

Systematic Transmission Electron Microscopy Study Investigating Lithium and Magnesium Intercalation in Vanadium Oxide Polymorphs

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Magnesium-ion based batteries promise a competitive alternative to conventional lithium-ion battery technology. Batteries combining Mg metal anode with a suitable intercalation-based cathode can offer much higher volumetric energy density, as well as significant cost and safety benefits over lithium ion batteries. Recent first-principles and experimental reports have established that orthorhombic α -V₂O₅ is a promising intercalation cathode for Mg ion batteries. However, several crucial aspects of the intercalation phenomenon, such as the specific intercalation sites for Mg within α -V₂O₅ or the formation of different phases upon Mg insertion into α -V₂O₅ remain unclear. Further systematic characterization of the Mg intercalation behaviour is therefore required.

This contribution will focus on systematic investigation of Mg intercalation into α -V₂O₅ by combining aberration-corrected scanning transmission electron microscopy (STEM) imaging, electron diffraction, electron energy loss (EEL) and energy dispersive x-ray spectroscopy (XEDS). More specifically, we will present a comparison of Mg insertion sites in two different samples: i) electrochemically cycled α -V₂O₅ cathode in a prospective full cell vs Mg metal anode and ii) chemically synthesized MgV₂O₅ sample. In the case of electrochemically cycled α -V₂O₅, our results determine the Mg intercalation sites and it is concluded that this sample exhibits the local formation of the ϵ -Mg_{0.5}V₂O₅ phase, as predicted by earlier first-principles density functional theory (DFT) calculations [1]. Figure 1a) and b) present atomic resolution high-angle annular dark-field (HAADF) and annular bright-field (ABF) images, respectively, for the electrochemically-cycled orthorhombic α -V₂O₅ cathode. Simulated HAADF and ABF images for the DFT predicted ϵ -Mg_{0.5}V₂O₅ phase are overlaid on the experimental STEM images. The structural model for the ϵ -Mg_{0.5}V₂O₅ phase is shown in Fig 1(c). We will also show that the chemically synthesized sample presents the δ -MgV₂O₅ phase [2].

Recent theoretical calculations have also predicted that the migration barrier for ionic intercalation can be decreased by exploiting different anion coordination environments in metastable vanadium oxide polymorphs, such as ζ -V₂O₅ [3]. Figure 2a) presents atomic-resolution HAADF image for ζ -V₂O₅ nanowires clearly showing the heavier V atoms and elucidating the tunnel structure for this novel polymorph; a structural model for the ζ -V₂O₅ phase is presented in Figure 2b). We have investigated the lithium intercalation in this tunnel-structured ζ -V₂O₅ polymorph, and will focus on showing that ζ -V₂O₅ nanowires show much better Li-cycling properties (i.e. reversibility) compared to orthorhombic α -V₂O₅ [4]. Moreover, Mg intercalation into ζ -V₂O₅ nanowires will be investigated in detail, comparing electrochemical performance at both low and high temperature cycling followed by systematic STEM characterization. The results obtained for this novel polymorph ζ -V₂O₅ will be directly compared with our previous work investigating Mg intercalation in α -V₂O₅ [2]. Other V₂O₅ polymorphs, such as ϵ -V₂O₅ will also be tested for their ability to intercalate Li or Mg [5].

References:

- [1] G. S. Gautam *et al*, Chemistry of Materials **10**, (2015), p. 1021.
 [2] A. Mukherjee *et al*, Chemistry of Materials **2017** (in print)
 [3] A. Parija *et al*, Chemistry of Materials **28** (2016), p. 5611.
 [4] A. Mukherjee *et al*, Direct observation of reversible topotactic lithium intercalation in tunnel structure ζ -V₂O₅ nanowire cathode, (*in preparation*)
 [5] This work is supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences.

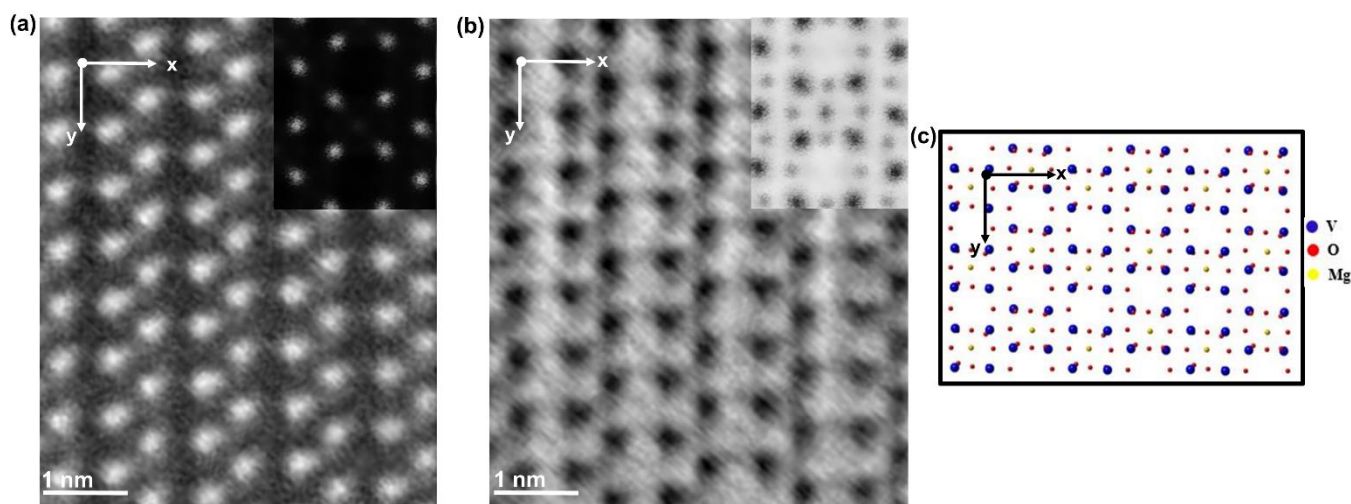


Figure 1. (a) Filtered atomic-resolution HAADF image of electrochemically cycled α -V₂O₅ cathode, simulated image overlaid (b) Filtered ABF image, simulated image overlaid (c) Structural model for DFT predicted ϵ -Mg_{0.5}V₂O₅ phase in [001] zone

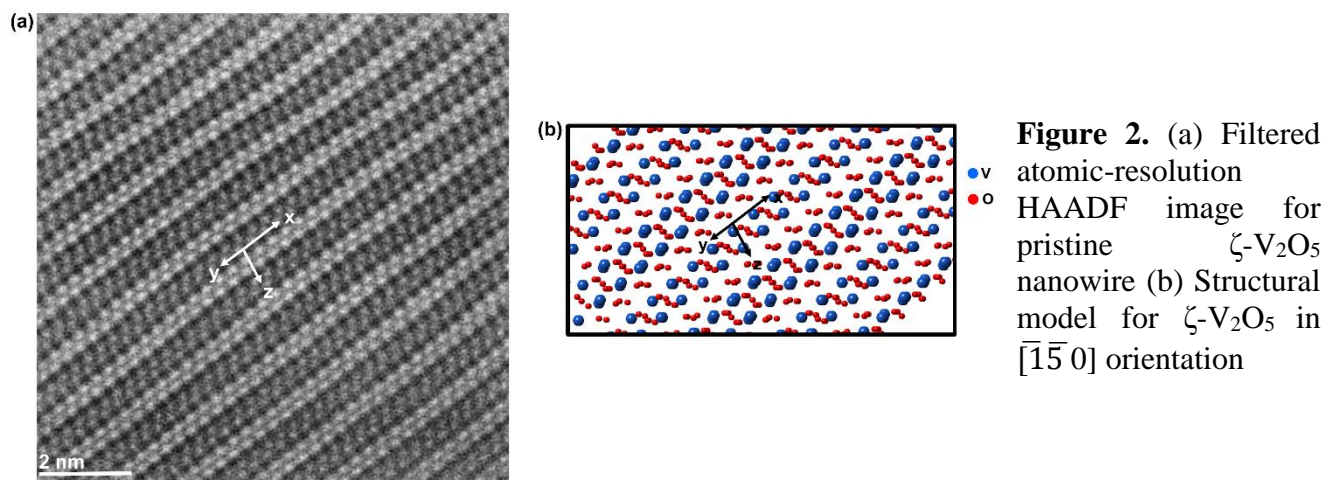


Figure 2. (a) Filtered atomic-resolution HAADF image for pristine ζ -V₂O₅ nanowire (b) Structural model for ζ -V₂O₅ in $[\bar{1}50]$ orientation