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Characterization of Metal-doped Mn_3O_4 Particles by Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy

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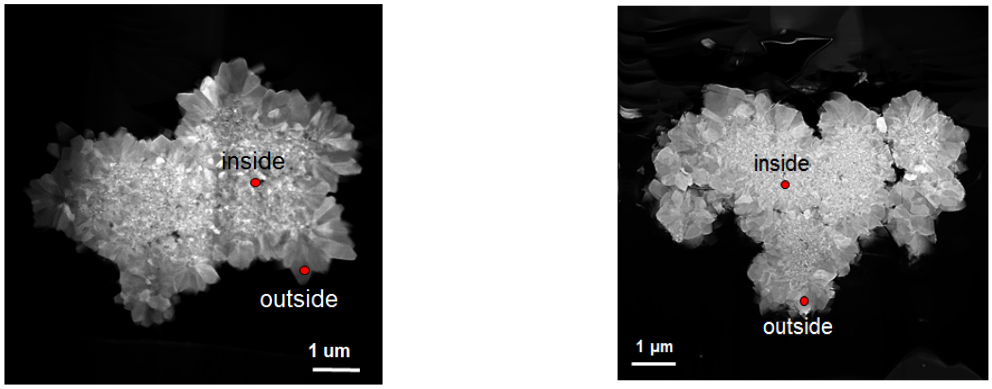
Metal-doped manganese oxides have been used as precursors of cathode materials for rechargeable lithium batteries due to their high capacity. A core-shell-structured material has been designed to improve the cycle life and safety of lithium batteries [1]. In this study, Co or Al-doped manganese oxides with core-shell structure were synthesized by co-precipitation method involving the precipitation of hydroxide particles from cobalt sulfide solutions. The grain structure and composition variation of metal-doped Mn3O4 particles were studied by transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). We also probed the electronic structure of the precursor materials at the nanometer scale by means of scanning transmission electron microscopy and electron energy loss spectroscopy.

Figure 1 shows cross-sectional STEM images of the Co or Al-doped manganese oxides obtained by co-precipitation process. The particles showed the core-shell structure with smaller grains inside and bigger grains outside, and they coalesce into bigger particles. The grain size inside the particles is ~ 20nm and outside ~5μm. In the case of Co-doped manganese oxides, the concentration of cobalt inside the particle is constant and outside increases towards the surface. In the case of Al-doped manganese oxides, the concentration of aluminum is constant inside and outside. EELS analysis probed that inside the particle, O K-edge shows the typical shape of O K-edge of Mn_3O_4 and outside, the first peak of O K-edge decreases. In the case of Co-doped manganese oxides, the ratio of the integrated intensities of the L_3 and L_2 white lines (L_3/L_2, the valency of the transition metals [2.3]) inside the particle was 2.8 of the typical value for Mn_3O_4 and outside 3.0 (Figure 2) It is found that the outer layer of higher cobalt concentration has lower oxidation state. In the case of Al-doped manganese oxides, the valency (L_3/L_2) of the transition metals inside the particle was 2.9 and outside 2.8 (Figure 3).

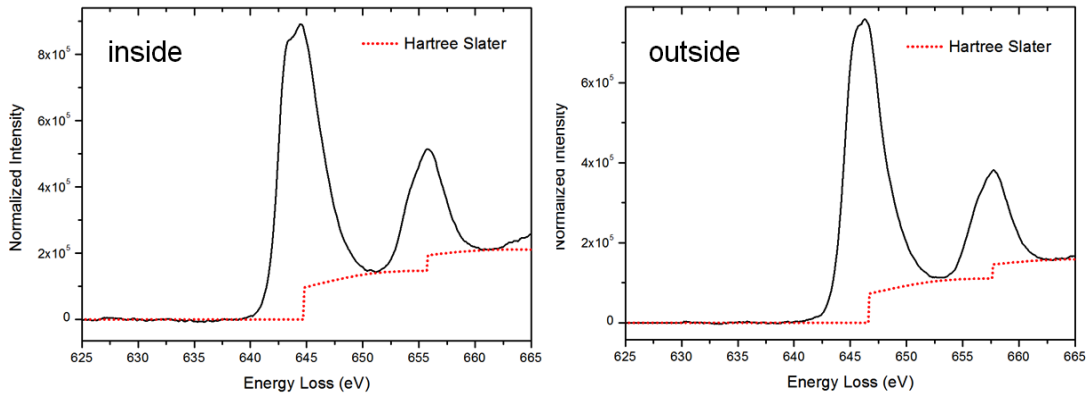
References:

[1] Y.K. Sun et al., Nature Materials **8** (2009) p. 320.
[2] L.Laffont et al., Materials Characterization **61** (2010) p. 1268.
[3] H.K. Schmid, W. Mader, Micron **37** (2006) p. 426.



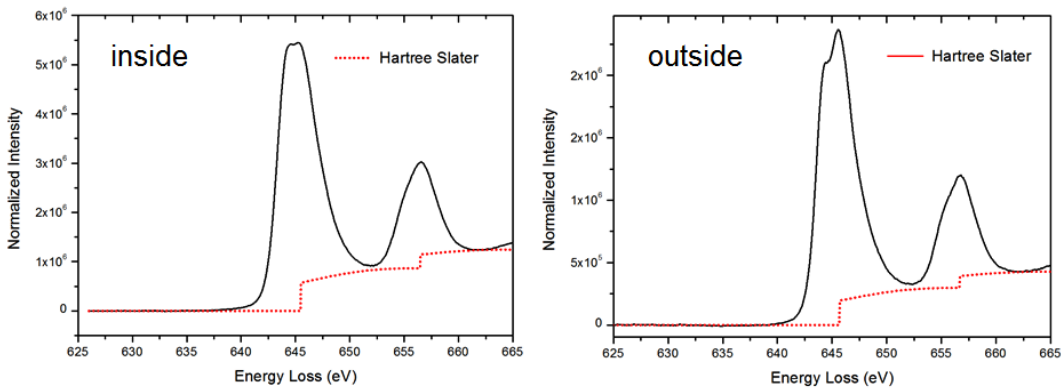
(a) (b)

Figure 1. STEM images of Co-doped Mn_30_4 particle (a) and Al-doped Mn_30_4 particle (b).



(a) (b)

Figure 2. EELS spectra showing Mn-$L_{2,3}$ edges obtained in the inside (a) and the outside (b) of Co-doped Mn_3O_4. The ratio of the integrated intensities of the L_3 and L_2 white lines inside the particle was 2.8 of the typical value for Mn_3O_4 and outside 3.0.



(a) (b)

Figure 3. EELS spectra showing Mn-$L_{2,3}$ edges obtained in the inside (a) and the outside (b) of Al-doped Mn_3O_4. The valency (L_3/L_2) of the transition metals inside the particle was 2.9 and outside 2.8.

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