



# 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  $\text{CuMn}_2\text{O}_4$  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.

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## 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 structures such as  $\text{Fe}_3\text{O}_4$  [1,2],  $\text{Mn}_3\text{O}_4$  [3,4] and  $\text{LiMn}_2\text{O}_4$  [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  $\text{MMn}_2\text{O}_4$  ( $M = \text{Mn, Mg, Li}$ ), 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]  $\text{CdMn}_2\text{O}_4$  can be used as an electrode material for NO gas sensors; [10]  $\text{NiMn}_2\text{O}_4$  [11], mesoporous  $\text{MnCo}_2\text{O}_4$  [12], and high surface area  $\text{CuMn}_2\text{O}_4$  [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  $\text{H}_2$  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  $\text{LiMn}_2\text{O}_4$  NWs by hydrothermal and solid state methods respectively; Lee et al. synthesized  $\text{MnGa}_2\text{O}_4$  NWs via thermal evaporation method; [25] Chen et al. obtained  $\text{MnCr}_2\text{O}_4$  NWs by heating stainless steel foil; [26] and Na et al. synthesized  $\text{Mn}_2\text{SnO}_4$  NWs using a chemical vapor deposition method [27]. To date, however, no reports exist for the synthesis of single-crystalline NWs of  $\text{Mg}_2\text{MnO}_4$  or  $\text{CuMn}_2\text{O}_4$ .

Cubic  $\text{Mg}_2\text{MnO}_4$  forms the inverse spinel structure, with half of the  $\text{Mg}^{2+}$  ions in the tetrahedral A-sites, and the octahedral B-sites occupied equally by  $\text{Mg}^{2+}$  and  $\text{Mn}^{4+}$  so as to maximize the crystal field stabilization energy of the  $\text{Mn}^{4+}$  cations. Both  $\text{Mg}^{2+}$  and  $\text{Mn}^{4+}$  are critical in determining the functionality of this compound. Izawa et al. found  $\text{Mg}_2\text{MnO}_4$  showed good lithium isotope selectivity in the ion exchange process in which  $\text{Li}^+$  ions replace  $\text{Mg}^{2+}$  in the  $\text{Mg}_2\text{MnO}_4$  [28].  $\text{Mg}_2\text{MnO}_4$  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  $\text{CuMn}_2\text{O}_4$ , 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

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cubic  $\text{CuMn}_2\text{O}_4$  which has  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  on the A-sites and  $\text{Cu}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  taking B-sites. This coexistence of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  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  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$  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  $\text{CuMn}_2\text{O}_4$ , however, is more complicated than that of the cubic phase. Shoemaker et al. [35] refined the tetragonal  $\text{CuMn}_2\text{O}_4$  structure with *c/a* ratio of 1.03399 and a 0.27 inversion degree. In this tetragonal spinel,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  ions all take tetrahedral sites, with octahedral sites occupied by  $\text{Cu}^{2+}$ ,  $\text{Cu}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ . In its bulk form,  $\text{CuMn}_2\text{O}_4$  is known to catalyze the oxidation of CO to  $\text{CO}_2$  at room temperature [13,36,37], and the reduction of  $\text{NO}_x$  [38].

With the many useful applications of  $\text{Mg}_2\text{MnO}_4$  and  $\text{CuMn}_2\text{O}_4$  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  $\text{LiMn}_2\text{O}_4$  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  $\text{Mg}_2\text{MnO}_4$  or  $\text{CuMn}_2\text{O}_4$  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  $\text{MnO}_2$  and  $\gamma\text{-MnOOH}$  NWs were synthesized using methods in the literature [44,45]. For  $\text{MnO}_2$ , 1.37 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (99% min, Sigma-Aldrich) and 0.086 g  $\text{NaClO}_3$  (99% min, Sigma-Aldrich) were dissolved in 36 mL distilled water and stirred for 15 min. The mixed solution was transferred to a 45 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 160 °C for 18 h. 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, 0.63 g  $\text{KMnO}_4$  (99% min, Alfa Aesar) and 0.45 g CTAB (98%, Alfa Aesar) were dissolved in 36 mL distilled water and stirred for 20 min. The mixed solution was transferred to a 45 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 180 °C for 12 h. 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  $\text{CuMn}_2\text{O}_4$  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 1–3 h in air. A similar procedure was applied to make  $\text{MgMn}_2\text{O}_4$  and  $\text{Mg}_2\text{MnO}_4$  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  $\text{CuO}$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{CuMn}_2\text{O}_4$ , and that calcining the magnesium-containing mixture below 850 °C results in  $\text{MgO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mg}_2\text{MnO}_4$ . In both cases, using calcination temperatures higher than 950 °C yielded large  $\text{CuMn}_2\text{O}_4$  and  $\text{Mg}_2\text{MnO}_4$  whiskers. Molar ratios of starting materials different from those listed yielded the same products but with additional impurity phases, implying that the chosen compositions ( $\text{CuMn}_2\text{O}_4$ ,  $\text{MgMn}_2\text{O}_4$ , and  $\text{Mg}_2\text{MnO}_4$ ) are the most stable under our reaction conditions.

Several further experiments were also performed using the  $\gamma\text{-MnOOH}$  NWs as precursor, and using copper and magnesium oxides as alternate metal sources to the hydroxides: To make  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$  NWs, and  $\text{Mn}_3\text{O}_4$  whiskers,  $\gamma\text{-MnOOH}$  NWs were calcined at 250 °C, 750 °C, and 950 °C respectively; by calcining  $\text{MnOOH}$  NWs and  $\text{LiOH}$  with 1:8 molar ratio,  $\text{LiMn}_2\text{O}_4$  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  $2\theta$  from 10° to 70°, using  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15406$  nm). Nanowire morphologies were observed using a scanning electron microscope (SEM, Hitachi S 4300) and transmission electron microscope (TEM, JEOL 2010 F), with energy dispersive x-ray detector to collect EDS spectra. X-ray photoelectron spectroscopy (XPS) was performed using a X-rays generated by a  $\text{Mg K}\alpha$  source (1253.6 eV, PHI 04-548 Dual Anode X-ray source), an 11 in. diameter hemispherical electron energy analyser with multichannel detector, with pass energies of 23.5 eV and 0.025 eV step sizes (PHI 5600) (Fig. 5(a)–(c)) and a Thermo Scientific Model K-Alpha XPS instrument, with a monochromated, microfocusing  $\text{Al K}\alpha$  X-ray source (1486.6 eV) (Figs. 5(d), S5(f), S5(g)). The base pressure in the analysis chamber is typically  $2 \times 10^{-9}$  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.  $\text{Ag}/\text{AgCl}$ . We used a Pt wire as the counter electrode and silver/silver chloride ( $\text{Ag}/\text{AgCl}$ ) 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 = 4 mm). 3 mg of catalyst mixed with 7 mg of carbon black were dispersed in 1 mL of acetone by sonicating for 30 min. Carbon black was added to increase the conductivity. 6  $\mu\text{L}$  of the as-prepared catalyst solution was dropped on the GC. After drying, 3  $\mu\text{L}$  of 2.5 wt% nafion was then applied to the catalyst. Current density ( $\text{A}/\text{cm}^2$ ) 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

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