Pyrolysis of a Three-Dimensional Mn\textsuperscript{II}/Mn\textsuperscript{III} Network To Give a Multifunctional Porous Manganese Oxide Material

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Manganese oxides with different oxidation states of manganese have applications in many different fields such as catalysis, lithium ion batteries, molecular sieves, and water treatment.\textsuperscript{[15–16]} Many efforts have been made to obtain different kinds of morphologies of manganese oxides and their properties have been investigated in the context of the above-mentioned purposes.\textsuperscript{[17–22]} Most of the methods employed have followed hydrothermal synthesis starting from different manganese salts.\textsuperscript{[17–22]} Manganese coordination compounds have rarely been used to prepare manganese oxides. In some cases unstable manganese complexes resulted in the formation of manganese oxides after decomposition.\textsuperscript{[23]} Being most versatile, MnO\textsubscript{2} has been investigated in the formation of manganese oxides after decomposition.\textsuperscript{[23]} Being most versatile, MnO\textsubscript{2} has been investigated in the context of the different kinds of catalytic activity and also pseudo-capacitance, but it has been rather less investigated.\textsuperscript{[24–30]} Herein we report a new way of preparing porous MnO\textsubscript{2}, starting from a 3D network of a coordination complex built up from a mixed-valent Mn\textsuperscript{II}/Mn\textsuperscript{III} cluster [(Mn\textsuperscript{II}\textsubscript{12}Mn\textsuperscript{III}\textsubscript{12})(µ-O\textsubscript{6})(glycH\textsubscript{12})(µ-1,1-N\textsubscript{3})(OH\textsubscript{2})\textsubscript{6}(N\textsubscript{3})\textsubscript{1.5}]\textsubscript{2+}Cl\textsubscript{4}·ca.7.5H\textsubscript{2}O(1), where (glycH)\textsuperscript{2} is the dianion of propan-1,2,3-triol (see Experimental Section).\textsuperscript{[31]} Pyrolysis of this compound results in the formation of a novel spongelike morphology of α-Mn\textsubscript{2}O\textsubscript{3}. Given the porous nature and thus higher accessible surface area of this material, the catalytic activity of the material in the oxidation of cyclohexene and the use in Li-ion battery anodes was tested successfully.

The crystal structure of compound 1 is shown in Figure 1A. The Mn\textsubscript{II\textsubscript{12}} cluster units are connected through mononuclear [Mn\textsuperscript{II}\textsubscript{I}(N\textsubscript{3})\textsubscript{6}] units. The smooth surfaces of fresh crystals were observed (Figure 1B) by using a scanning electron microscope (SEM). A view inside the crystal was also obtained by cutting the surface using a dual-beam FIB (focused ion beam)/SEM, which allowed a comparison with the structure of the heated compound.

Thermogravimetric analysis (TGA) of compound 1 showed that the compound is thermally stable up to approximately 200°C after which it decomposes rapidly to Mn\textsubscript{2}O\textsubscript{3}. The resulting material was checked after pyrolysis, and a spongelike morphology was observed by using a SEM (Figure 1D). The TGA plot (see the Supporting Information) indicates the loss of lattice water molecules above 100°C. Together with the X-ray powder diffraction (XRPD, Figure 2) data this suggests that the compound still remains crystalline after heating at 100°C, and a single-crystal X-ray structure determination performed after heating overnight at 120°C suggests complete loss of crystal water from the structure.\textsuperscript{[32]} A systematic XRPD study was performed on the compound after heating at different temperatures (Figure 2), which shows that the compound loses crystallinity around 200°C, going through an amorphous intermediate state before finally becoming crystalline Mn\textsubscript{2}O\textsubscript{3} with a very small amount (1.1% according to TGA) of MnO at 500°C. The XRPD data collected after pyrolysis at 500°C has sharp peaks characteristic for α-Mn\textsubscript{2}O\textsubscript{3}, and very small peaks, which indicate a small amount of MnO.

Furthermore, electron backscattered diffraction (EBSD) data recorded on the sample after pyrolysis at 500°C were indexed and are consistent with the presence of Mn\textsubscript{2}O\textsubscript{3} and traces of MnO (Figure 3). From the infrared spectra the loss of lattice water was evident from the disappearance of the IR peak at 1630 cm\textsuperscript{-1} at higher temperatures (see the Supporting Information).\textsuperscript{[33]} A peak at 1384 cm\textsuperscript{-1}, characteristic of the symmetric stretch of

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NO$_3^-$, appears when the compound is heated to 120°C. The broad band around 1590 cm$^{-1}$ can be assigned to the antisymmetric stretch of the NO$_3^-$ group. One possible route for the formation of nitrate from reaction between lattice water and the azide ions is shown in Equation (1). Another possibility is the aerial oxidation of azide ions at higher temperature (Equation (2)). To see which pathway is more likely, the sample was heated in a nitrogen atmosphere and checked by using IR spectroscopy, which showed the characteristic peaks for nitrate, suggesting that the azide ion is indeed oxidized by the lattice water according to Equation (1).

\[
\text{N}_3^- + 3\text{H}_2\text{O} \rightarrow \text{N}_2 + 3\text{H}_2 + \text{NO}_3^- \tag{1}
\]

\[
2\text{N}_3^- + 3\text{O}_2 \rightarrow 2\text{N}_2 + 2\text{NO}_3^- \tag{2}
\]

A systematic SEM investigation was performed on the heated compound. The SEM images show that when the compound is heated at 190°C, the smooth surface of the fresh crystals disappears and holes form on the surface (Figure 4). This most likely results from the evaporation of crystal water and degassing of N$_2$ and H$_2$ through the surface. After heating at higher temperature, the compound loses crystallinity, and finally changes to Mn$_2$O$_3$ at 500°C as shown in the XRPD (Figure 2). At this temperature, the material becomes porous and adopts a spongeliike morphology (Figure 1D). A few extrusions were observed on the surface after pyrolysis (Figure 5). One such extrusion was cut using a dual-beam FIB/SEM and micrometer-sized compartments were observed. This highly porous structure most likely forms due to expulsions of the gases that form during the combustion of the ligands inside the lattice at high temperature. The 3D network structure of the compound likely plays the role of a template for porous manganese oxide formation. This therefore can be seen as a cooperative phenomenon that leads to the resulting morphology. A BET surface area analysis was performed on the porous material, and a specific surface area of 52 m$^2$ g$^{-1}$ was observed at 77 K. This value is higher than that of the commercially available Mn$_2$O$_3$ (Aldrich, 99.99%), which has a specific surface area of 4.0 m$^2$ g$^{-1}$. The surface area obtained is also higher than that of some reported Mn$_2$O$_3$ nanocrystals (23 m$^2$ g$^{-1}$), but lower than the value reported for some mesoporous Mn$_2$O$_3$ (283 m$^2$ g$^{-1}$).

Mn$_2$O$_3$ is known to show pseudo-capacitance which arises due to highly reversible surface redox reactions.\[27,36,37\] Observing the porous nature of the α-Mn$_2$O$_3$ produced by pyrolysis of 1, it was expected that the compound may show high capacitance due to the large accessible surface area for electrochemical redox reactions. Therefore, the porous ma-

![Figure 1](image1.png)

Figure 1. A) Crystallographic view of the three-dimensional coordination network 1. B) Smooth surface of the crystals viewed using SEM. C) Inside-view of fresh crystal seen by cutting a crystal using focused ion beam (FIB). D) Spongeliike porous morphology of manganese oxide (α-Mn$_2$O$_3$ and trace amount of MnO) after pyrolysis. E) A close up view of the porous surface. Scale bars: 20 µm, 3 µm, 2 µm, and 200 nm for B, C, D, and E, respectively.

![Figure 2](image2.png)

Figure 2. XRPD pattern at different temperatures showing the loss of crystallinity at higher temperature. At 500°C, the (211) peak indicates the presence of α-Mn$_2$O$_3$. For the full range XRPD pattern of Mn$_2$O$_3$, see the Supporting Information.
Material was cycled galvanostatically in a two-electrode coin cell against a Li metal counter-electrode at voltages between 3.0 V and 0.05 V. In the first discharge, a first plateau with some substructure was found at voltages between 1.7 V and 0.4 V (Figure 6A). Subsequently, a very flat plateau is visible at 0.4 V, which is characteristic of a two-phase reaction regime. Overall, seven Li ions can be inserted per formula unit of Mn₂O₃, corresponding to a discharge capacity of 1191 mAh g⁻¹. In the following charge and discharge processes about four Li ions can be removed and re-inserted, respectively, and the shape of the voltage profile remains essentially unaltered with a charge plateau at 1.2 V and a discharge plateau at 0.6 V. This corresponds to a reversible capacity of about 650 mAh g⁻¹, which is higher than that of the graphite anode (370 mAh g⁻¹) commonly used in commercial batteries. Corresponding features can be found in the cyclic voltammogram of an identical cell (Figure 6B). In the first reduction process some smaller peaks are visible at voltages between 1.6 V and 0.6 V followed by an intense, narrow peak at 0.12 V. In the following oxidation and reduction processes the shape of the voltammogram remains unaltered and is dominated by broad oxidation peaks around 1.3 V and reduction peaks at 0.3 V. Further research is ongo-

Figure 3. EBSD data with the Kikuchi lines indexed for Mn₂O₃ (top) and MnO (bottom)

Figure 4. Holes formed on the surface after degassing at 190°C. Scale bars: 20 μm (A), 10 μm (B)

Figure 5. A) Extrusion on the surface after pyrolysis. B, C) The sponge-like porous morphology inside the extrusions was viewed by cutting it using a focused ion beam (dual-beam FIB/SEM). D) Micrometer-size compartments are shown inside the material. Scale bars: 10 μm (A), 30 μm (B), 40 μm (C), 2 μm (D).

Figure 6. A) Voltage profile during galvanostatic cycling of Mn₂O₃ against a Li metal counter-electrode. B) Cyclic voltammogram of an identical cell.
ing to investigate the long-term stability of this material during electrochemical Li insertion/extrusion.

Catalytic activity of the porous manganese oxide was also checked successfully by using in a catalytic amount (1 mol %) in the oxidation of cyclohexene by H₂O₂. Full conversion to cyclohexene oxide, 2-cyclohexene-1-ol, and 2-cyclohexenone (1:8:43:57:52:25) was found after reaction for 25 h at 70°C. The heterogeneous nature of the catalysis was checked by filtering off the catalyst and no further catalytic activity was observed in the filtrate. The recovered catalyst was checked by XRPD (see the Supporting Information) and no significant changes were observed, which suggests that the material did not decompose during catalysis.

In summary, a new route for the synthesis of a novel morphology of Mn₂O₃ has been described. By using this kind of templated synthesis, depending on the molecular structure of the starting compound it may be possible to induce different kinds of morphologies in the resulting metal oxides. Metal–organic frameworks thus can be potential precursors to synthesize novel porous metal oxides. Owing to the resulting high surface area, application of such materials in fields such as high-efficiency battery materials and heterogeneous catalysis is promising as we have successfully shown here.

Experimental Section

Synthesis: Compound I was synthesized according to the reported procedure.[10] MnCl₂·4H₂O (198 mg, 1 mmol) was added with stirring to a solution of propan-1-2,3-triol (73 µL, 1 mmol) in methanol (20 mL). The resulting solution was added with stirring to a solution of sodium azide (approximately 30% yield). For the preparation of the SEM sample, compounds were checked by filtering off the catalyst and no further catalytic activity was observed in the filtrate. The recovered catalyst and EDAX/C29s Phase Identification software.

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