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

UNIVERSITÄT DES SAARLANDES

Tobias Benjamin Straub, Guido Kickelbick*

Saarland University, Inorganic Solid State Chemistry, Saarbrücken, Germany

Introduction: What is mechanochemistry

IUPAC defines mechanochemistry as a: "**Chemical reaction that is induced by the direct absorption of mechanical energy**."[1]

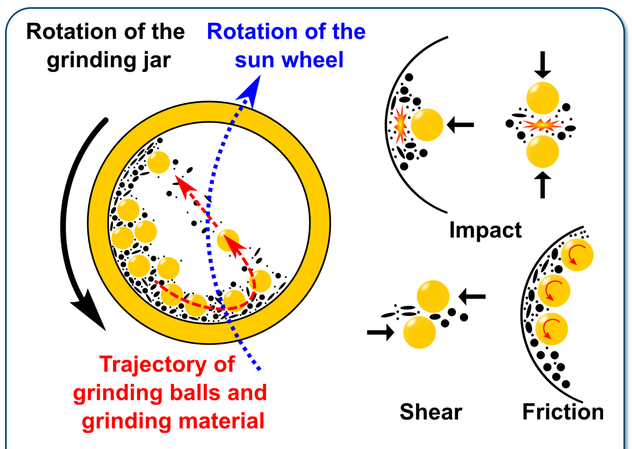


***Fig.1**: Working principle of a planetary mill and main forces acting on powder particles during milling.[2]*

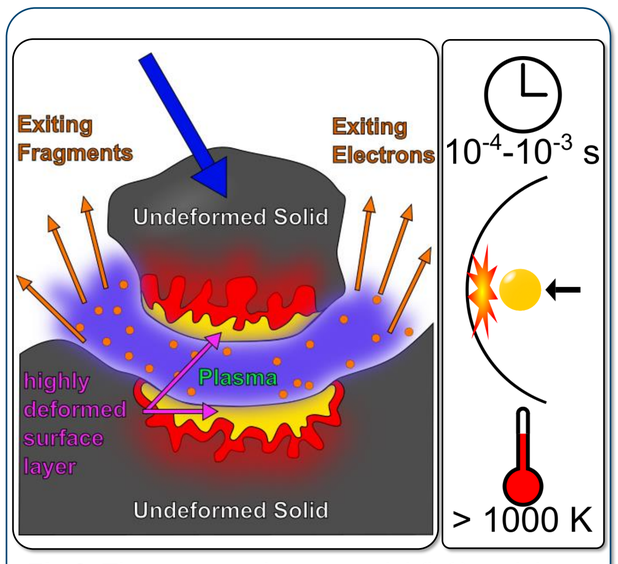


***Fig.2**: The magma-plasma model (left) and the hot-spot model (right) are two of the most commonly used explanations for describing the processes in a mechanochemical reaction.[4]*

Advantages:

- increased defect formation
- metastable phases can be obtained
- lower reaction temperatures,
- shorter reaction times
- absence of solvents, reduction of by-products
- new synthetic pathways are realized[3]

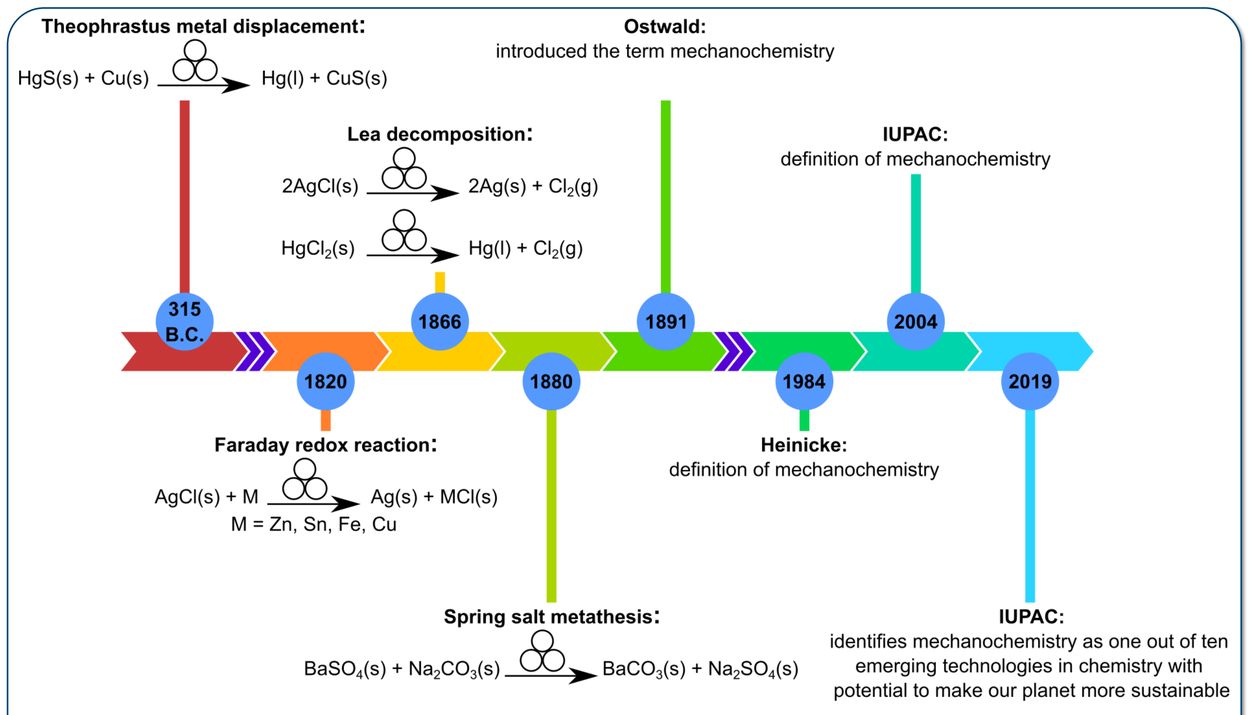


***Fig.3**: Timeline with milestones in the historical development of mechanochemistry.[6]*

Current Research and Results

Defect Formation in Manganese Dioxide through High Energy Ball Milling

$MnO_2 \xrightarrow{\text{hebm}} MnO_{2-x} + x/2\ O_2$ (x is up to 0.1)

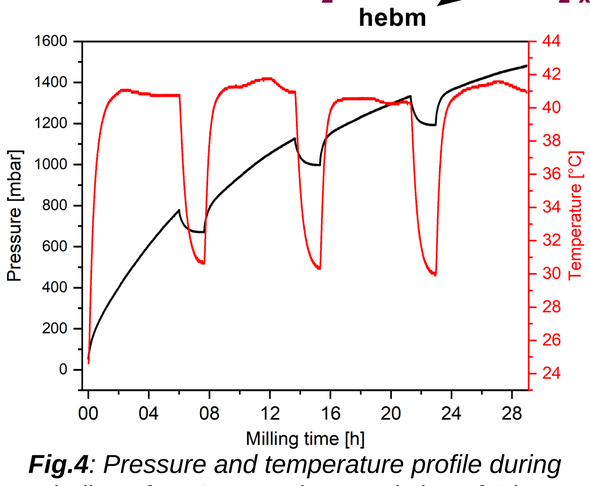


***Fig.4**: Pressure and temperature profile during grinding of MnO_2. 4 cycles consisting of 6 hours of grinding at 400 rpm and 99 minutes pause.*

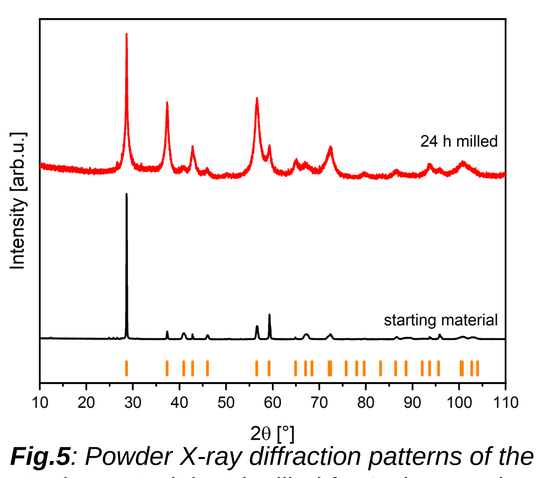
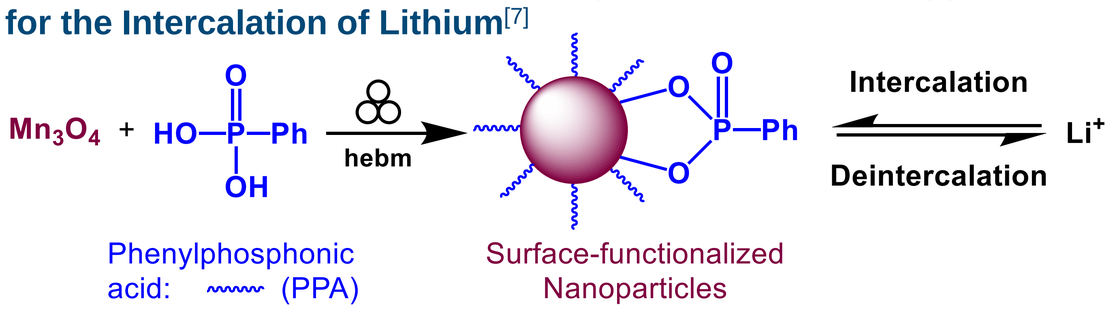


***Fig.5**: Powder X-ray diffraction patterns of the starting material and milled for 24 hours. The orange lines indicate the hkls of MnO_2.*

- Continuous pressure increase during the grinding process
- No pressure drop to the initial value even after the cooling phase
- No formation of any other product or minor phase visible in the XRD
- Only a peak broadening due to crystallite size diminution (226(5) nm to 9.7(2) nm)
- Defect formation up to 10% (calculated via non-temperature related pressure rise)

→ High energy ball milling (hebm) can induce oxygen vacancies

Surface Functionalized Oxidic Nanoparticles and their Application for the Intercalation of Lithium[7]



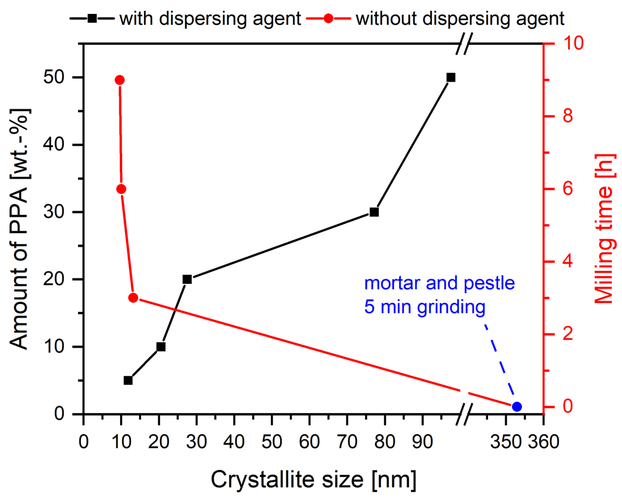


***Fig.6**: Crystallite size as a function of milling time with constant amount of PPA (red) and as a function of different amounts of PPA (black).*

- Surface functionalization was confirmed via IR-Spectroscopy, thermogravimetry and elementary analysis of washed and unwashed samples
- Milling with a dispersing agent causes the crystallite size to decrease with longer milling times
- Using higher amounts of PPA and a dispersing agent leads to a larger crystallite size at constant milling times
- Influence on de-/intercalation still needs to be investigated

→ hebm can be used for surface functionalization

Influence of Mechanochemical Activation on the Lithiation Behaviour[8]

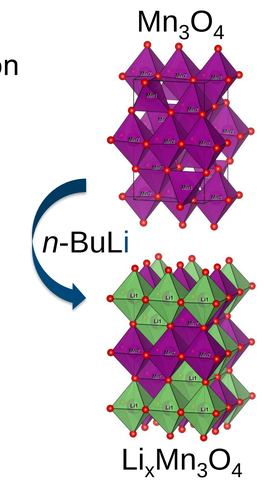
Conventional thermal synthesis:

$MnCO_3 \xrightarrow[\text{ssr}]{1100\ °C} Mn_3O_4$ (coarse grained) $\xrightarrow[1\ h,\ RT]{Li}$ no intercalation observable

High energy ball milling:

$MnO + Mn_2O_3 \xrightarrow{\text{hebm}} Mn_3O_4$ (nanocrystalline) $\xrightarrow[1\ h,\ RT]{Li}$ $Li_xMn_3O_4$, x ≈ 1, > 50% yield

n-BuLi, 7 d, reflux



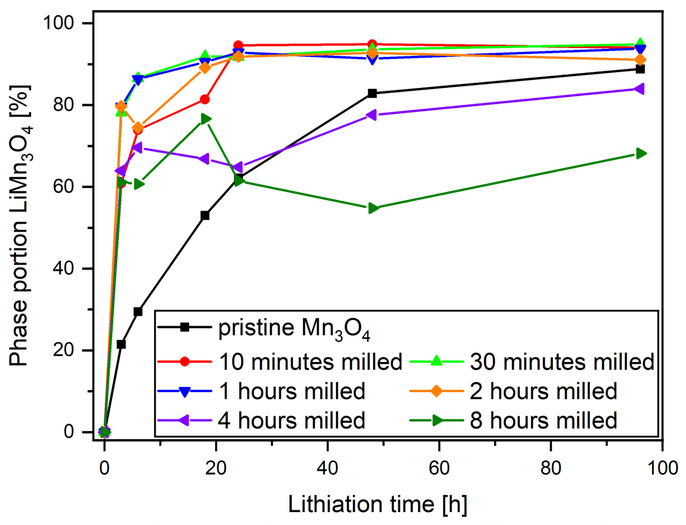


***Fig.7**: Phase portion of $LiMn_3O_4$ at different lithiation times for different milling time lengths of Mn_3O_4.*

- Mechanochemical activation of coarse grained Mn_3O_4 leads to faster lithiation behaviour already at short milling times.
- Longer milling times lead to a reduced phase fraction of $LiMn_3O_4$. The reason for this is still under investigation.

→ hebm can facilitate the lithiation of Mn_3O_4

Conclusions

During mechanochemical activation of metal oxides, crystallite sizes and defect concentration are affected. Both processes can lead to changes in chemical behavior in intercalation chemistry, e.g., for lithium or sodium ions. By pressure and temperature *in situ* measurements during the grinding of MnO_2, the formation of oxygen vacancies can be observed. Surface functionalization with PPA leads to different crystallite sizes depending on the milling conditions. Short mechanochemical activation of Mn_3O_4 produced via high temperature synthesis facilitates its lithiation.

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