

RIETVELD REFINEMENT ANALYSIS OF EMD XRD POWDER PATTERNS AND A STRUCTURAL INTERPRETATION

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A structural model is developed for Electrolytic Manganese Dioxide (EMD) and Chemical Manganese Dioxide (CMD) based on rietveld refinement of x-ray diffraction patterns and Transmission Electron Microscopy (TEM) data. Rietveld refinement results indicate that both EMD and CMD are composed of gamma- and epsilon-manganese dioxide ($\gamma\text{-MnO}_2$ and $\epsilon\text{-MnO}_2$, respectively) with an occasional occurrence of pyrolusite ($\beta\text{-MnO}_2$). The principal structural feature observed is that the crystallite domain values for $\gamma\text{-MnO}_2$ decrease from 50 to 15 angstroms as EMD surface area increases from 10 to 86 m²/g. Also, the $\epsilon\text{-MnO}_2$ crystallite domain size decreases from 150 to 60 angstroms. Quantitative data shows that the ratio of $\gamma\text{-MnO}_2$ to $\epsilon\text{-MnO}_2$ is essentially constant. However, transmission electron microscope evaluation indicates that only $\gamma\text{-MnO}_2$ structure is observed, i.e., the TEM's reveal only crystal planes with a separation of approximately 4 angstroms.

By definition, $\epsilon\text{-MnO}_2$ is composed of a framework of hexagonally close-packed oxygen atoms with one-half of the octahedral sites randomly filled with manganese atoms. In contrast, $\gamma\text{-MnO}_2$ has the one-half of the octahedral sites filled with manganese atoms in an ordered configuration. Likewise, ($\beta\text{-MnO}_2$) has its manganese atoms arranged in one-half of the octahedral sites in a second ordered configuration. Finally, it has been proposed that both micro twinning and pyrolusite inter-growths occur within the $\gamma\text{-MnO}_2$ structure. The $\gamma\text{-MnO}_2$ micro-twin boundaries register on the x-ray pattern as the small crystallite domain size of the $\gamma\text{-MnO}_2$ phase, i.e.; the twin boundary is the crystallite boundary.

A structural model is proposed for both EMD and CMD materials, which are, composed of only small crystallite domains of $\gamma\text{-MnO}_2$ crystallites in the range of 15 to 50 angstroms. The $\epsilon\text{-MnO}_2$ pattern observed in x-ray diffraction patterns is an expression of the larger hexagonal close-packed oxygen framework and does not exist as a discrete phase in the material. Rietveld crystallite domain sizes for the $\epsilon\text{-MnO}_2$ is two to three times as large as that for $\gamma\text{-MnO}_2$ in any given sample. Therefore, it is proposed that the $\epsilon\text{-MnO}_2$ is a signature of the oxygen framework crystallite domain size and not a discrete phase in EMD or CMD materials.