papp, C.-W., Liu, Y.-S., Lun, Z., Clément, R. J., Shi, T., McCloskey, B. D., Guo, J., Balasubramanian, M., Ceder, G. (2018) *Nature* **556**, 185-190.

[2] Uchaker, E., Zheng, Y. Z., Li, S., Candelaria, S. L., Hu, S., Cao, G. Z. (2014) *J. Mater. Chem. A* **2**, 18208-18214.

[3] Lee, J., Urban, A., Li, X., Su, D., Mautier, G., Ceder, G. (2014) *Science* **343**, 519-522.

[4] Christensen, C. K., Ravnsbæk, D. B. (2021) *J Phys Energy* DOI: 10.1088/2515-7655/abf0f1

Keywords: Total scattering, Pair distribution function analysis, disorder, nano-crystalization, battery electrode materials

The Carlsberg Foundation, the Independent Research Fund Denmark and the Novo Nordic Foundation are thanked for funding.

Acta Cryst. (2021), A**77**, C499