Chemical Bonds and Structural Evolution of Electrochromic WO_3 Films during Electrochemical Cycles

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Amorphous tungsten oxide (WO_3) had received many attentions because of the potential application of electrochromic devices as smart windows in energy-saving area. The optical properties of WO_3 could be changed by double injection of electrons and hydrogen ion (H^+) and alkali ions (Li^+, Na^+, K^+·····) from the external circuit in a reversible way. After the insertion of Li ions and electrons into WO_3 films, the W^{+6} ions could be reduced into valence state of W^{+5}. The electrons close to W^{+5} ions can absorb the energy from solar photons and transfer to W^{+6} ions, and attain the effect of coloration. The reaction can be described as following equation:

$$h\nu + W^{+5}(A) + W^{+6}(B) \rightarrow W^{+6}(A) + W^{+5}(B)$$

However, the arrangement and the bonding between tungsten and oxygen will influence the electrochromic properties. The X-ray absorption spectroscopy data were using synchrotron radiations at NSRRC 17C1 beamline.

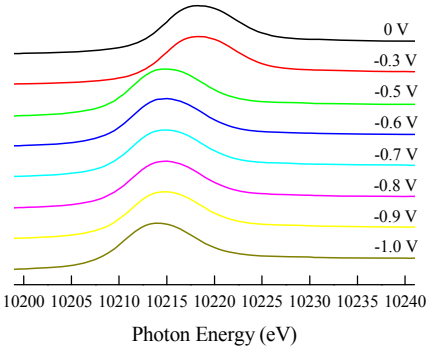

Figure 1. The X-ray absorption near edge structure (XANES) of W L_{III}-edge under various applied potential.

The XANES results were showed in Fig. 1. The binding energy of WL_{III} edge of as-deposited WO_3 film was 10218 eV. By continuously applying potential to -0.5 V, we found that the binding energy of W L_{III} edge had shifted to lower energy, 10215 eV. It was very reasonably that the as-deposited WO_3 film received electrons and Li ions from external circuit and the W^{+6} ions were reduced into W^{+5} ions. This phenomenon was consisted with the result of TEM. By this reduction of chemical state, the nuclear screening effect of W^{+5} ions were lowered and decreased the binding energy of W^{+5} ions to outer orbital electrons. Furthermore, the energy shift of W L_{III} edge continued to decrease to 10214 eV at external circuit potential of -1 V.

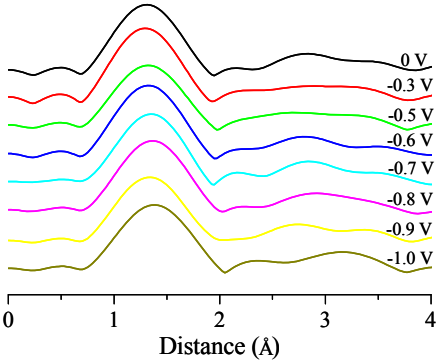

Figure 2. Radial distribution function of WO_3 films under different applied potentials.

The RDF results had shown in Fig. 2. The lengthening of bonding distance could be explained by the fact that the W^{+6} ion gained an electron and a Li ion from external circuit. The Li ion entered the interstitial site of WO_3 cell. The inserted electron was trapped by a W^{+6} ion and reduced the W^{+6} ion into a W^{+5} state.