Digging deeper into the irreversible disordering of nanocrystalline TiO_2-rutile electrodes

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Nanosizing TiO_2-rutile has been shown to improve its Li-ion storage capacity significantly. During the initial discharge, the nanocrystalline material distorts monoclinically and disorders gradually. Upon deep discharge (high degree of lithiation), the material undergoes an irreversible structural reconstruction into a layered α-$NaFeO_2$-like structure with grain boundaries possessing a structural motif resembling that of TiO_2-columbite (TiO_2-II) [1]. Herein, the initial discharge of nanocrystalline TiO_2-rutile in electrodes of Li-ion batteries is investigated in greater detail. The various structural transformations are being resolved by employing a lower current rate and the individual features of the discharge curve are explained by the individual steps of the phase evolution.

The nanocrystalline nature and the disordering hampers Rietveld analysis in reciprocal space and the analysis in real space through PDF analysis gets highly challenging, as the various nanocrystalline phases largely resemble each other in real space, especially at low *r*. The task calls for a versatile toolbox. Inspired by the cloud-based service 'PDF in the cloud' (PDFitc) [2], various model-free tools are employed to shed light on the phase evolution during the initial discharge. When needed, experimental data are denoised using principal component analysis (PCA) to improve visualization of delicate structural features. Inspired by the similarityMapping app on PDFitc, the onset of phase transitions and the phase similarity at various states of charge are probed through Pearson correlation analysis. Inspired by the nmfMapping app on PDFitc [3-4], non-negative matrix factorization (NMF) is used to determine the number of components (phases) needed to describe the trends in the *operando* data and to characterize the phase evolution through the NMF weights.

All the various model-free analyses allow for detailed structural modelling of the *operando* PDF data to dig deeper into the irreversible disordering of nanocrystalline TiO_2-rutile when used in electrodes for rechargeable Li-ion batteries.

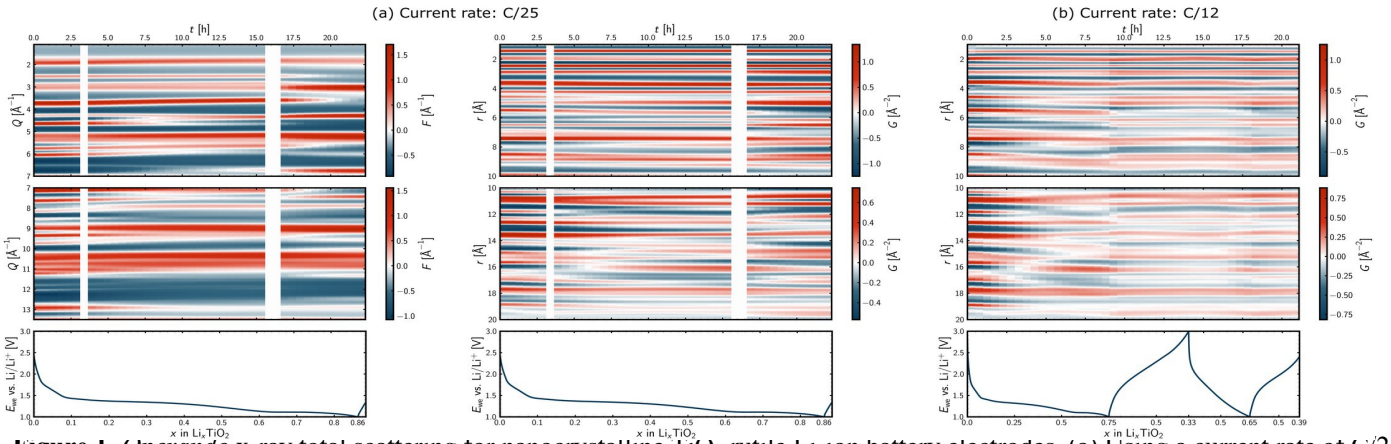

Figure 1. *Operando* x-ray total scattering for nanocrystalline TiO_2-rutile Li-ion battery electrodes. (a) Using a current rate of C/25. Left: reduced total scattering structure function, *F(Q)*. Right: reduced atomic pair distribution function (PDF), *G(r)*. Both the *operando F(Q)* and *G(r)* have been denoised using principal component analysis. Beamline P02.1, PETRA III, Deutsches Elektronen- Synchrotron. (b) *Operando* PDF when using a current rate of C/12. Beamline 11-ID-B, Advanced Photon Source, Argonne National Lab.

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