Simple Synthetic Route to Manganese-Containing Nanowires with the Spinel Crystal Structure

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Abstract: This report describes a new route to synthesize single-crystalline manganese-containing spinel nanowires (NWs) by a two-step hydrothermal and solid-state synthesis. Interestingly, a nanowire or nanorod morphology is maintained during conversion from $\text{MnO}_2/\text{MnOOH}$ to $\text{CuMn}_2\text{O}_4/\text{Mg}_2\text{MnO}_4$, despite the massive structural rearrangement this must involve. Linear sweep voltammetry (LSV) curves of the products give preliminary demonstration that CuMn_2O_4 NWs are catalytically active towards the oxygen evolution reaction (OER) in alkaline solution, exhibiting five times the magnitude of current density found with pure carbon black.

1. Introduction

Manganese containing spinels have interested researchers for decades, both for the versatility of the spinel-type crystal structure with its many interstices, and for the multiple oxidation states of the manganese and different properties of the resulting spinels. Spinel such as Fe_3O_4 , [1,2]

Mn_3O_4 , [3,4] and LiMn_2O_4 , [5,6] for example, are known to perform well as electrodes for lithium ion batteries; of particular interest are the tests performed by Thackeray *et al.* [7] and Feltz *et al.* [8] who tested the lithiation kinetics for manganese-containing spinels MMn_2O_4 ($\text{M} = \text{Mn}, \text{Mg}, \text{Li}$), and found that the reducibility of the manganese cations was a crucial factor for lithiation. Besides their use as battery electrodes, manganese based spinels are also good catalysts for oxidation and reduction reactions: [9] CdMn_2O_4 can be used as an electrode material for NO gas sensors; [10] NiMn_2O_4 , [11] mesoporous MnCo_2O_4 , [12] and high surface area CuMn_2O_4 [13] have been shown to catalyze CO oxidation at ambient temperatures, exhibiting robust stabilities. Cu-Mn spinel oxides are also highly active for production of H_2 from methanol. [14] In addition, manganese spinels are reactive towards electro-organic redox catalysis with comparative stability. [15]

Since Tarascon *et al.* found that nanoscale transition-metal oxides were able to enhance lithium reactivity, [16] which is fundamental for lithium ion battery performance, researchers have studied several promising nanoscale metal oxides, particularly nanoscale manganese-containing spinels. Based on this research, these nanoscale spinels have better performance than bulk materials for lithium ion batteries. [17,18] Additionally, nano-sized manganese spinels are also more desirable for catalytic processes taking place at active surfaces, since they have larger surface-to-volume ratios than dense spinels. Though some reports exist on the synthesis of manganese-containing spinels with nanoparticle [19–22] and nanorod [23] morphology, a nanowire morphology is still quite challenging to synthesize and only a limited number of reports regarding the manganese-containing spinel NW synthesis exist. For example, Hosono *et al.* [24] and Lee *et al.* [6] reported the synthesis of single crystalline LiMn_2O_4 NWs by hydrothermal and solid state methods respectively; Lee *et al.* synthesized MnGa_2O_4 NWs via

thermal evaporation method;[25] Chen *et al.* obtained MnCr_2O_4 NWs by heating stainless steel foil;[26] and Na *et al.* synthesized Mn_2SnO_4 NWs using a chemical vapor deposition method.[27] To date, however, no reports exist for the synthesis of single-crystalline NWs of Mg_2MnO_4 or CuMn_2O_4 .

Cubic Mg_2MnO_4 forms the inverse spinel structure, with half of the Mg^{2+} ions in the tetrahedral A-sites, and the octahedral B-sites occupied equally by Mg^{2+} and Mn^{4+} so as to maximize the crystal field stabilization energy of the Mn^{4+} cations. Both Mg^{2+} and Mn^{4+} are critical in determining the functionality of this compound. Izawa *et al.* found Mg_2MnO_4 showed good lithium isotope selectivity in the ion exchange process in which Li^+ ions replace Mg^{2+} in the Mg_2MnO_4 . [28] Mg_2MnO_4 is also a good electrocatalyst for the oxygen evolution reaction, due to its high ion mobility enhanced by the tetravalent manganese ions within the spinel structure.[29,30]

In the case of CuMn_2O_4 , it is known to exist in both a cubic[31,32] and a tetragonal[33] phase, with differing structurally-dependent properties. Waskowska *et al.*[34] synthesized 0.8 inverted cubic CuMn_2O_4 which has Cu^+ and Mn^{2+} on the A-sites and Cu^{2+} , Mn^{3+} and Mn^{4+} taking B-sites. This coexistence of Mn^{3+} and Mn^{4+} cations on the octahedral sites is believed to be the driving force for its high electrical conductivity. Despite the presence of two Jahn-Teller (J-T) active ions, the proportion of Cu and Mn cations with the J-T active Cu^{2+} and Mn^{3+} oxidation states is smaller than the critical amount required to cause an overall J-T distortion,[34] and the structure therefore forms a cubic phase. The structure of tetragonal CuMn_2O_4 , however, is more complicated than that of the cubic phase. Shoemaker *et al.*[35] refined the tetragonal CuMn_2O_4 structure with c/a ratio of 1.03399 and a 0.27 inversion degree. In this tetragonal spinel, Cu^+ , Cu^{2+} , Mn^{2+} , Mn^{3+} ions all take tetrahedral sites, with octahedral sites occupied by Cu^{2+} , Cu^{3+} ,

Mn^{3+} , Mn^{4+} . In its bulk form, CuMn_2O_4 is known to catalyze the oxidation of CO to CO_2 at room temperature,[13,36,37] and the reduction of NO_x .[38]

With the many useful applications of Mg_2MnO_4 and CuMn_2O_4 as enumerated above, it would be highly desirable to have a reliable, inexpensive, and scalable route for the production of single-crystalline NWs of these materials. 1-D nanomaterials have the advantage of possessing high aspect ratios and high surface areas, which are particularly crucial for catalyst applications, and may be fabricated into 2-D membranes for easier manipulation in industrial applications.[39–42] In addition, since catalysts have preferred faces for catalytic activity,[38,43] single-crystalline materials – especially those with specific crystalline facets – are needed. Given these reasons, and the fact that syntheses of ternary oxides in NW form can be notoriously tricky, we were intrigued by the report by Lee *et al.*[6] of LiMn_2O_4 NW synthesis, using a binary manganese oxide or oxyhydroxide NW precursor to essentially “lock-in” the NW morphology, and a simple solid-state reaction to convert the material to the desired ternary oxide spinel phase; this is a remarkable result given the very different crystal structures of the starting NWs (which are rutile-type) and the product (which are spinel-type).

In this report, we expand on the approach of Lee *et al.*,[6] to introduce a new route to synthesize other single-crystalline manganese-containing spinel NWs by the solid state reaction of binary manganese-containing NW precursors with metal hydroxides. Our study is the first report of the synthesis of Mg_2MnO_4 or CuMn_2O_4 in single-crystalline NW or nanorod (NR) morphology. Powder x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and linear sweep voltammetry (LSV) have been used to characterize phase purity, crystal structure,

morphology, oxidation states of elements, and electrochemical catalytic performance with regards to the oxygen evolution reaction (OER).

2. Materials and methods

The precursor MnO_2 and $\gamma\text{-MnOOH}$ NWs were synthesized using methods in the literature.[44,45] For MnO_2 , 1.37g $\text{MnSO}_4\cdot\text{H}_2\text{O}$ (99% min, Sigma-Aldrich) and 0.086g NaClO_3 (99% min, Sigma-Aldrich) were dissolved in 36 mL distilled water and stirred for 15 minutes. The mixed solution was transferred to a 45 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 160 °C for 18h. After the system was allowed to cool to room temperature, the product was collected and washed with distilled water several times, then dried at 60 °C overnight. In a typical procedure for $\gamma\text{-MnOOH}$ NWs, 0.63g KMnO_4 (99% min, Alfa Aesar) and 0.45g CTAB (98%, Alfa Aesar) were dissolved in 36 mL distilled water and stirred for 20 minutes. The mixed solution was transferred to a 45 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 180 °C for 12h. The system was again allowed to cool to room temperature, the product collected and washed with distilled water several times, and then dried at 60 °C overnight.

To make CuMn_2O_4 NWs, a mixture of Mn-containing precursor NWs and well-ground $\text{Cu}(\text{OH})_2$ (Alfa Aesar) with molar ratio 2:1 was dispersed with methanol in a crucible and stirred for 20 min to make an even mixture. This was dried on a hot plate to produce a pellet which was annealed at 900 °C for 1-3h in air. A similar procedure was applied to make MgMn_2O_4 and Mg_2MnO_4 NWs, using the correct molar ratio of Mn-containing precursor NWs and well-ground $\text{Mg}(\text{OH})_2$ (Alfa Aesar). Samples were quenched in liquid nitrogen to reduce the formation of secondary impurity phases during cooling. Optimization of the experimental parameters (leading to the choice of the above conditions) revealed that calcining the copper-containing mixture

below 850 °C results in a mixture of CuO, Mn₂O₃ and CuMn₂O₄, and that calcining the magnesium-containing mixture below 850 °C results in MgO, Mn₂O₃, Mg₂MnO₄. In both cases, using calcination temperatures higher than 950 °C yielded large CuMn₂O₄ and Mg₂MnO₄ whiskers. Molar ratios of starting materials different from those listed yielded the same products but with additional impurity phases, implying that the chosen compositions (CuMn₂O₄, MgMn₂O₄, and Mg₂MnO₄) are the most stable under our reaction conditions.

Several further experiments were also performed using the γ -MnOOH NWs as precursor, and using copper and magnesium oxides as alternate metal sources to the hydroxides: To make MnO₂ and Mn₂O₃ NWs, and Mn₃O₄ whiskers, γ -MnOOH NWs were calcined at 250 °C, 750 °C, and 950 °C respectively; by calcining MnOOH NWs and LiOH with 1:8 molar ratio, LiMn₂O₄ NWs were produced. The results of these experiments are summarized in the schematic in supporting information (Fig. S1), but do not form the focus of the current paper.

Structural Characterization: Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Discover X-Ray diffractometer at an angle of 2 θ from 10° to 70°, using Cu K α radiation (λ =0.15406 nm). Nanowire morphologies were observed using a scanning electron microscope (SEM, Hitachi S 4300) and transmission electron microscope (TEM, JEOL 2010F), with energy dispersive x-ray detector to collect EDS spectra. X-ray photoelectron spectroscopy (XPS) was performed using a X-rays generated by a Mg K- α source (1253.6 eV, PHI 04-548 Dual Anode X-ray source), an 11 inch diameter hemispherical electron energy analyser with multichannel detector, with pass energies of 23.5 eV and 0.025 eV step sizes (PHI 5600) (Figs. 5 (a-c)) and a Thermo Scientific Model K-Alpha XPS instrument, with a monochromated, microfocusing Al K α X-ray source (1486.6 eV) (Figs. 5(d), S5(f), S5(g)). The base pressure in the analysis chamber is typically 2 x 10⁻⁹ mbar or lower. Survey spectra (0-1350 eV) were

acquired with a pass energy of 200 eV and the high resolution spectra were collected with a pass energy of 50 eV. Peak fitting was performed using mixed Gaussian/Lorentzian peak shapes and a Shirley/Smart type background.

Electrochemical Characterization: Linear sweep voltammetry (LSV) curves were obtained with a scan rate of 10 mV/s in the potential range of 0-1 V vs. Ag/AgCl. We used a Pt wire as the counter electrode and silver/silver chloride (Ag/AgCl) as the reference electrode. 0.1 M KOH solution was used as an electrolyte. For the working electrode, the mixture of catalysts and carbon black were deposited onto a glassy carbon (GC) current collector (diameter = 4mm). 3 mg of catalyst mixed with 7 mg of carbon black were dispersed in 1 mL of acetone by sonicating for 30 minutes. Carbon black was added to increase the conductivity. 6 μ L of the as-prepared catalyst solution was dropped on the GC. After drying, 3 μ L of 2.5 wt % nafion was then applied to the catalyst. Current density (A/cm^2) was obtained by normalizing current by the geometric area of electrodes. A difference in surface roughness of each electrode was not counted. Finally, the LSV curves of the spinel NWs for the oxygen evolution reaction were corrected for iR effect. The electrical resistance (R) of the NW electrode was determined by electrochemical impedance spectroscopic technique at the DC potential of 1.0 V vs. Ag/AgCl. LSVs were plotted as a function of potential versus hydrogen electrode (RHE).

3. Results and Discussion

The solid-state reaction of MnO_2 NWs with the rutile-type pyrolusite structure with polycrystalline $Cu(OH)_2$ was performed, to obtain NWs of $CuMn_2O_4$ with the spinel-type crystal structure. Shown in Fig. 1 are SEM images and indexed XRD patterns from both the MnO_2 NW starting material, and the resulting $CuMn_2O_4$ NWs. Remarkably, though the reaction of rutile-

type NWs to form spinel NWs represents a massive structural change, the anisotropic morphology of the starting material is retained during the transformation to the resulting a wire- or rod-shaped crystals, though admittedly with some degradation of wire quality. Fully-indexed XRD patterns show that a conversion from MnO_2 to CuMn_2O_4 was achieved, with both phase-pure reactant and product, proceeding via the following proposed solid-state reaction:

Further characterization of the crystallinity and composition of the CuMn_2O_4 NWs was performed using the TEM to collect higher resolution images, which are shown in Fig. 2, with accompanying fast Fourier transform (FFT) and EDS analysis. Inspection of the images and indexing of the FFT confirms the expected spinel structure, and that the wires are single-crystalline; indeed, in every case for which a wire was sufficiently thin to enable high-resolution imaging, the wire was a single crystal. Exact values for the relative concentration of Cu and Mn were challenging to obtain using EDS, since the wires are somewhat too large for a Cliff-Lorimer correction, yet possibly too small for the standard “ZAF” correction. With this caveat in mind, ZAF-corrected estimates of the Cu and Mn concentrations for the wire shown in Fig. 2 are consistent with a 1:2 ratio of Cu:Mn. Full results of the quantitative analysis of EDS spectra collected from three CuMn_2O_4 NWs are given in Fig. S2 of supporting information.

Our crystal structure model for CuMn_2O_4 was built using CrystalMaker software. By analysis of the calculated spectra, we found that certain relative peak intensities change with degree of inversion (defined by the occupancy of the spinel crystal A- and B-sites), though the peak positions remain the same. These results are shown in Fig. S3 of supporting information. The intensity of the (011) and (022) reflections increase, while that of (112) and (020) decrease with an increasing degree of inversion. Though not conclusive, since peak intensities would also depend on crystalline anisotropy resulting from the one-dimensional rod morphology, this allows

us to estimate an inversion degree of about 0.9 for our CuMn_2O_4 NR samples where the intensity of (011) lies between that of (112) and (020), while (020) and (022) have about the same intensity, which is consistent with the same four sharp peaks of our experimental XRD pattern. The breadth of the (013) peak makes intensity comparison of this reflexion difficult to include in the comparison.

Fig. 3 shows XRD patterns and SEM images of MgMn_2O_4 and Mg_2MnO_4 NWs using an analogous synthetic approach, for which the following solid state reactions were expected:

For these reactions, however, XRD reveals that the products are not phase pure, and in each case comprise a dominant phase of the expected structure, with secondary spinel and binary oxide phases. One explanation for this is that the MgMn_2O_4 — Mg_2MnO_4 system forms a limited solid solution, phase separating into cubic spinel on the Mg-rich end, and tetragonal spinel on the Mn-rich end, with mass-conservation achieved by the formation of small amounts of MgO and Mn_3O_4 respectively.

To attempt to access a phase-pure region, we tried a further experiment, using γ - MnOOH NWs as an alternate precursor to replace MnO_2 , which for the composition Mg_2MnO_4 produced improved results. SEM images and XRD patterns from both the γ - MnOOH and resulting Mg_2MnO_4 NWs are shown in Fig. 3. In this case, though SEM images suggest that our MnOOH starting material is a single material, XRD analysis reveals that it is a mixture of MnOOH and KMnO_2 structure types, and a small (unidentified) impurity phase. (It should be noted that both our SEM and XRD results for γ - MnOOH NWs appear indistinguishable from those of γ - MnOOH NWs used in the published report[44] on which we based our synthesis.) Despite the mixture of structures in the starting material, both types of wires apparently react to form

Mg₂MnO₄ NWs in the solid state reaction step, as indicated by the XRD from this product, for which all but one peak (at 12.5°) can be assigned to cubic Mg₂MnO₄. For the γ -MnOOH starting material, we propose the following solid-state reaction, and we speculate that the KMnO₂ wires must react similarly, though additionally producing a gas-phase or amorphous potassium-containing side product:

The high resolution TEM image and FFT of a representative Mg₂MnO₄ NW in Fig. 4 shows that similar to the CuMn₂O₄, these wires are single-crystalline, and EDS analysis with a ZAF correction is again consistent with the expected ratio of Mg to Mn (quantitative results for two wires are included in Fig. S2). TEM and EDS analysis were additionally performed on a secondary morphology present in our samples, with a small particle (as opposed to NW) morphology (Fig. S4). EDS reveals that this phase is very rich in Mg (Fig. S2).

For completeness, we further performed the reaction of Cu(OH)₂ with the γ -MnOOH NW precursor, with similar results in terms of phase-purity, crystallinity, and morphology. In this case we speculate that the dominant solid-state reaction proceeds as follows:

The XRD pattern from CuMn₂O₄ (Fig. S5) matches the calculated spectrum (using the tetragonal space group I4₁/amd, with a=5.798Å, and c =8.791Å), except for three minor CuO impurity peaks and one unidentified peak at 12.5°. Given the small powder samples available, and small crystallite size, a Rietveld refinement to further identify these peaks was not possible. CuMn₂O₄ NWs are confirmed to be single-crystalline using high resolution TEM imaging (Fig. S5), and EDS is again consistent with the expected Cu:Mn ratio. The minor (non wire-like) particle phases have also been analysed by TEM and EDS (Fig. S4), but in this case appear to have the same composition as the nanowire morphologies (Fig. S2).

One of the key factors determining the catalytic properties of these nanowires is the oxidation states of the cations, which we determined for three samples, using XPS: CuMn_2O_4 using the MnO_2 starting material (as shown in Figs. 1 & 2), tetragonal MgMn_2O_4 using the MnO_2 starting material (as in Fig. 3), and cubic Mg_2MnO_4 using the $\gamma\text{-MnOOH}$ starting material (as in Figs. 3 & 4). The binding energy of copper is related to its valence state and its coordination environment. The intense peak at 931.1 eV in the XPS spectra of Cu 2p_{3/2} (Fig. 5(a)) is assigned to Cu^+ on the spinel B site. According to previous XPS studies of CuMn_2O_4 , [46–48] the two broad peaks at 932.8 eV and 934.1 eV could be due to Cu^+ on the A site and Cu^{2+} on the B site. Shoemaker *et al.*, however, assigned the peak at 934.75 eV to Cu^{3+} on the B site. From the XPS spectrum, it is evident that significantly more copper cations reside on B sites than A sites, which is consistent with the high inversion degree calculated from CrystalMaker. Manganese is also known to show mixed oxidation states in manganese containing spinels. In Fig. 5b, peaks at 640.5 eV, 642.1 eV and 644.4 eV can be assigned to Mn^{2+} , Mn^{3+} and Mn^{4+} . [49] The CuMn_2O_4 NWs are therefore seen to contain Mn^{2+} , Mn^{3+} and Mn^{4+} . In contrast, MgMn_2O_4 and Mg_2MnO_4 NWs contain only Mn^{3+} and Mn^{4+} , heavily dominated by Mn^{3+} in the MgMn_2O_4 sample, and by Mn^{4+} in the Mg_2MnO_4 sample.

The catalytic activity of these same three samples towards the oxygen evolution reaction (OER): $4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^-$ was evaluated from linear sweep voltammetry curves comparing NW samples with pure carbon black (Fig. 6). Though all curves were collected with the same mass of sample loaded onto the GC (at 0.143 mg/cm^2), the electrocatalytic activity of CuMn_2O_4 NWs toward the OERs was found to be superior to those of magnesium-containing spinels and pure carbon black, with around five times the current density determined at 2.0V.

The onset potential of CuMn_2O_4 was measured to be 1.6 V vs. RHE, which is comparable to the values reported for LaCo_3O_4 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ perovskite oxides, and $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ spinel structures.[50–52] The OER current of CuMn_2O_4 NWs is significantly larger than those of Mg-containing NWs and carbon black, although the surface roughness of Mg_2MnO_4 is expected to be much lower due to lower expected Brunauer-Emmett-Teller (BET) surface areas, suggesting that optimizing the surface area of the CuMn_2O_4 NW sample would lead to a highly catalytic sample. Despite of large differences in BET surface areas between two catalysts, calibration of the LSV data with respect to BET surface areas was not attempted, since it is difficult to estimate the area available for catalysis, and the surface area is in any case dominated by that of carbon black. We speculate that the multiple oxidation states of Cu and Mn induce the strong adsorption of OH-reactants on catalyst surfaces, and also provide enough density of states to support fast electron transfer.

Oxidation state variance of the metals in Mg_2MnO_4 and CuMn_2O_4 are expected to affect the catalytic properties. Studies have shown that the key factor determining catalytic activity towards the OER for cubic Mg_2MnO_4 is the large amount of tetravalent manganese ions on the octahedral sites.[30] Interestingly, for tetragonal CuMn_2O_4 , however, the material is more catalytically-active but has fewer tetravalent manganese ions on the octahedral sites. Reported characterization of this material suggests that half of the tetravalent manganese ions reside on the octahedral sites, along with one third of the trivalent manganese ions and a small number of Cu^{2+} and Cu^{3+} cations.[35] It is possible that having both multivalent copper as well as manganese in CuMn_2O_4 might provide a synergy which promotes catalytic activity.

4. Conclusions

In this report, we described a new route to make single crystalline Mg_2MnO_4 NWs and CuMn_2O_4 NWs by the simple solid state reaction of MnO_2 and $\gamma\text{-MnOOH}$ NWs with metal hydroxide metal sources in such a way that the metal diffuses into the nanowire, undergoing a rutile to spinel crystal structure transformation, while preserving an anisotropic wire- or rod-like morphology. Linear sweep voltammetric results revealed the electrocatalytic activity Cu_2MnO_4 NWs for oxygen evolution reaction in alkaline solution. We believe this synthetic route may be extended as a general way to synthesize many manganese-containing spinel NWs, as well as other ternary oxides.

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References

- [1] C. He, S. Wu, N. Zhao, C. Shi, E. Liu, J. Li, Carbon-Encapsulated Fe_3O_4 Nanoparticles as a High-Rate Lithium Ion Battery Anode Material, *ACS Nano*. 7 (2013) 4459–4469. doi:10.1021/nn401059h.
- [2] F.-S. Ke, L. Jamison, L. Huang, B. Zhang, J.-T. Li, X.-D. Zhou, S.-G. Sun, Negative electrode comprised of Fe_3O_4 nanoparticles and Cu nanowires for lithium ion batteries, *Solid State Ion*. 262 (2014) 18–21. doi:10.1016/j.ssi.2013.08.034.
- [3] S.-Z. Huang, J. Jin, Y. Cai, Y. Li, H.-Y. Tan, H.-E. Wang, G.V. Tendeloo, B.-L. Su, Engineering single crystalline Mn_3O_4 nano-octahedra with exposed highly active {011} facets for high performance lithium ion batteries, *Nanoscale*. 6 (2014) 6819–6827. doi:10.1039/C4NR01389A.
- [4] H. Tang, Y. Sui, X. Zhu, Z. Bao, Synthesis of Mn_3O_4 -Based Aerogels and Their Lithium-Storage Abilities, *Nanoscale Res. Lett.* 10 (2015). doi:10.1186/s11671-015-0960-x.

- [5] B. Ammundsen, J. Paulsen, Novel Lithium-Ion Cathode Materials Based on Layered Manganese Oxides, *Adv. Mater.* 13 (2001) 943–956. doi:10.1002/1521-4095(200107)13:12/13<943::AID-ADMA943>3.0.CO;2-J.
- [6] H.-W. Lee, P. Muralidharan, R. Ruffo, C.M. Mari, Y. Cui, D.K. Kim, Ultrathin Spinel LiMn₂O₄ Nanowires as High Power Cathode Materials for Li-Ion Batteries, *Nano Lett.* 10 (2010) 3852–3856. doi:10.1021/nl101047f.
- [7] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, Lithium insertion into manganese spinels, *Mater. Res. Bull.* 18 (1983) 461–472. doi:10.1016/0025-5408(83)90138-1.
- [8] A. Feltz, F.-H. Beck, B. Neidnicht, Redox reactions in condensed oxide systems XIII: Li insertion reaction of MgTiO₃ and the spinels Mg₂TiO₄, MgNiMnO₄ and MMn₂O₄ (M Mn, Mg, Ni), *J. Alloys Compd.* 176 (1991) 347–355. doi:10.1016/0925-8388(91)90043-U.
- [9] G.C. Allen, J.A. Jutson, Carbon deposition on iron–manganese–chromium spinels, *J. Mater. Chem.* 1 (1991) 73–78. doi:10.1039/JM9910100073.
- [10] S.J. S. Kiiding, YSZ-cells for potentiometric nitric oxide sensors, *Ionics*. 9 (2003) 151–154. doi:10.1007/BF02376552.
- [11] D. Mehandjiev, E. Zhecheva, G. Ivanov, R. Ioncheva, Preparation and catalytic activity of nickel–manganese oxide catalysts with an ilmenite-type structure in the reactions of complete oxidation of hydrocarbons, *Appl. Catal. Gen.* 167 (1998) 277–282. doi:10.1016/S0926-860X(97)00312-8.
- [12] J. Zhu, Q. Gao, Mesoporous MCo₂O₄ (M = Cu, Mn and Ni) spinels: Structural replication, characterization and catalytic application in CO oxidation, *Microporous Mesoporous Mater.* 124 (2009) 144–152. doi:10.1016/j.micromeso.2009.05.003.
- [13] Z.-R. Tang, S.A. Kondrat, C. Dickinson, J.K. Bartley, A.F. Carley, S.H. Taylor, T.E. Davies, M. Allix, M.J. Rosseinsky, J.B. Claridge, Z. Xu, S. Romani, M.J. Crudace, G.J. Hutchings, Synthesis of high surface area CuMn₂O₄ by supercritical anti-solvent precipitation for the oxidation of CO at ambient temperature, *Catal. Sci. Technol.* 1 (2011) 740–746. doi:10.1039/C1CY00064K.
- [14] J. Papavasiliou, G. Avgouropoulos, T. Ioannides, Combined steam reforming of methanol over Cu–Mn spinel oxide catalysts, *J. Catal.* 251 (2007) 7–20. doi:10.1016/j.jcat.2007.07.025.
- [15] E. Lodowicks, F. Beck, Basic characteristics of spinel type manganese mixed oxide/titanium composite anodes for electroorganic redox catalysis, *Chem. Eng. Technol.* 17 (1994) 338–347. doi:10.1002/ceat.270170508.
- [16] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature*. 407 (2000) 496–499. doi:10.1038/35035045.
- [17] J.C. Arrebola, A. Caballero, L. Hernán, J. Morales, Improving the Performance of Lithium-Ion Batteries by Using Spinel Nanoparticles, *J. Nanomater.* 2008 (2008) e659397. doi:10.1155/2008/659397.
- [18] J. Gao, M.A. Lowe, H.D. Abruña, Spongelike Nanosized Mn₃O₄ as a High-Capacity Anode Material for Rechargeable Lithium Batteries, *Chem. Mater.* 23 (2011) 3223–3227. doi:10.1021/cm201039w.

- [19] K.M. Shaju, P.G. Bruce, A Stoichiometric Nano-LiMn₂O₄ Spinel Electrode Exhibiting High Power and Stable Cycling, *Chem. Mater.* 20 (2008) 5557–5562. doi:10.1021/cm8010925.
- [20] C.-Z. Lu, G.T.-K. Fey, Nanocrystalline and long cycling LiMn₂O₄ cathode material derived by a solution combustion method for lithium ion batteries, *J. Phys. Chem. Solids.* 67 (2006) 756–761. doi:10.1016/j.jpcs.2005.11.008.
- [21] G. Jian, Y. Xu, L.-C. Lai, C. Wang, M.R. Zachariah, Mn₃O₄ hollow spheres for lithium-ion batteries with high rate and capacity, *J. Mater. Chem. A.* 2 (2014) 4627–4632. doi:10.1039/C4TA00207E.
- [22] J. Cabana, T. Valdés-Solís, M.R. Palacín, J. Oró-Solé, A. Fuertes, G. Marbán, A.B. Fuertes, Enhanced high rate performance of LiMn₂O₄ spinel nanoparticles synthesized by a hard-template route, *J. Power Sources.* 166 (2007) 492–498. doi:10.1016/j.jpowsour.2006.12.107.
- [23] C. Wang, L. Yin, D. Xiang, Y. Qi, Uniform Carbon Layer Coated Mn₃O₄ Nanorod Anodes with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries, *ACS Appl. Mater. Interfaces.* 4 (2012) 1636–1642. doi:10.1021/am2017909.
- [24] E. Hosono, T. Kudo, I. Honma, H. Matsuda, H. Zhou, Synthesis of Single Crystalline Spinel LiMn₂O₄ Nanowires for a Lithium Ion Battery with High Power Density, *Nano Lett.* 9 (2009) 1045–1051. doi:10.1021/nl803394v.
- [25] J.Y. Lee, D.S. Kim, C.W. Na, J. Park, MnGa₂O₄ and Zn-doped MnGa₂O₄ 1-Dimensional Nanostructures, *J. Phys. Chem. C.* 111 (2007) 12207–12212. doi:10.1021/jp072232r.
- [26] Y. Chen, Z. Liu, S.P. Ringer, Z. Tong, X. Cui, Y. Chen, Selective Oxidation Synthesis of MnCr₂O₄ Spinel Nanowires from Commercial Stainless Steel Foil, *Cryst. Growth Des.* 7 (2007) 2279–2281. doi:10.1021/cg070514a.
- [27] C.W. Na, D.S. Han, J. Park, Y. Jo, M.-H. Jung, Ferrimagnetic Mn₂SnO₄ nanowires, *Chem. Commun.* (2006) 2251. doi:10.1039/b601404f.
- [28] N. Izawa, T. Oi, Ion and lithium isotope selectivities of sorbents prepared from Mg₂MnO₄, *J. Mater. Sci.* 32 (1997) 675–679. doi:10.1023/A:1018587702508.
- [29] A. de Kock, M.H. Rossouw, L.A. de Picciotto, M.M. Thackeray, W.I.F. David, R.M. Ibberson, Defect spinels in the system Li₂O.yMnO₂ (y>2.5): A neutron-diffraction study and electrochemical characterization of Li₂Mn₄O₉, *Mater. Res. Bull.* 25 (1990) 657–664. doi:10.1016/0025-5408(90)90032-W.
- [30] N. Garg, Menaka, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, Nanostructured dimagnesium manganese oxide (Spinel): Control of size, shape and their magnetic and electro catalytic properties, *J. Solid State Chem.* 197 (2013) 392–397. doi:10.1016/j.jssc.2012.08.063.
- [31] N.K. Radhakrishnan, A.B. Biswas, A neutron diffraction study of the spinel oxide CuMn₂O₄, *Phys. Status Solidi A.* 44 (1977) 45–49. doi:10.1002/pssa.2210440103.
- [32] A. Miller, Determination of the valence state of copper in cubic CuMn₂O₄ spinel by X-ray absorption edge measurements, *J. Phys. Chem. Solids.* 29 (1968) 633–639. doi:10.1016/0022-3697(68)90032-2.
- [33] B. Gillot, S. Buguet, E. Kester, Oxidation mechanism and valence states of copper and manganese in tetragonal CuMn₂O₄, *J. Mater. Chem.* 7 (1997) 2513–2517. doi:10.1039/A703731G.

- [34] A. Waskowska, L. Gerward, J.S. Olsen, S. Steenstrup, E. Talik, CuMn₂O₄: properties and the high-pressure induced Jahn-Teller phase transition, *J. Phys. Condens. Matter.* 13 (2001) 2549. doi:10.1088/0953-8984/13/11/311.
- [35] D.P. Shoemaker, J. Li, R. Seshadri, Unraveling Atomic Positions in an Oxide Spinel with Two Jahn–Teller Ions: Local Structure Investigation of CuMn₂O₄, *J. Am. Chem. Soc.* 131 (2009) 11450–11457. doi:10.1021/ja902096h.
- [36] G.G. Xia, Y.G. Yin, W.S. Willis, J.Y. Wang, S.L. Suib, Efficient Stable Catalysts for Low Temperature Carbon Monoxide Oxidation, *J. Catal.* 185 (1999) 91–105. doi:10.1006/jcat.1999.2484.
- [37] Y. Tanaka, T. Utaka, R. Kikuchi, K. Sasaki, K. Eguchi, Water gas shift reaction over Cu-based mixed oxides for CO removal from the reformed fuels, *Appl. Catal. Gen.* 242 (2003) 287–295. doi:10.1016/S0926-860X(02)00529-X.
- [38] D. Fang, J. Xie, D. Mei, Y. Zhang, F. He, X. Liu, Y. Li, Effect of CuMn₂O₄ spinel in Cu–Mn oxide catalysts on selective catalytic reduction of NO_x with NH₃ at low temperature, *RSC Adv.* 4 (2014) 25540–25551. doi:10.1039/C4RA02824D.
- [39] B. Lan, L. Yu, T. Lin, G. Cheng, M. Sun, F. Ye, Q. Sun, J. He, Multifunctional Free-Standing Membrane from the Self-assembly of Ultralong MnO₂ Nanowires, *ACS Appl. Mater. Interfaces.* 5 (2013) 7458–7464. doi:10.1021/am401774r.
- [40] Y. Yang, P. Wang, Z. Zhang, H. Liu, J. Zhang, J. Zhuang, X. Wang, Nanowire membrane-based nanothermite: towards processable and tunable interfacial diffusion for solid state reactions, *Sci. Rep.* 3 (2013) 1694. doi:10.1038/srep01694.
- [41] X. Zhang, A.J. Du, P. Lee, D.D. Sun, J.O. Leckie, TiO₂ nanowire membrane for concurrent filtration and photocatalytic oxidation of humic acid in water, *J. Membr. Sci.* 313 (2008) 44–51. doi:10.1016/j.memsci.2007.12.045.
- [42] N. Liu, J. Li, W. Ma, W. Liu, Y. Shi, J. Tao, X. Zhang, J. Su, L. Li, Y. Gao, Ultrathin and Lightweight 3D Free-Standing Ni@NiO Nanowire Membrane Electrode for a Supercapacitor with Excellent Capacitance Retention at High Rates, *ACS Appl. Mater. Interfaces.* 6 (2014) 13627–13634. doi:10.1021/am503108x.
- [43] T. Maiyalagan, K.R. Chemelewski, A. Manthiram, Role of the Morphology and Surface Planes on the Catalytic Activity of Spinel LiMn_{1.5}Ni_{0.5}O₄ for Oxygen Evolution Reaction, *ACS Catal.* 4 (2014) 421–425. doi:10.1021/cs400981d.
- [44] X. Xiao, L. Wang, D. Wang, X. He, Q. Peng, Y. Li, Hydrothermal synthesis of orthorhombic LiMnO₂ nano-particles and LiMnO₂ nanorods and comparison of their electrochemical performances, *Nano Res.* 2 (2009) 923–930. doi:10.1007/s12274-009-9094-8.
- [45] Y. Jia, J. Xu, L. Zhou, H. Liu, Y. Hu, A simple one step approach to preparation of γ -MnOOH multipods and β -MnO₂ nanorods, *Mater. Lett.* 62 (2008) 1336–1338. doi:10.1016/j.matlet.2007.08.041.
- [46] E. Kester, B. Gillot, P. Perriat, P. Dufour, C. Villette, P. Tailhades, A. Rousset, Thermal Behavior and Cation Distribution of Submicron Copper Ferrite Spinel CuxFe_{3-x}O₄ (0 ≤ x ≤ 0.5) Studied by DTG, FTIR, and XPS, *J. Solid State Chem.* 126 (1996) 7 – 14. doi:10.1006/jssc.1996.0302.

- [47] B. Gillot, S. Buguet, E. Kester, Oxidation mechanism and valence states of copper and manganese in tetragonal CuMn_2O_4 , *J. Mater. Chem.* 7 (1997) 2513–2517. doi:10.1039/A703731G.
- [48] M. Lenglet, A. D’Huysser, J. Kasperek, J.P. Bonnelle, J. Dürr, Caractérisation des états d’oxydation du cuivre et du manganèse dans quelques manganites par analyse des spectres XPS, d’émission X et des seuils d’absorption X, *Mater. Res. Bull.* 20 (1985) 745–757. doi:10.1016/0025-5408(85)90053-4.
- [49] J. Töpfer, A. Feltz, D. Gräf, B. Hackl, L. Raupach, P. Weissbrodt, Cation Valencies and Distribution in the Spinel NiMn_2O_4 and $\text{M}_2\text{NiMn}_2\text{O}_4$ ($\text{M} = \text{Li}, \text{Cu}$) Studied by XPS, *Phys. Status Solidi A*. 134 (1992) 405–415. doi:10.1002/pssa.2211340211.
- [50] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles, *Science*. 334 (2011) 1383–1385. doi:10.1126/science.1212858.
- [51] C. Jin, X. Cao, L. Zhang, C. Zhang, R. Yang, Preparation and electrochemical properties of urchin-like $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ perovskite oxide as a bifunctional catalyst for oxygen reduction and oxygen evolution reaction, *J. Power Sources*. 241 (2013) 225–230. doi:10.1016/j.jpowsour.2013.04.116.
- [52] F. Cheng, J. Shen, B. Peng, Y. Pan, Z. Tao, J. Chen, Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts, *Nat. Chem.* 3 (2011) 79–84. doi:10.1038/nchem.931.

Figure Legends

Figure 1. Structural characterization of MnO_2 to CuMn_2O_4 conversion. SEM images of (a) MnO_2 and (b) CuMn_2O_4 nanowires; and powder XRD patterns of (c) MnO_2 nanowires, indexed to the pyrolusite phase (pdf card # 01-071-0071), and (d) CuMn_2O_4 nanowires, indexed to CuMn_2O_4 spinel (using the tetragonal space group $I4_1/amd$, with $a=5.798\text{\AA}$, and $c=8.791\text{\AA}$).

Figure 2. Crystallinity and compositional analysis of a CuMn_2O_4 nanowire (synthesized from MnO_2 precursor). (a) TEM image demonstrating NW facets. (b) High-resolution TEM image with FFT inset, demonstrating single-crystallinity. (c) EDS spectrum showing the presence of Cu, Mn, and O within the wire (quantitative analysis in supporting information). Ni peak due to the TEM grid marked in blue.

Figure 3. Structural characterization of Mg-containing nanowire syntheses. SEM images of (a) tetragonal spinel NWs with nominal composition MgMn_2O_4 (synthesized from MnO_2 precursor NWs); (b) cubic spinel NWs with nominal composition Mg_2MnO_4 (synthesized from MnO_2 precursor NWs); (c) $\gamma\text{-MnOOH}$ NWs; and (d) cubic spinel Mg_2MnO_4 NWs (synthesized from $\gamma\text{-MnOOH}$ precursor NWs). (e) – (h) Powder XRD patterns from (a) – (d) respectively.

Figure 4. Crystallinity and compositional analysis of a Mg_2MnO_4 nanowire (synthesized from $\gamma\text{-MnOOH}$ precursor). (a) High-resolution TEM image with FFT inset, demonstrating single-crystallinity. (b) EDS spectrum showing the presence of Mg, Mn, and O within the wire (quantitative analysis in supporting information). Cu peak due to the TEM grid marked in blue.

Figure 5. XPS spectra for the $2p_{3/2}$ region of (a) Cu cations in CuMn_2O_4 (from MnO_2); (b) Mn cations in CuMn_2O_4 (from MnO_2); (c) Mn cations in MgMn_2O_4 (from MnO_2); and (d) Mn cations in Mg_2MnO_4 (from $\gamma\text{-MnOOH}$).

Figure 6. Linear sweep voltammetry curves of CuMn_2O_4 , Mg_2MnO_4 , and MgMn_2O_4 , compared with carbon black (iR -corrected).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Step 1. Hydrothermal reaction

Pyrolusite: MnO_2

Step 2. Calcination

Spinel ternary oxide:
 CuMn_2O_4 or Mg_2MnO_4

- Structure changed
- Nanowire morphology retained