# Mechanochemical activation of metal oxides – Synthesis, modification, and application of manganese oxides



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## Introduction

Manganese oxides are promising energy storage materials and catalysts.<sup>[1-3]</sup> An important representative of this group is  $\alpha$ -Mn<sub>3</sub>O<sub>4</sub>, which crystallizes in the spinel structure (space group 14,1/amd) and exhibits a Jahn-Teller distortion of the Mn<sup>3+</sup> (d<sup>4</sup>) ions.<sup>[4]</sup> Another important manganese oxide is MnO<sub>2</sub> which has a rutile structure ( $P4_2/mnm$ ).<sup>[5]</sup> We have already shown that the mechanochemical activation of metal oxides has a strong influence on the crystallite sizes and the defect concentration.<sup>[6]</sup> Both properties can lead to changes in the reactivity of the oxides, e.g., their intercalation chemistry for lithium or sodium ions. For example, Li intercalation is drastically enhanced in mechanochemically prepared  $Mn_3O_4$  compared to samples synthesized under conventional high-temperature conditions.<sup>[7]</sup> In this study, we



### **Results and Discussion**



Fig.1: Diffraction patterns (a) and crystallite sizes (b) of  $Mn_3O_4$  milled at 400 rpm for different time lengths. The ball to powder ratio hereby was 23:1. The purple lines indicate the hkls of  $Mn_3O_4$  (ICSD) #167411). The crystallite size was determined by Rietveld refinement.



a)

The diffractograms of the mechanochemical activated Mn<sub>3</sub>O<sub>4</sub> do not show any phase transitions, only a broadening of the reflections can be observed due to the reduction of the crystallite size during the grinding process.

b) c) d)

**Defect Formation in Manganese Oxides through High Energy Ball Milling** 

$$2Mn_{Mn}^{X} + O_{O}^{X} \xrightarrow{A_{r}} 2Mn_{Mn}^{'} + V_{O}^{\bullet\bullet} + \frac{1}{2}O_{2}^{\uparrow}$$



**Fig.4:** Pressure and temperature profile during grinding of  $MnO_2$  (a): consisting of 4 cycles of 6 hours of grinding at 400 rpm and 99 minutes pause and  $Mn_3O_4$  (b): 2 cycles consisting of 12 hours of grinding at 400 rpm and 1 minute pause. The temperature-dependent pressure increase was considered.



Grinding of MnO<sub>2</sub> leads to the formation of up to 10% oxygen defects, in contrast to the grinding of  $Mn_3O_4$ .

#### Effect of Surface Functionalization of Mn<sub>3</sub>O<sub>4</sub> on Crystallite Size



**Fig.3:** Phase portion (a) of lithiated  $Mn_3O_4$  depending on different milling times and time of lithiation. Phase portion (b) of lithiated  $Mn_3O_4$  depending on different rotational speeds at a constant time (10 min) and duration of lithiation. Lithiation was performed with 2.5 equivalents n-butyllithium. The phase portion of  $LiMn_3O_4$  was determined by Rietveld refinement.



Hebm can facilitate the lithiation of  $Mn_3O_4$ . Mechanochemical activation of coarse grained Mn<sub>3</sub>O<sub>4</sub> with a rotational speed of 400 rpm or more leads to faster lithiation behavior already at short milling times. Long milling times or low rotation speed (200 rpm) lead to a reduced phase fraction of LiMn<sub>3</sub>O<sub>4</sub>.

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# Conclusions

amounts of PPA (black curve).

phase transformation or formation of by-products are observed during the No mechanochemical activation of the two manganese oxides, only the reduction of the crystallite size is visible. By pressure and temperature in situ measurements during the grinding of MnO<sub>2</sub>, the formation of oxygen vacancies can only be observed. Short mechanochemical activation of  $Mn_3O_4$  produced via high temperature synthesis at sufficient speed facilitates its lithiation. Extended milling times or small rotational speeds lead to less lithium intercalation in  $Mn_3O_4$ .



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