



# Characterisation of Hydrrous Manganite ( $\gamma$ -MnOOH) Surfaces - An XPS Study

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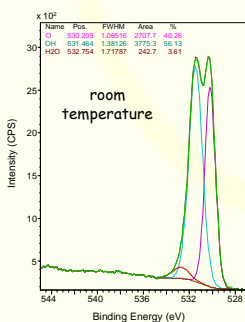
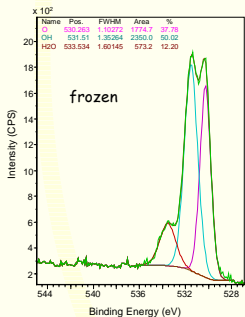
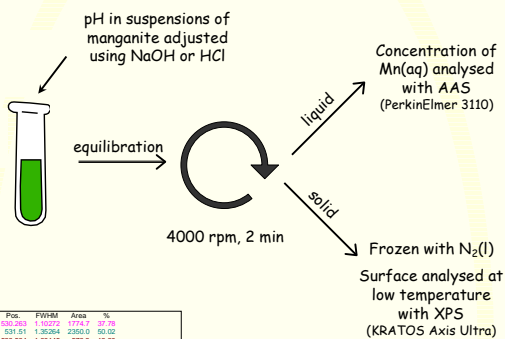
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## Objective

The objective of this work is to examine the surface of pure manganite at different pH values with X-ray Photoelectron Spectroscopy (XPS) in order to develop an understanding for the acid-base properties of manganite. This knowledge serves as a foundation for continued metal sorption studies.

## Sample Preparation and Analysis

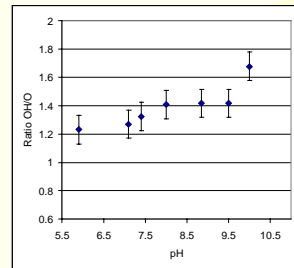
To understand the processes at the manganite surface in water suspensions it is important to have conditions during the analysis that do not alter the mineral-water interface. However, it has been noticed that during the drying of samples the interface does change. To avoid this, a method to freeze samples with liquid nitrogen has been examined, which enables measurements of samples as frozen pastes.



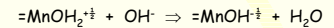
As shown in the two O 1s spectra to the left, the freezing procedure keeps the water at the surface, in contrast to, analysis performed at room temperature.

These two spectra also show that it is possible to resolve the two types of oxygen present in manganite, i.e. the O and OH group. A third component is always observed even in dried samples and this component is thought to be sorbed water or, in the dried sample, protonated OH groups.

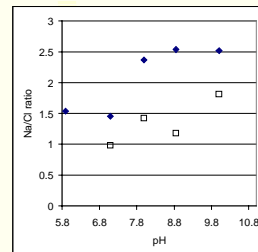
## Surface Changes with pH



The ratio between the OH and O component of the O 1s spectra increases with pH. A possible mechanism for this increase of OH could be:



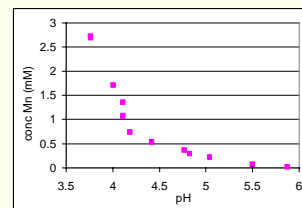
The OH<sub>2</sub> component, in O 1s spectra, is thought to be situated at similar binding energy to water and is, thus, difficult to quantify.



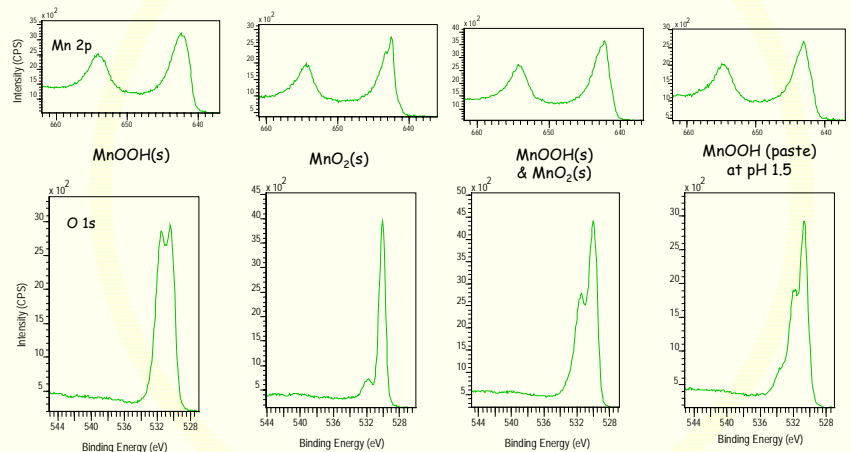
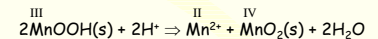
The suspensions were prepared with 10 mM NaCl as ionic medium and, as a consequence, the ratio between Na and Cl can be used as a measure of the charging of the surface. With pH > 7.8 the surface is negatively charged which leads to an increase in the Na/Cl ratio as a function of pH.

Filled diamonds = wet paste, empty squares = warmed sample

## Dissolution of Manganite



Manganite dissolves at pH below 6 and this dissolution is illustrated by the concentration of manganese in solution after 24 hrs of equilibration. The dissolution is assumed to occur according to:



Spectra of the dissolved surface with XPS should, thus, show Mn(IV) at the surface. The Mn 3s spectra that were acquired did not show any significant change in the split between the satellite and the main peak. However, slight changes can be observed in the shape of the Mn 2p line (See graphs above) which can be interpreted as an increased amount of Mn(IV) at the surface. Also, drastic changes in the O 1s spectra can be seen which are interpreted as increased amounts of a Mn(IV) oxide at the surface. A mixture of MnOOH and MnO<sub>2</sub> shows the same changes in spectra, which supports this hypothesis.