

Crystal Surfaces and Their Role on Electrochemical Activity in MgV_2O_4 Crystals

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Spinel vanadium oxides are a promising material for electrochemical studies because they have been shown to cycle Mg^{2+} ions at capacities higher than their Mn and Cr-doped counterparts [1]. These high-capacity nanocrystals are typically on the order of a few nm in radius and thus present challenges to studies using electron microscopy techniques. As part of this contribution, we will show that elevating the thermal annealing temperature during synthesis significantly increases the size of MgV_2O_4 crystals and improves their crystallinity. This has opened the way for studies focused on understanding electrochemical activity in single particles. Here, we will present a study concentrating on the role of crystal surface types to electrochemical activity in MgV_2O_4 crystals using atomic-resolution scanning transmission electron microscopy (STEM) and electron-probe spectroscopy techniques.

This study will be conducted using an aberration-corrected cold field emission JEOL ARM200CF operated at 200kV primary electron energy. Imaging and spectroscopic measurements will be conducted with the emission current at 15 μA . The electron probe will be operated at 24 mrad convergence semi-angle and the inner angle detector will be set to 75 mrad for high angle annular dark field imaging and 30mrad for low angle annular dark field imaging. The microscope is also equipped with an Oxford XMAX100TLE X-ray detector and a post-columns Gatan Continuum GIF spectrometer. Beam induced structural changes to the unoccupied density of states will be tracked with LIVE EELS beta software from Gatan.

In this contribution, we will use atomic-resolution imaging and sub-nanometer EELS mapping to demonstrate that electrochemical activity can be correlated to structural transformations on the surface of MgV_2O_4 crystals. By mapping the vanadium *L*-edge and oxygen *K*-edge, we were able to isolate the source of electrochemical activity to a surface layer on the order of 5 nm in thickness. Fig. 1a shows that this region is likely amorphous since lattice fringes visible in the core of the particle terminate abruptly at the upon entering the surface layer. Fig. 1b points to distinct electronic structure between the core and surface of the particle, namely we observe a chemical shift to higher energies in the V *L*-edge onset, as well as changes to the fine structure near the O *K*-edge onset (ELNES). The chemical shift towards higher energies in the *L*-edges is consistent with an increase vanadium valences state, as expected for with a local extraction of Mg^{2+} .

From atomic-resolution images collected along a variety of crystal orientations, we will study how structural transformation- and consequently electrochemical activity- develop along different crystal surfaces. Figure 1. outline this process: (a) an ABF image allows us to determine the orientation of the particle, and (b), (c) show magnified images highlighting how different crystal surface types impact the

propagation of electrochemical activity. Here we observe the abrupt termination of the surface layer along the [111] surface while the [110] shows nonuniform surface terminations [2].

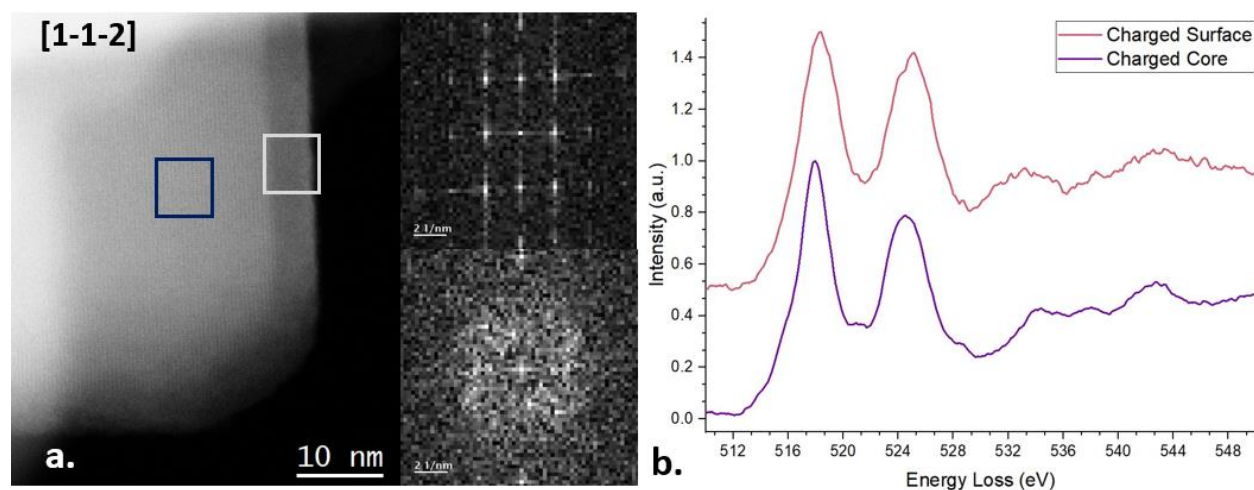


Figure 1. (a) Fast Fourier Transforms showing reduced crystallinity in charged MgV_2O_4 surface layer. (b) Comparison of the V L-edge and O K-edge acquired in the core and surface of the charged particle. The presence of higher energy peaks in the vanadium L-edge indicate an increase to the vanadium confined to the surface of the crystal.

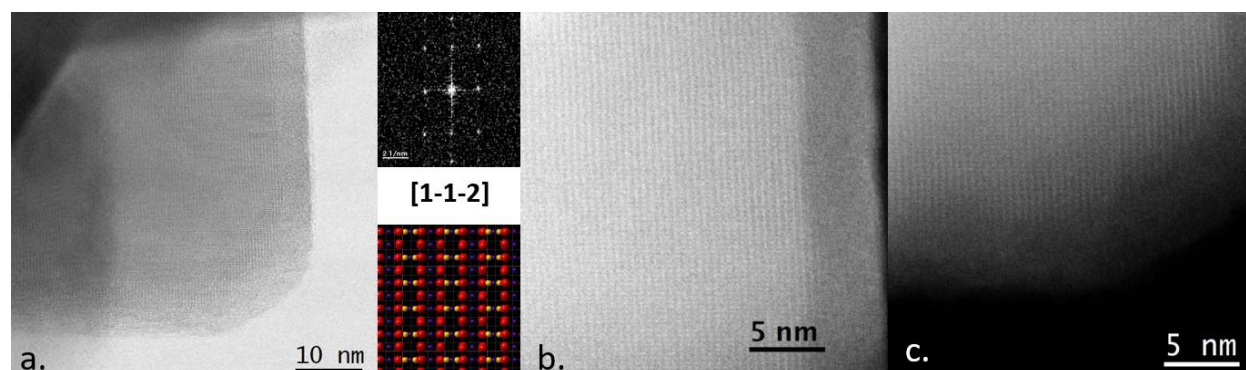


Figure 2. (a) ABF image of a charged MgV_2O_4 crystal, FFT and expected crystal structure. (b) HAADF image showing surface transformation along the $[-11-1]$ surface and (c) HAADF image showing surface transformation along $[110]$ surface

References:

[1] L Hu et al., *ACS Energy Letters*, **5**(8) (2020), p. 2721.

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