

## Disordering mechanism during Li-ion intercalation in nano-rutile TiO<sub>2</sub>

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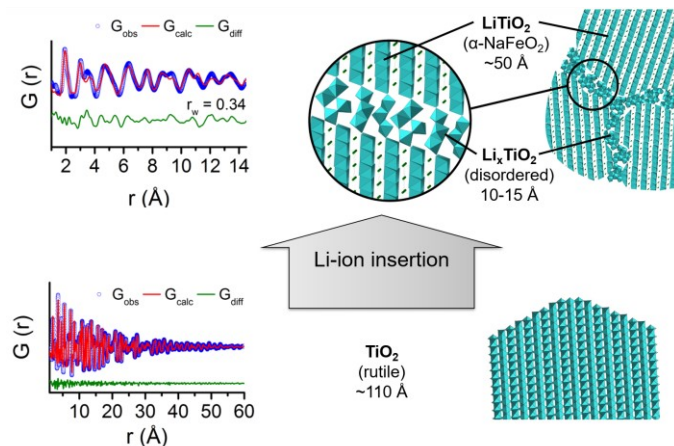
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Traditional Li-ion battery electrodes are highly crystalline materials in which the ions are intercalated between atomic layers or channels in the atomic lattice. Such electrodes are typically characterized by retaining their crystallinity for many charge-discharge cycles. However, a number of electrode materials undergo an irreversible loss of crystallinity upon Li-intercalation. Examples of such materials are rutile TiO<sub>2</sub> and orthorhombic V<sub>2</sub>O<sub>5</sub>, which loses long range order upon intercalation of >0.8 and >2 Li, respectively [1,2]. Very little is presently known about neither the mechanism of such order-disorder phenomena nor about how ion storage occurs in disordered structures in subsequent charge-discharge cycles. This is in spite that such materials represent cheap and effective alternatives to their crystalline counterparts, i.e. recently amorphous V<sub>2</sub>O<sub>5</sub> was shown to reversibly store close to double the amount of Na-ions as compared to crystalline V<sub>2</sub>O<sub>5</sub> [3].

Herein, we investigate the structural evolution during Li-intercalation and the associated disordering process in nano-rutile TiO<sub>2</sub> by means of combined *ex situ* and *operando* synchrotron radiation powder X-ray diffraction and total scattering with pair distribution function (PDF) analysis. We find that, the disorder mechanism entails a reconstructive phase transformation with formation of a distorted  $\alpha$ -NaFeO<sub>2</sub> structure. Furthermore, small disordered domains form due to extensive dislocations between the distorted  $\alpha$ -NaFeO<sub>2</sub> domains [4].



**Figure 1:** PDF fit of initial TiO<sub>2</sub> rutile structure model (bottom) and discharged LiTiO<sub>2</sub> with  $\alpha$ -NaFeO<sub>2</sub> structure and disordered grain boundaries (top).

After amorphization, TiO<sub>2</sub> reversibly stores ~200 mAh/g with ion storage occurring via solid solution reactions with remarkable small volume changes between the end-members. Our results suggest that these materials may hold potential as cheap electrode materials despite the fact that they lose long range order. Also our methodology opens for investigating a wide range of order-disorder phenomena in electrochemically driven phase transitions.

[1] Borghols, W. J. H., Wagemaker, M., Lafont, U., Kelder, E. M. & Mulder, F. M. (2008). *Chem. Mater.* **20**, 2949.

[2] Delmas, C., Cognac-Auradou, H., Cocciantelli, J.M., M6n6tder, M. & Doumerc, J.P. (1994). *Solid State Ionics* **69**, 257.

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

[4] Christensen, C. K., Balakrishna, A. R., Iversen, B. B., Chiang, Y.-M. & Ravnsbæk, D. B. (2019). *Nanoscale* **11**, 12347.

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