



Synthesis–structure correlations of manganese–cobalt mixed metal oxide nanoparticles[☆]

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ABSTRACT

Mixed metal oxides in the nanoscale are of great interest for many aspects of energy related research topics as water splitting, fuel cells and battery technology. The development of scalable, cost-efficient and robust synthetic routes toward well-defined solid state structures is a major objective in this field. While monometallic oxides have been studied in much detail, reliable synthetic recipes targeting specific crystal structures of mixed metal oxide nanoparticles are largely missing. Yet, in order to meet the requirements for a broad range of technical implementation it is necessary to tailor the properties of mixed metal oxides to the particular purpose. Here, we present a study on the impact of the nature of the gas environment on the resulting crystal structure during a post-synthesis thermal heat treatment of manganese–cobalt oxide nanoparticles. We monitor the evolution of the crystal phase structure as the gas atmosphere is altered from pure nitrogen to synthetic air and pure oxygen. The particle size and homogeneity of the resulting nanoparticles increase with oxygen content, while the crystal structure gradually changes from rocksalt-like to pure spinel. We find the composition of the particles to be independent of the gas atmosphere. The manganese–cobalt oxide nanoparticles exhibited promising electrocatalytic activity regarding oxygen evolution in alkaline electrolyte. These findings offer new synthesis pathways for the direct preparation of versatile utilizable mixed metal oxides.

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1. Introduction

Manganese based spinel type oxides have attracted a lot of attention recently which is due to the broad range of beneficial properties like several valencies, low toxicity and high abundance. Therefore this class of materials has miscellaneous possible applications as (super)-capacitors [1], electrode materials for batteries and as a catalyst for energy storage and conversion in electrolyzers and fuel cells [2–5].

The development of synthesis strategies for nanoparticles with high surface area is of great importance to yield highly-efficient and cost-effective catalysts. This is especially valid for the electrochemical energy conversion applications such as oxygen reduction reaction (ORR) as cathodic reaction in polymer electrolyte fuel cells and oxygen evolution reaction (OER) for water electrolysis [6].

Common methods for the synthesis of metal oxide- and mixed metal oxide (MMO) particles are mechanical mixing of metallic precursors [7], spray pyrolysis [8], sol–gel decomposition [9,10] and hydrothermal decomposition [1,11–13]. The latter one is advantageous since it applies moderate temperatures resulting in improved control of particle size and accessibility of metastable phases. Pure manganese oxides have been successfully synthesized in spinel structure without additional oxidizing agents [14,15]. The synthesis of MMOs faces additional challenges concerning the homogeneity, particle size distribution and phase purity especially if the metal ions do not naturally crystallize in the same structure. Control over the properties associated with the crystal structure is somewhat limited by the chosen metal ions or rather their radii. Furthermore the crystal structure depends on the initial composition of the mixture and the synthesis conditions. Amongst those synthesis parameters, the reaction temperature, solvent and reaction time have been varied in several synthesis routes [12,14].

In the following, we will present recent findings on the influence of the gas atmosphere during synthesis on the crystal structure of MMO nanoparticles (NP). We investigated manganese–cobalt oxides as model system using a microwave-assisted synthesis route wherein the surfactant and solvent are identical. This

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allows the use of inexpensive precursors and leads to an easily scalable synthesis for the cost efficient preparation of large amounts of phase pure, crystalline nanoparticles. The use of a microwave has several advantages over the common heating jacket e.g. the homogeneous heat transfer, high heating rates, very good reproducibility and temperature control. The resulting nanoparticles were characterized with respect to their composition using inductively-coupled plasma optical emission spectroscopy (ICP-OES) and energy-dispersive spectroscopy (EDX). The crystal structure was determined using X-ray diffraction and the particle size and morphology by transmission electron microscopy (TEM). We could show that the presence of O₂ during synthesis leads to a distorted spinel-type crystal structures whereas low O₂ amount yields in rocksalt structures. The homogeneity and particle size has been found to be increasing with O₂ content in the atmosphere during synthesis. Finally, this selected catalyst was tested for the electrocatalytic activity for OER in alkaline electrolyte.

2. Experimental

2.1. Synthesis

All catalysts were prepared using a microwave assisted solvothermal synthesis. Mixtures of one equivalent Manganese(II)acetate-tetrahydrate (Sigma-Aldrich, ≥99.0%) and two equivalents Cobalt(II)acetate-tetrahydrate (Alfa-Aesar, 99.999%) were dispersed in Oleylamine (Aldrich, ≥98%) and stirred. The dispersion was degassed with N₂, synthetic air or O₂ respectively for 5 min. For the thermal treatment, a microwave autoclave (Anton Paar Monowave 300) was used. The samples were heated to 200 °C for 20 min. After the thermal treatment the dispersion was washed three times with ethanol (VWR, 100%) [16,17] and subsequently dispersed in cyclohexane (Roth, Rotisolv®, ≥99.5%).

2.2. Physicochemical characterization

2.2.1. XRD

X-ray diffraction patterns were recorded using a Bruker D8 Advance equipped with a scintillation counter between 10° and 75° with a step size of 0.06° and a counting time of 10 s. Therefore, the NP-dispersion was deposited on Si(100) wafer and dried in air for 120 min at RT.

2.2.2. TEM/EDX

TEM/EDX Electron microscopy was performed on a FEI Tecnai G² 20 S-TWIN with LaB₆ cathode, 200 kV accelerating voltage, and resolution limit of 0.24 nm. For preparation, a Cu grid with 200 mesh was used. Electron microscope include energy-dispersive X-Ray spectroscopy device (EDX) with an EDAX r-TEM SUTW Detector.

2.2.3. ICP-OES

Compositional analysis was performed using a715-ES inductively coupled plasma (ICP) analysis system (Varian). The standard concentrations were 1, 0.1 and 0.01 ppm for Mn and Co. The chosen wavelengths for concentration determination were 257.61 nm; 259.37 nm, 294.92 nm for manganese, as well as 228.62 nm; 236.38 nm; 237.86 nm; 238.89 nm for cobalt.

2.2.4. Electrochemical measurements

The catalyst dispersion in cyclohexane was pipetted onto a glassy carbon (GC) cylinder (HTW, ø10 mm) which had been polished until mirror-like finish and cleaned in an ultrasonic bath using ultrapure water and acetone. After deposition of the colloidal solution, the sample was calcined at 320 °C for 120 min to remove residues of oleylamine. For the electrochemical investigations

Table 1. Composition of as-prepared MMO-NPs as determined from ICP-OES.

Gas	Mn fraction (%)	Co fraction (%)
N ₂	55.5	44.5
Synthetic air	52.5	47.5
O ₂	57.2	42.8

a standard three electrode cell with a platinum mesh as counter electrode and a commercial reversible hydrogen electrode (Hydroflex, Gaskatel) as reference electrode were used and connected with a Haber-Luggin capillary. As potentiostat we used a SP150 from Biologic and a PINE rotator for the RDE. The measurements were carried out in a 0.1 M KOH solution which was degassed with N₂ for 20 min before the measurement which was switched to overflow over the electrolyte when the measurement was started. The electrode was introduced into the electrolyte under a potential of 1 V versus RHE. The working electrode was rotated at 1600 rpm. All electrode potentials were corrected for ohmic losses using electrochemical impedance spectroscopy (PEIS) and will be referred to as RHE. To determine the ohmic resistance, impedance spectra were recorded at every potential step between 1 Hz and 10 kHz with a modulation amplitude of 10 mV.

3. Results and discussion

In this work, we investigated the crystal structures of manganese-cobalt oxides with respect to the gas atmosphere during their synthesis. Commonly, the synthesis of MMOs requires an additional oxidizing agent e.g. H₂O₂ [18] or a subsequent thermal oxidation [19]. The latter, however, makes it difficult to control the oxidation and crystallization process. We have developed a synthesis route which utilizes gaseous O₂ during synthesis instead. This offers the option for a direct formation of a broad range of MMO-NPs with tunable crystal structures.

MnCoO_x-NPs were prepared using microwave-assisted synthesis. The metal precursors were dispersed in oleylamine and degassed using N₂, synthetic air or O₂ prior to the heating procedure. The resulting colloidal dispersion was extensively washed using ethanol to remove oleylamine, redispersed in cyclohexane and subsequently characterized with respect to composition, particle size and crystal structure. Table 1 shows the ICP-OES results for MMO-NPs synthesized in N₂, synthetic air and O₂.

The catalyst composition showed a Co/Mn ratio of about 1:1 for each sample. These results were in good agreement with EDX results where we found a Co:Mn ratio of 42:58, 43:57 and 51:48 for MnCoO_x-N₂, MnCoO_x-air and MnCoO_x-O₂, respectively. These results showed that the gas atmosphere during synthesis had no effect on the resulting composition of the MMO-NPs.

The particle size distribution and morphology of the MnCoO_x-NPs were determined using TEM and the corresponding micrographs and histograms are shown in Fig. 1. The micrographs evidenced that the nanoparticles exhibited largely spherical shapes regardless of the employed gas atmosphere. Mean diameters were estimated from counting at least 200 particles per sample. The mean diameter of the MnCoO_x-NPs increased from 4 nm in N₂ and synthetic air to 6 nm in O₂ while the size distribution was narrower under the presence of O₂ during the synthesis.

The crystal structure of the MnCoO_x-NPs prepared under different gas atmospheres during synthesis was then investigated using XRD and the diffraction patterns are shown in Fig. 2. The diffraction pattern for the MnCoO_x-N₂ material annealed under pure Nitrogen showed reflections at 2θ = 37°, 42° and 62° which can be attributed to reflections of rocksalt-like M²⁺O structure assigned with (111), (200) and (220) of CoO (PDF#00-048-1719),

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