

Investigation of Li ion and Multivalent Battery Systems Using In situ TEM and High Resolution EELS

Arijita Mukherjee¹, Hasti Asayesh Ardakani², Patrick J. Phillips¹, Reza S. Yassar², Robert F. Klie¹

¹ Department Of Physics, University Of Illinois At Chicago, 845 West Taylor Street, Chicago, Illinois 60607, United States

² Department of Mechanical Engineering-- Engineering Mechanics, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, United States

Energy storage research is of utmost relevance today with demands for higher energy density, faster cycling times, safer and more cost effective options. Research is underway both for exploring novel cathode materials for traditional Li ion batteries and also multivalent elements such as Mg, Ca (both divalent) or trivalent Al to replace Li ion for next generation batteries. V_2O_5 has been proposed as a promising cathode host for multiple reasons: its layered structure can potentially intercalate Li or other multivalent ions (e.g., Mg); a shorter Li diffusion path and high Li ion mobility has been reported for nanostructured V_2O_5 ; its theoretical energy density is higher than conventional Li ion battery electrodes; and, its low cost. [1]

The following contribution will focus on various in-situ transmission electron microscopy (TEM) experiments using a biasing electrochemical holder, with a Li metal anode and V_2O_5 nanowires as the cathode, over a variable bias window within an open cell battery approach. This approach has shown considerable success for in-situ experiments involving Li-ions and SnO_2 nanowire cathodes. [2] Electron diffraction patterns of the V_2O_5 nanowire cathode collected before and after bias application have shown significant change from the crystalline phase before to some polycrystalline, possibly intercalated phase afterwards. Electron energy-loss spectroscopy (EELS) analysis of the nanowires both before and after bias application also manifested peak shifts indicating a change in the valence state of Vanadium (initially V^{5+}). The primary goal is to identify the dominant lithiated phase upon in-situ cycling. Preliminary indexing of polycrystalline diffraction pattern indicates $\gamma Li_2V_2O_5$ as the dominant phase. EELS analysis will be used to verify this. [3]. Figure 1 shows EELS spectra of the cathode collected before and after bias application at around -2.5 V for in-situ lithiation; the peak shifts indicate a definite change in the Vanadium valence state following the bias application. Figure 2 presents selected area electron diffraction patterns, captured from the nanowire tip which was in contact with Li; the phase change from crystalline (before bias, pristine V_2O_5) to a polycrystalline state (after bias) also confirms Li intercalation. The polycrystalline rings have been indexed to γLiV_2O_5 . (JCPDS card 48-0076).

Results will also be discussed regarding multivalent systems such as Ca or Mg, using a similar approach as outlined above, and an appropriate ionic liquid electrolyte. Preliminary results have shown some changes in the diffraction pattern following attempted Ca intercalation and further experiments are planned. Also, in operando TEM will be discussed using electrochemical liquid cells and appropriate electrolyte and cathode configuration.

References

- [1] Zhiguo Wang et al, *Phys.Chem. Chem. Phys.*, **15** (2013), p.8705
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 [3] Candace K Chan et al, Fast, Completely Reversible Li Insertion in Vanadium Pentoxide Nanoribbons, *Nano Letters*,**7**(2)(2007),p.490
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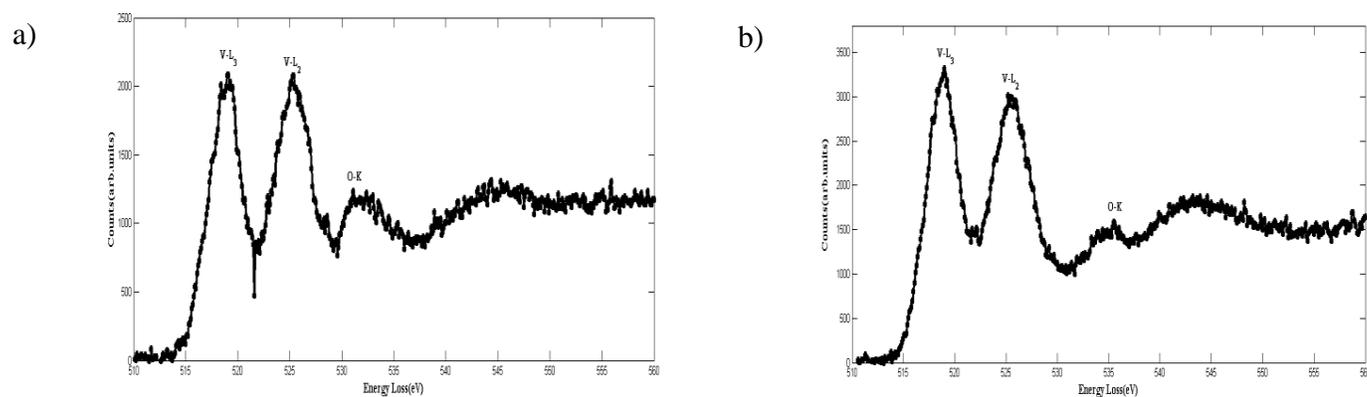


Figure 1. (a) EELS spectra of V₂O₅ nanowire before and (b) after bias application for in situ lithiation experiment

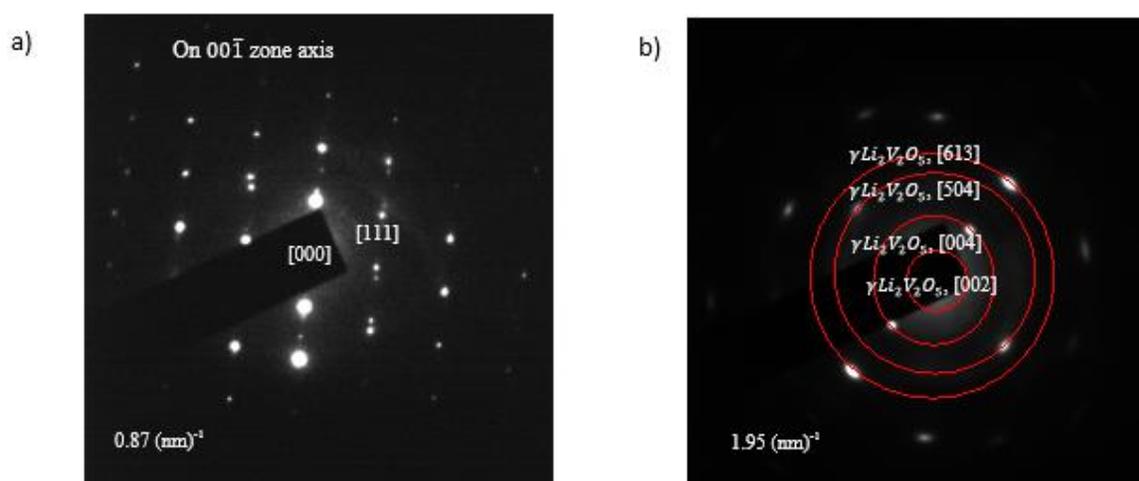


Figure 2. (a) Electron Diffraction Pattern of V₂O₅ nanowire before and (b) after bias application for in situ lithiation experiment