Understanding the signatures of Mn valency variations in the valence energy loss spectra of Li-Mn-Ni-O cathode materials

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Valence energy loss spectrum (VEELS) characterized by interband transitions, and plasmon excitations is rarely used in spectroscopy of Li ion battery materials. One reason being the large number of different excitations observed in this region as well as the difficulty in interpreting their nature and origin.[1] We have determined the spectral features observed in the VEELS spectra of Lithium-Manganese-Nickel spinel oxides (Li-Mn-Ni-O) with respect to Mn valency changes after insertion/extraction of lithium ion.[2] Li-Mn-Ni-O spinel oxides are of interest primarily due to their applications as cathode materials in Li-ion batteries.[2] In Li-ion batteries, phase stability, voltage limits, and safety are closely related to the character of the transition metal ion in the cathode materials. This includes valency, spin state, co-ordination, and covalency. [3]

Here we have determined the nature and origin of the spectral features observed in the VEELS spectra with respect to Mn valency changes during the lithiation of $LiNi_{0.5}Mn_{1.5}O_4$ to Lithium rich $Li_2Ni_{0.5}Mn_{1.5}O_4$.[1] The lithiation process is characterized by a Mn valency change from Mn 4+ in $LiNi_{0.5}Mn_{1.5}O_4$ to Mn 3+ in Lithium rich $Li_2Ni_{0.5}Mn_{1.5}O_4$. Figure 1 shows the VEELS spectra from $Li_2Ni_{0.5}Mn_{1.5}O_4$ (thin dotted curve) and $LiNi_{0.5}Mn_{1.5}O_4$ (thick solid curve). The VEELS spectra of $LiNi_{0.5}Mn_{1.5}O_4$ is characterized by sharp peaks around 7-10 eV whose intensity decrease with lithiation to $Li_2Ni_{0.5}Mn_{1.5}O_4$.

Using band-structure calculations and molecular orbital considerations we show that the intense peaks in the VEELS spectra of $LiNi_{0.5}Mn_{1.5}O_4$ have a large contribution from ligand-metal-charge transfer (LMCT) transitions. Figure 2 displays a Molecular orbital (MO) schematic for a MnO_6^{9-} cluster with Mn valency of Mn 3+. [4] The figure shows hybridized molecular orbitals formed from Mn and O atomic orbitals. The dark squares represent filled states and the unfilled rectangles show the unfilled states. The solid arrows show the occupying spin of the electron, while dashed arrows show the possible interband transitions. LMCT transitions giving rise to sharp peaks observed in the VEELS spectra of $LiNi_{0.5}Mn_{1.5}O_4$ arise from the mainly O 2p non-bonding t_{2u} and bonding t_{1u} orbitals to the mainly Mn 3d anti-bonding t^*_{2g} and e^*_g orbitals. We discuss the origins of the observed valence spectra differences between the two phases in relation to peaks shift, variations in occupancy, and variations in covalency as result of Mn valency changes occurring during lithiation.

References

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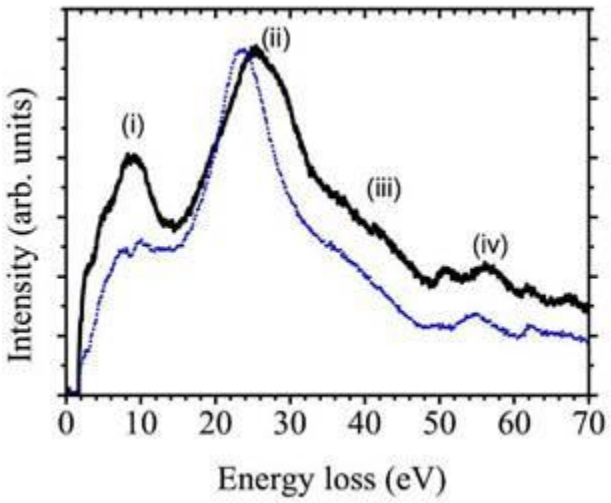

FIG. 1. Valence loss electron energy loss spectra (VEELS) obtained from lithium rich $Li_2Ni_{0.5}Mn_{1.5}O_4$ (thin dotted curve) and $LiNi_{0.5}Mn_{1.5}O_4$ (thick solid curve)

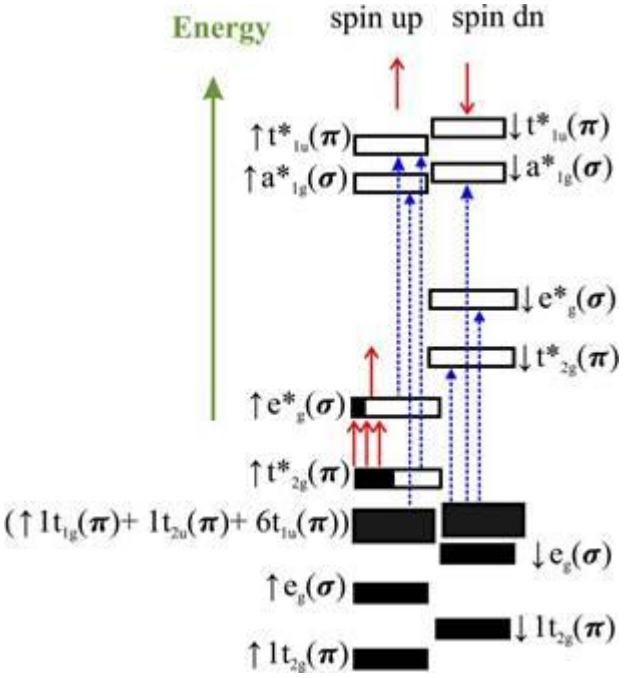

FIG. 2. A schematic molecular orbital diagram from a MnO_6^{9-} cluster with Mn 3+. The dark squares represent filled states and the unfilled rectangles show the unfilled states. The solid arrows show the occupying spin of the electron, while dashed arrows show the possible interband transitions.