

Nano-Area Electron Diffraction for Studies of Energy-Related Nanomaterials

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The future use of electrical energy requires the development of next-generation chemical energy storage systems based on portable and lightweight batteries suitable for low-cost transportation, storage and easy to use for consumers. The natural choice for such endeavor is the use of rechargeable lithium-ion batteries with A/C-electrodes that often consist of nanopowdered materials for improved Li-conversion process. Therefore local structure analysis for such a state of matter was always challenging due to limited choice of sensitive nanostructural methods available.

In the present work we examined the microstructure of promising Li-cathode nanomaterial FeF_2 made via microwave heated precursor synthesis with typical grain size ≤ 6 nm (Fig. 1a). To analyze the large number of nanoparticles, we applied an automated Nano-Area Electron Diffraction (NAED) scanning technique we developed to determine structure properties of the FeF_2 nanomaterial, including (a) “single crystal” reciprocal-space analysis for single grains, (b) establishing reliable (HKL) diffraction conditions for major FeF_2 nanophase, (c) crystallographic space group choice for FeF_2 nanostructure, (d) analysis of minor impurity phases and, finally, (e) real-space texture mapping of NAED data intensities (Fig. 2) by selecting specific diffraction features in NAED patterns with flexible “digital” objective apertures that are not available for conventional TEM or STEM instruments. These data were extracted from single NAED data scan ($30 \times 30 = 900$ patterns) marked by the square contour in Fig. 1 a.

Here the local NAED information is limited only by collimated e-beam size and scanning step-like potential applied to beam deflection coils in S/TEM. Due to the very small probed sample volume by almost parallel nanobeam, the observed NAEDs retain many features of single crystal patterns. They appear to be much less sensitive to strong double-diffraction effects in “forbidden” reflections (marked by crosses in Fig. 1 c-e) as observed in Fourier transforms of HRTEM images leading to incorrect FeF_2 crystal symmetry. NAED data also help in statistical verification of reliable (HKL) diffraction conditions and the space-group determination for new nanomaterials. In addition, NAED data quality can be improved by the removal of inelastic scattering via Gatan Image Filter (GIF), thus making important step towards general diffraction solution of phase retrieval problem [1] in TEM. Furthermore, the GIF spectroscopy mode can help to correlate NAED scans with Li-composition mapping derived from EELS [2].

In summary, from NAED data analysis we found that FeF_2 film has mostly random crystal-grain orientations with some weak texture towards the sample edge (Figs. 2 d-g) consistent with film morphology in Fig 1 b. High purity major FeF_2 nanocrystalline phase shows some traces for FeF_3 impurity phase revealed by few individual NAED patterns, apparently not displayed by the averaged ring diffraction pattern shown in Fig. 1 b. Nanocrystals in FeF_2 film have a rutile-type structure with S.G. $P4_2/mnm$ similar to its bulk counterpart, as follows directly from single-crystal diffraction conditions and relative diffraction intensities examined in Figs. 1 c-e. These results demonstrate an importance of novel microscopy characterization techniques and point a new way to tailoring nanomaterials' properties by controlling their structures [3].

References

- [1] V.V. Volkov, J. Wall and Y. Zhu, *Ultramicroscopy* **108** (2008) 741-749.
- [2] F. Wang, et al, *ACS Nano*, DOI: 10.1021/nn1028168 (2011).
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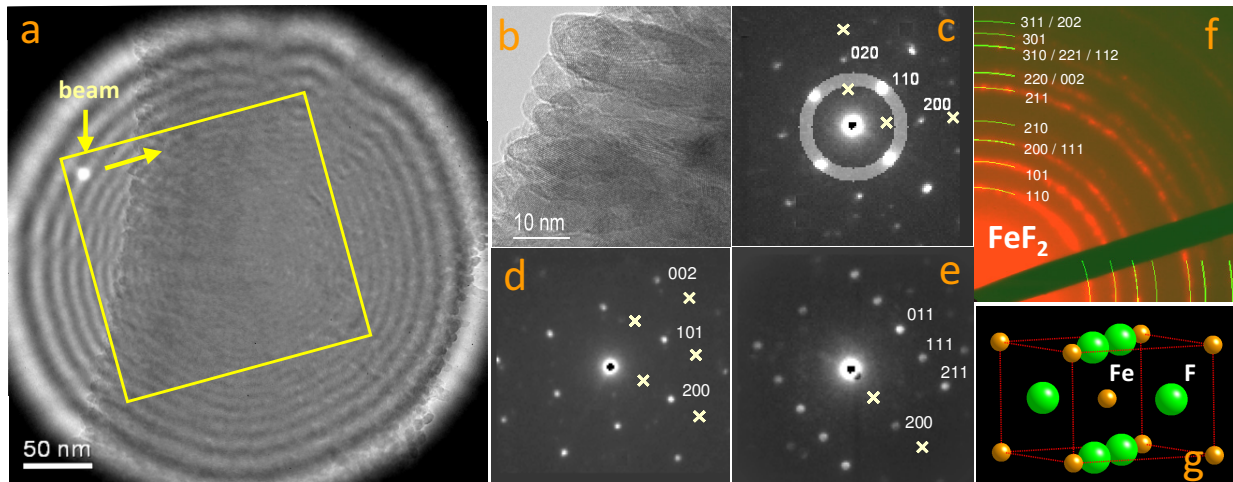


Fig. 1 Details of the automated Nano-Area Electron Diffraction (NAED) scan for FeF_2 nanomaterial suitable for Li-batteries: (a) Local area of the NAED scan is outlined by the squared (yellow) contour with the initial nanobeam position located at the top left corner. The recorded NAED patterns ($30 \times 30 = 900$ for Fig. 1 a) are stored as 4D-data array on the hard drive for offline analysis. (b) Magnified local image showing the weak preferred orientation for nanobar grains oriented towards the sample edge. (c-e) The most common three NAED patterns with “single-crystal” data establishing correct (HKL) diffraction conditions: (c) Zone [001]: $H00$: $H=2n$; $0K0$: $K=2n$; (d) Zone [010]: $H0L$: $H+L=2n$ and $00L$: $L=2n$, eq. to Zone [100]: $0KL$: $K+L=2n$; (e) Additional zone [01-1] with $H00$: $H=2n$. These conditions are consistent only with tetragonal S.G. $P4_2/mmm$ (136). Forbidden reflections are marked for clarity by crosses only in one quadrant of NAED patterns. (f) Appropriate conventional diffraction ring pattern. (g) Crystal structure for FeF_2 ($P4_2/mmm$) consistent with NAED data analysis. In Fig. 1d we show an example of flexible choice for “digital” objective ring aperture used to map all (110) reflections in Fig. 2d. Such “digital” apertures may have several different shapes to pick-up any diffraction feature and map it the real space.

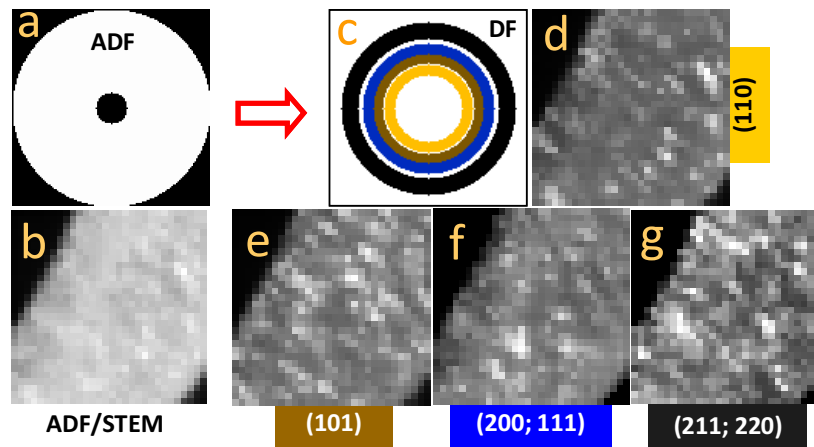


Fig. 2 Example of real-space mapping for NAED data scan by using different selection criteria for flexible “digital” apertures: (a) Fixed geometry for conventional ADF detector and (b) appropriate ADF-STEM image FeF_2 all radial and azimuthal diffraction information averaged and practically lost. (c) In contrast, a set of ring-like “digital” filters (DF) shown here by different colors is used for selective (d, e, f, g) mapping of nanobar grains FeF_2 with several operating reflections. The observed weak diffraction texture in (d-g) images follows from the preferred orientation for FeF_2 nanobar grains towards the sample edge in agreement with film morphology shown in Fig. 1 b.