Electrochemical Performance and \textit{ex situ} Analysis of ZnMn\textsubscript{2}O\textsubscript{4} Nanowires as Anode Materials for Lithium Rechargeable Batteries

Sung-Wook Kim\textsuperscript{1,§}, Hyun-Wook Lee\textsuperscript{2,§}, Pandurangan Muralidharan\textsuperscript{2,§}, Dong-Hwa Seo\textsuperscript{2}, Won-Sub Yoon\textsuperscript{3}, Do Kyung Kim\textsuperscript{2} (✉), and Kisuk Kang\textsuperscript{2,4} (✉)

1 Research Institute of Advanced Materials, Seoul National University, 599 Kwanak-ro, Kwanak-gu, Seoul 151-742, Republic of Korea
2 Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea
3 School of Advanced Materials Engineering, Kookmin University, 861-6 Jeongneung-dong, Seongbuk-gu, Seoul 136-702, Republic of Korea
4 Department of Materials Science and Engineering, Seoul National University, 599 Kwanak-ro, Kwanak-gu, Seoul 151-742, Republic of Korea

§ These authors contributed equally to this work

Received: 2 November 2010 / Revised: 10 January 2011 / Accepted: 12 January 2011
© Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2011

ABSTRACT
One-dimensional ZnMn\textsubscript{2}O\textsubscript{4} nanowires have been prepared and investigated as anode materials in Li rechargeable batteries. The highly crystalline ZnMn\textsubscript{2}O\textsubscript{4} nanowires about 15 nm in width and 500 nm in length showed a high specific capacity of about 650 mAh·g\textsuperscript{−1} at a current rate of 100 mA·g\textsuperscript{−1} after 40 cycles. They also exhibited high power capability at elevated current rates, i.e., 450 and 350 mAh·g\textsuperscript{−1} at current rates of 500 and 1000 mA·g\textsuperscript{−1}, respectively. Formation of Mn\textsubscript{3}O\textsubscript{4} and ZnO phases was identified by \textit{ex situ} X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies after the initial discharge–charge cycle, which indicates that the ZnMn\textsubscript{2}O\textsubscript{4} phase was converted to a nanocomposite of Mn\textsubscript{3}O\textsubscript{4} and ZnO phases immediately after the electrochemical conversion reaction.

KEYWORDS
Energy storage, lithium rechargeable battery, anode, ZnMn\textsubscript{2}O\textsubscript{4} nanowire

1. Introduction
Increasing demand for higher energy capability Li rechargeable batteries has led the extensive research efforts on the development of electrode materials with higher specific capacity [1–4]. In particular, materials that store Li ions through a conversion reaction (e.g., CoO, Co\textsubscript{2}O\textsubscript{4}, FeO, Mn\textsubscript{2}O\textsubscript{3}) or an alloying reaction (e.g., Si, Ge, Sn) have been suggested as promising alternative anode materials due to their intrinsically high specific capacity [5–9]. However, these materials typically undergo significant volume change during lithiation and delithiation due to the large Li uptake in the structure and accompanying phase transformation. In addition, electron (or Li-ion) conduction is often severely restricted during the electrochemical reaction. In this respect, fabrication of nanosized particles of these materials has been intensively explored and, in some cases, proven to effectively accommodate strain induced by volume change and give improved electron/Li-ion conduction [10–14].

Recent studies have shown that Si anodes exhibit promising electrochemical performance when properly...
designed with nanosized particles [12–14]. However, fabrication of Si nanostructures frequently involves complex processes which require special chemical agents or apparatus, resulting in high production costs and restricting their potential for commercial development.

On the other hand, nanostructured transition metal oxides can be obtained even from simple basic processes such as solid-state, sol–gel, and hydrothermal synthesis methods [15–17]. Commercialization of these simple processes is therefore much more feasible. Nanostructured Co$_3$O$_4$ has been demonstrated as a promising anode material due to its high electrochemical activity and specific capacity (~900 mAh·g$^{-1}$) [5, 11], although the high cost and toxicity of Co remain as major drawbacks.

Recently, compounds involving partial or total substitution of Co in Co$_3$O$_4$, such as ZnCo$_2$O$_4$, NiCo$_2$O$_4$, and ZnMn$_2$O$_4$ have been proposed [18–21] as alternatives to Co$_3$O$_4$. Of these, ZnMn$_2$O$_4$ is particularly interesting because all the Co ions have been substituted by cheap and non-toxic Zn and Mn ions [20, 21]. Interestingly, ZnMn$_2$O$_4$ can store Li ions through both conversion and alloying reactions because Zn, one of the products of the conversion reaction, further alloys with Li to form LiZn. Yang et al. and Xiao et al. investigated ZnMn$_2$O$_4$ nanoparticles and nanoflowers, which showed specific capacities as high as 569 and 626 mAh·g$^{-1}$, respectively [20, 21].

In this study, we fabricate one-dimensional ZnMn$_2$O$_4$ nanowires by a simple synthesis process and demonstrate their use as a high performance anode material. Ex situ X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analysis of the nanowire single crystals has been used to investigate structural changes associated with the discharge–charge cycles.

### 2. Experimental

ZnMn$_2$O$_4$ nanowires were fabricated by a solid-state reaction of $\alpha$-MnO$_2$ nanowires and Zn(CH$_3$COO)$_2$ (Aldrich, 99.99%). $\alpha$-MnO$_2$ nanowires were synthesized by hydrothermal reaction using Mn(CH$_3$COO)$_2$·4H$_2$O (Aldrich, 99.99%) and (NH$_4$)$_2$SO$_4$ (Aldrich 98%) [22]. A stoichiometric amount of the $\alpha$-MnO$_2$ nanowires and Zn(CH$_3$COO)$_2$ were homogeneously dispersed in high purity ethanol and diethylamine, and ground for several hours to form a fine mixture. Finally, the mixture was calcined at 480 °C at low pressure in an O$_2$ atmosphere (2 mbar) for 12 h to form ZnMn$_2$O$_4$ nanowires.

The morphology of the ZnMn$_2$O$_4$ nanowires was confirmed by field emission scanning electron microscopy (SEM, Hitachi S-4800) and field emission TEM (JEOL JEM-2100F and Tecnai G$^2$ F30 S-Twin). The crystal phase of ZnMn$_2$O$_4$ was identified by XRD using Cu $K\alpha$ radiation (Rigaku D/MAX 2500). The electrochemical cells were assembled as CR2016-type coin cells composed of a ZnMn$_2$O$_4$ nanowire electrode, a Li metal counter electrode, a polymer membrane separator (Celgard 2400), and an organic electrolyte of 1 mol/L LiPF$_6$ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate. A slurry composed of 60 wt.% ZnMn$_2$O$_4$ nanowire mixture, 30 wt.% carbon black, and 10 wt.% polyvinylidene fluoride binder was dissolved in N-methyl-2-pyrrolidone and manually mixed, cast onto Al foil, and then dried to form a test electrode. Electrochemical tests were performed using an automatic battery cycler (WonAtech, WBCS3000). Galvanostatic discharge–charge tests were performed in the voltage range 0.01–3.0 V at current rates from 100 to 1000 mA·g$^{-1}$ and cyclic voltammetry (CV) was carried out in the same voltage range with a scan rate of 0.1 mV·s$^{-1}$.

### 3. Results and discussion

The XRD pattern shown in Fig. 1(a) indicates that the fabricated powder is a conventional tetragonal ZnMn$_2$O$_4$ structure with the space group $I4_1/amd$ (JCPDS no. 24-1133). Figures 1(b)–1(d) show the typical morphology of the fabricated ZnMn$_2$O$_4$ nanowires which are about 15 nm wide and 500 nm long. Individual ZnMn$_2$O$_4$ nanowires are interwoven with each other to form a complex network structure. Compared with a simple spherical nanopowder, such a network structure is expected to improve the electrochemical performance, due to its higher resistance against separation or isolation of individual nanowires during the electrochemical reaction. This will be particularly critical for electrode materials experiencing
a large volume change. The HRTEM image shown in Fig. 1(d) indicates that the ZnMn$_2$O$_4$ nanowires are highly crystalline. The measured interplanar distance is about 2.86 Å which matches well to the (200) plane of ZnMn$_2$O$_4$.

Electrochemical tests were performed using the ZnMn$_2$O$_4$ nanowire electrode as shown in Fig. 2. The galvanostatic discharge–charge profiles for the first five cycles at a current rate of 100 mA·g$^{-1}$ are shown in Fig. 2(a). The first discharge capacity is about 1400 mAh·g$^{-1}$ which is higher than the theoretical value (1008 mAh·g$^{-1}$). The formation of solid-electrolyte-interphase layers at the ZnMn$_2$O$_4$/electrolyte interface may contribute to the extra capacity at the first discharge [20, 21]. The specific capacity is saturated at ca. 650 mAh·g$^{-1}$ after several cycles, and this is comparable to that for ZnMn$_2$O$_4$ nanoflowers reported by Xiao et al. [21]. Figure 2(b) shows a comparison of the specific capacity of ZnMn$_2$O$_4$ nanowires at different current rates. High rate performance of an electrode is especially important for high power applications, and the ZnMn$_2$O$_4$ nanowire exhibits good reversibility during the electrochemical reaction even at elevated current rates. The specific capacities were about 450 and 350 mAh·g$^{-1}$ at a current rate of 500 and 1000 mA·g$^{-1}$, respectively. This is the first report of such a high rate performance for a ZnMn$_2$O$_4$ anode material as far as we know. Considering that the highest power capability reported so far for ZnCo$_2$O$_4$ is about 350 mAh·g$^{-1}$ at a current rate of 630 mA·g$^{-1}$ [18] our ZnMn$_2$O$_4$ nanowire exhibits promising power capability.

Figure 2(c) shows the CV peaks of the ZnMn$_2$O$_4$ nanowire electrode. Compared to other ZnMn$_2$O$_4$ anodes with different morphologies [20, 21], the first irreversible reactions occurred at higher voltage near 1.6 and 1.3 V. It seems that the morphology of a
nanoparticle influences the irreversible reaction voltage. After the irreversible reaction, the cathodic properties were comparable to those of other ZnMn$_2$O$_4$ anodes [20, 21]. On the other hand, the anodic peaks showed different behavior from these other ZnMn$_2$O$_4$ anodes. Xiao et al. suggested that the products after the first discharge—LiZn, Mn, and Li$_2$O—are converted to ZnO and MnO upon full delithiation [21]. They argued that anodic peaks near 1.2 and 1.5 V in a subsequent cycle are related to the conversion reactions of MnO and ZnO, respectively. However, one additional anodic peak near 2.2 V appeared for our material indicating that an additional oxidation step occurred during the delithiation.

In order to clarify the discharge–charge mechanism of ZnMn$_2$O$_4$, we performed a structural investigation using ex situ XRD and TEM. Figure 3(a) shows ex situ XRD patterns of the materials after the first discharge and charge, with that of pristine ZnMn$_2$O$_4$ for comparison. The crystalline ZnMn$_2$O$_4$ phase is completely destroyed after the initial discharge giving an amorphous-like phase, and is not recovered after the initial charge. This behavior is consistent with the Ref. [21]. Because it is hard to understand the reaction mechanism by XRD alone, we performed ex situ TEM analysis. In fact, it turns out that the use of single nanowires is beneficial for TEM structure analysis, since clear bulk images are readily obtained. Figure 3(b) shows the HRTEM images after initial discharge and charge. There are two crystalline domains clearly observed in the tested electrode. The interplanar distances in the two regions are about 2.49 Å and 2.82 Å, which

---

**Figure 2** (a) Galvanostatic discharge–charge profiles of ZnMn$_2$O$_4$ nanowires for the first five cycles at a current rate of 100 mA·g$^{-1}$. (b) Specific capacity of ZnMn$_2$O$_4$ nanowires over 40 cycles at different current rates. (c) CVs of ZnMn$_2$O$_4$ nanowires for the first two cycles at a scan rate of 0.1 mV·s$^{-1}$

---

**Figure 3** (a) Ex situ XRD patterns of ZnMn$_2$O$_4$ nanowires after the initial discharge–charge cycle. (b) Two crystalline domains of a ZnMn$_2$O$_4$ nanowire after the initial discharge–charge process, as observed by ex situ TEM
match to that of the (211) plane of the Mn3O4 phase (JCPDS no. 18-0803), and the (100) plane of the ZnO phase (JCPDS no. 36-1451), respectively. Considering that the oxidation reaction from CoO to Co3O4 occurs near 2.4 V during the charge process in a ZnCo2O4 anode [18], the additional CV peak observed near 2.2 V shown in Fig. 2(c) seems to be related to the oxidation of MnO to Mn3O4, which is consistent with the \textit{ex situ} TEM analysis. While Xiao et al. argued that the ZnMn2O4 phase converts to ZnO and MnO phases after electrochemical reaction [21], our results suggest that the ZnMn2O4 phase is transformed to ZnO and Mn3O4. This discrepancy may be resolved by adding an additional oxidation step to the mechanism proposed by Xiao et al. during the charge process, as follows

\[ \text{ZnMn}_2\text{O}_4 + 9\text{Li}^+ + 9\text{e}^- \rightarrow \text{LiZn} + 2\text{Mn} + 4\text{Li}_2\text{O} \]  
(1st discharge)

\[ \text{LiZn} \leftrightarrow \text{Zn} + \text{Li}^+ + \text{e}^- \]  
(charge/discharge)

\[ \text{Zn} + \text{Li}_2\text{O} \leftrightarrow \text{ZnO} + 2\text{Li}^+ + \text{e}^- \]  
(charge/discharge)

\[ 2\text{Mn} + 2\text{Li}_2\text{O} \leftrightarrow 2\text{MnO} + 4\text{Li}^+ + 4\text{e}^- \]  
(charge/discharge)

\[ 2\text{MnO} + 2/3\text{Li}_2\text{O} \leftrightarrow 2/3\text{Mn}_3\text{O}_4 + 4/3\text{Li}^+ + 4/3\text{e}^- \]  
(additional charge/discharge)

We speculate that the additional electrochemical activity from MnO is possibly due to the enhanced kinetics of the nanowire electrode. More detailed studies to confirm this will be performed using \textit{in situ} analysis in the near future.

4. Conclusion

ZnMn2O4 nanowires have been fabricated and electrochemically characterized as an anode material for Li rechargeable batteries. A ZnMn2O4 nanowire electrode can store and release Li⁺ ions reversibly with a high specific capacity of ca. 650 mAh·g⁻¹ at a current rate of 100 mA·g⁻¹ and high power capability, with specific capacities of 450 and 350 mAh·g⁻¹ at current rates of 500 and 1000 mA·g⁻¹, respectively. From \textit{ex situ} TEM analysis of the nanowire electrode, we found that the ZnMn2O4 phase is converted to ZnO and Mn3O4 after the discharge–charge cycle. These ZnMn2O4 nanowires are expected to be a useful high performance anode material for future Li rechargeable battery applications.

Acknowledgements

This research was supported by the Energy Resource Technology Development program (No. 2008-E-EL11-P-08-3-010) and the Energy Resources Technology R&D program (No. 20092020100040) under the Ministry of Knowledge Economy. This research was also supported by the Nuclear R&D program (No. 2010-0018524), Engineering Research Center program (No. 2008-0062206) through the National Research Foundation (NRF) and Korea Science and Engineering Foundation (KOSEF) grant (No. R01-2008-000-20480-0) funded by the Ministry of Education, Science, and Technology (MEST). This research was also supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2009-0094219). The \textit{ex situ} TEM analysis was supported by “The Support Program for the Advancement of National Research Facilities and Equipment”, funded by the Korean government (MEST). P. M. was financially supported by the Priority Research Centers Program through the NRF funded by MEST (No. 2009-0094041). H. W. L. was supported by the NRF of Korea Grant funded by MEST (No. 2010-0029031).

References


