Interactions Between Cations and Nanoparticulate Layered Mn Oxides Using X-ray Atomic Pair Distribution Functions (PDF)

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Due to large surface area and abundant structural defects, layered Mn oxides possess extraordinary abilities to sorb metal cations. X-ray absorption spectroscopy (XAS) has been extensively used in charactering metal sorption structure. Here, we used X-ray pair distribution function (PDF) analyses to investigate Zn^{2+} and Ni^{2+} sorption geometry on δ-MnO_2 and impacts of H^+ on crystal structure of δ-MnO_2. Differential PDFs (d-PDFs) of Zn- and Ni-sorbed δ-MnO_2 at pH 4 list well-defined 3 Zn/Ni-O and 6 Zn/Ni-Mn pair correlation peaks within 10 Å, supporting that the metal adsorption occurs on vacant sites rather than edge sites. PDF modeling suggests significant structural variations caused by H^+ (pH). As pH increased from pH 1 to 7 in $NaNO_3$ solutions, the unit cell expanded in three crystallographic directions, particularly in the *c* direction (from 7.09 to 7.33 Å) while the stacking vector (β) decreased from 98.6^o to 96.1^o.