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A ZnO-MnO composite was synthesized using a simple solvothermal method combined with a high-temperature treatment. To observe the phase change during the heating process, in situ high-temperature XRD analysis was performed under vacuum conditions. The results indicated that $ZnMn_2O_4$ transformed to the ZnO-MnO composite phase starting from 500 °C and that this composite structure was retained until 700 °C. The electrochemical performances of the ZnO-MnO composite electrode were evaluated through galvanostatic discharge-charge tests and cyclic voltammetry analysis. Its initial coulombic efficiency was significantly improved to 68.3% compared to that of $ZnMn_2O_4$ at 54.7%. Furthermore, the ZnO-MnO composite exhibited improved cycling performance and enhanced rate capability compared with untreated $ZnMn_2O_4$. To clarify the discharge-charge mechanism of the ZnO-MnO composite electrode, the structural changes during the charge and discharge processes were also investigated using ex situ XRD and TEM.

Introduction

Transition metal oxides (TMOs) (M=Co, Ni, Cu, Fe, Mn, etc.) have been receiving considerable attention because of their higher reversible capacities compared to those of conventional carbonaceous materials.¹⁻⁵ The chemical and electrochemical Li-reduction of TMOs was thoroughly studied in the 1980s,⁶⁻⁸ and it was recently demonstrated that bulk particles of transition metal salts TMX (TM=Co, Ni, Cu, Fe, Mn, etc.; X=O, S, N, P, F, etc.) electrochemically react with lithium to form composite particles composed of amorphous or poorly crystallized Li-X acting as a matrix for nanometric metallic TM⁰ particles.^{1,9-12} Poizot et al¹ reported that lithium can be stored reversibly in TMOs through the following heterogeneous conversion reaction:

$Li + TMO \leftrightarrow Li_2O + TM$

Recent works have reported a capacity of 900 mAh g⁻¹ after 25 cycles¹ and of 700 mAh g⁻¹ after 100 cycles¹³ with Co_3O_4 . However, because of its toxicity and high cost, many efforts are devoted to replacing Co_3O_4 , partially by eco-friendly and less expensive alternative metals.¹⁴

Various types of TMOs have been reported to have high capacities and relatively stable capacity retention during cycling. Despite all the efforts, however, one of the crucial drawbacks of TMOs for use as an alternative anode material for lithium ion batteries is their low initial coulombic efficiency. According to previous reports,^{1,15} there are two possible mechanisms for the low initial coulombic efficiency in TMOs. Poizot et al¹ reported that a solid electrolyte interphase (SEI) film was formed on the oxide anode material by electrolyte decomposition during the first discharge process and that this film was retained during the first charge process. Thus, the initial coulombic efficiency of the oxide anode material decreased. The formation of the SEI film on the electrode surface appeared to be one of the possible reasons for the low initial coulombic efficiency of TMOs. On the other hand, because TMOs are discharged or charged by the formation or decomposition of Li_2O , which is well known to be an electrochemically irreversible material, the incomplete decomposition of Li₂O during the first charge process also causes deterioration of the initial coulombic efficiency in TMOs.

 $ZnMn_2O_4$ has been synthesized using various methods.¹⁶⁻²⁰ However, $ZnMn_2O_4$ has a critical weak point in terms of initial coulombic efficiency. Its initial coulombic efficiency (first charge/first discharge = %) is one of the lowest among all types of anode materials. To use $ZnMn_2O_4$ as a substitute for graphite as an anode material, its initial coulombic efficiency should be improved; in other words, its initial irreversible capacity loss should be reduced.

In this work, a ZnO-MnO composite was synthesized starting from $ZnMn_2O_4$ using a simple solvothermal method combined with a heat treatment under a reducing atmosphere, and its formation processes were monitored using in situ high-temperature X-ray diffraction and TGA. The electrochemical properties of the ZnO-MnO composite materials were evaluated. Furthermore, its structural changes

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during the first charge and discharge processes were also investigated using ex situ XRD and TEM.

Experimental

Synthetic procedures

The ZnO-MnO composite was synthesized using a simple solvothermal method combined with a high-temperature treatment under a reducing atmosphere. First, $ZnMn_2O_4$ was prepared using a solvothermal process, as we described previously.²¹ All of the reactants and solvents were of analytical grade and were used without any further purification. For ZnMn₂O₄, the preparation of cetyltrimethylammonium bromide (C19H42BrN), citric acid $(C_6H_8O_7)$ and zinc nitrate $(Zn(NO_3)_2 \cdot 6H_2O)$ were dissolved in 170 mL of anhydrous ethanol and vigorously stirred for 3 h. Then, 30 mL of a 1 mmol manganese nitrate $(Mn(NO_3)_2 \cdot xH_2O)$ solution was added dropwise to the stirred solution. After stirring for an additional 3 h, the resulting solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 200 mL, which was then heated to 160 °C and maintained at this temperature for 24 h. The calculated atomic molar ratio of zinc and manganese in the reaction system was maintained at 1:2. After the autoclave cooled to room temperature, the dark brown precipitates were filtered, washed several times with anhydrous ethanol, and dried overnight at 100 °C. Finally, the ZnO-MnO composite was obtained by heat treating the ZnMn₂O₄ at 700 °C for 6 h under an Ar + H₂ atmosphere.

Characterization

The crystal structures of ZnMn₂O₄ and of the ZnO-MnO composite were characterized by powder X-ray diffraction (XRD; Rigaku, D/MAX-2500V/PC). The XRD data were collected in the 2 θ range from 10° to 80° at a scan rate of 4° min⁻¹. In situ high-temperature XRD measurements were performed using a D/MAX-2500V/PC diffractometer with a SHT-1500 high-temperature chamber under vacuum conditions. The temperature of the sample was increased at a rate of 5 °C min ¹ to a certain temperature, and then an XRD pattern was recorded. Then, the process was repeated at the elevated temperature with a step of 100 degrees. The morphologies of these materials were observed using a scanning electron microscope (SEM; FEI, NOVA nanoSEM200) and a transmission electron microscope (TEM; FEI, Technai G2) equipped with an energy-dispersive spectrometer (EDS). Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT from room temperature to 1000 °C under an Ar + H₂ atmosphere at a heating rate of 5 °C min⁻¹. The specific surface area and porosity were measured by N₂ adsorption-desorption isotherms at 77 K using a BELSORP mini II system.

Electrode fabrication and electrochemical measurements

ZnMn₂O₄ and ZnO-MnO composite electrodes were prepared using acetylene black as the active material and polyvinylidene fluoride (PVdF) as the binder in a weight ratio of 80:12:8. The slurry was coated on copper foil and dried under vacuum overnight at 80 °C. The mass of active material loaded on each disk (16 mm in diameter, punched from the Cu foils) was approximately 2.2 mg cm⁻². The electrochemical properties of the $ZnMn_2O_4$ and ZnO-MnO electrodes were evaluated in a 2032 coin-type cell, in which the lithium electrode was used as both the counter and reference electrodes. The electrolyte used was 1 M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 by volume). Cyclic voltammetry (CV) measurements were performed over the range of 0.01 - 3.0 V at a scan rate of 0.1 mV s⁻¹ using a VSP (France). Discharge-charge measurements were performed over the range of 0.01 - 3.0 V at a current rate from 0.1 to 10 C using a Maccor series 4000 (USA).

Results and discussion

The XRD patterns of the as-prepared ZnMn₂O₄ and its reduced form of ZnO-MnO composite at 700 °C for 6 h in an Ar + H₂ atmosphere are shown in Figure 1. All the diffraction peaks can be indexed to those from ZnMn₂O₄ (JCPDS No. 24-1133), ZnO (JCPDS No. 36-1451), and MnO (JCPDS No. 78-0424). No other crystalline phases were observed. Surprisingly, ZnMn₂O₄ was transformed to ZnO and MnO, as indexed in Figure 1(b) after heat treatment in an Ar + H₂ atmosphere.



Fig. 1 XRD patterns of (a) $ZnMn_2O_4$ and (b) ZnO-MnO composite.

To monitor the phase changes during the thermal process under the reducing atmosphere, in situ high-temperature XRD was performed under vacuum conditions. The changes in the XRD patterns for $ZnMn_2O_4$ powder depending on the temperature, from room temperature to 1000 °C, are shown in Figure 2. Its spinel crystal structure at room temperature was maintained up to 400 °C. Additional peaks appeared at 500 °C, which were identified as MnO peaks. Other additional peaks appeared at 600 °C, which were characteristic peaks of ZnO. At

700 °C, the original spinel peaks were completely removed, and all the crystal phases were transformed to ZnO and MnO. Additionally, when the temperature was increased from 700 °C to 1000 °C, the ZnO peaks gradually disappeared, and finally, only peaks corresponding to MnO remained. This result appeared to be caused by the evaporation of ZnO.



Fig. 2 In situ XRD patterns of $ZnMn_2O_4$ depending on the temperature from 28 °C to 1000 °C under a vacuum condition.

To understand the phase transition during the heat treatment under a reducing atmosphere, thermogravimetric analysis (TGA) was performed, as shown in Figure 3. The slight weight loss below 350 °C is attributed to the evaporation of water absorbed on the surface of $ZnMn_2O_4$ powder. The weight loss between 350 and 500 °C corresponds to the loss of oxygen due to the reduction of Mn^{3+} to Mn^{2+} (weight loss: calculated, 1.302 mg, experimental, 1.481 mg).



Fig. 3 TGA curves of $ZnMn_2O_4$ heated between 28 °C and 1000 °C under a flow of Ar + $H_2.$

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Above 700 °C, a large mass loss is observed due to the evaporation of ZnO (weight loss: calculated, 6.627 mg, experimental, 6.107 mg). Consistent with the in situ high-temperature XRD analysis, the corresponding phase transformation from ZnMn₂O₄ to ZnO-MnO begins near 500 °C and finishes at 700 °C, at which point ZnMn₂O₄ has been reduced to the ZnO-MnO composite phase. The possible phase transformation mechanism of the ZnMn₂O₄ could be expressed as the following reaction:

$$ZnMn_2O_4 \rightarrow ZnO + 2MnO + 1/2O_2$$
(1)



Fig. 4 N_2 adsorption-desorption isotherms and pore size distributions (insets) of (a) $ZnMn_2O_4$ and (b) ZnO-MnO composite.

To monitor the changes in the physical structure following the phase transformation, the specific surface areas and porosities of $ZnMn_2O_4$ and ZnO-MnO composite were measured using the Brunauer-Emmett-Teller (BET) gas-sorption method, and the N_2 adsorption-desorption isotherms at 77 K are presented in Figure 4, with the insets showing their corresponding Barrett-Joyner-Halenda (BJH) pore-size distributions. The $ZnMn_2O_4$ and ZnO-MnO exhibit similar isotherms, which can be classified as type IV with a type H1 hysteresis loop, indicating that these pore structures are mesoporous.²² According to the corresponding BJH plots (the inset) recorded from the nitrogen isotherms, the average pore sizes of $ZnMn_2O_4$ and ZnO-MnO are 16.3 nm and 46.3 nm, respectively. The BET specific surface areas and total pore

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volumes are 15.13 m² g⁻¹ and 0.06 cm³ g⁻¹ for ZnMn₂O₄ and 2.55 m² g⁻¹ and 0.03 cm³ g⁻¹ for ZnO-MnO, respectively. The asprepared ZnO-MnO composite exhibits a smaller surface area and higher density compared with ZnMn₂O₄.





The concomitant morphology changes were also investigated using SEM and TEM. As shown in Figure 5, the surface of ZnMn₂O₄ particles (a, b) appeared to be rougher than the surface of the ZnO-MnO particles, although it is not very clear. In contrast, the low-magnification TEM image of the ZnO-MnO composite in Figure 6 (a) shows that the sizes of the individual ZnO-MnO composite particles ranged from 20 to 30 nm, whereas the sizes of the $ZnMn_2O_4$ particles (Figure 6 (c)) are considerably smaller than those of the ZnO-MnO composite. The differences in particle size between the ZnO-MnO composite and ZnMn₂O₄ are in good agreement with the BET results. The HR-TEM image shown in Figure 6 (b) indicates that the measured interplanar distance values are 0.247 and 0.222 nm, corresponding to the (101) plane of ZnO and the (200) plane of MnO, respectively. The TEM studies clearly show the simultaneous presence of ZnO and MnO crystal lattices in the composite particles.



Fig. 6 TEM image of the (a) ZnO-MnO composite and SAED patterns in the inset, (b) its high-resolution lattice image, and TEM image of (c) $ZnMn_2O_4$ and SAED patterns in the inset.

The electrochemical performances of the $ZnMn_2O_4$ and ZnO-MnO composite electrodes were evaluated in a half-cell configuration using lithium metal as both reference and counter electrodes. The theoretical capacity of the ZnO-MnO composite material was calculated from the composition of ZnO : MnO = 1 : 2 as shown below:

ZnO-MnO composite:

 $(33.3\% \text{ x } 978 \text{ mAh } \text{g}^{-1}) + (66.7\% \text{ x } 755 \text{ mAh } \text{g}^{-1}) = 828 \text{ mAh } \text{g}^{-1}$

where the theoretical capacities of ZnO and MnO are 978 and 755 mAh g^{-1} , respectively.



Fig. 7 Cycle performances of the $ZnMn_2O_4$ and ZnO-MnO composite electrodes at a current rate of 0.1 C.

Figure 7 shows the discharge-charge cycling performances of the ZnMn₂O₄ and ZnO-MnO composite electrodes at a current rate of 0.1 C for 50 cycles. The reversible capacity of the ZnMn₂O₄ electrode rapidly faded as the number of cycles increased, finally delivering a capacity of 345 mAh g⁻¹ after the 50th cycle, which is 49.3% of the initial reversible capacity. In contrast, the ZnO-MnO composite electrode exhibited fascinating cycling stability. At the end of the 50th cycle, the reversible capacity is 625 mAh g⁻¹, which is 89.8% of the initial reversible capacity. The ZnO-MnO composite electrode exhibited a remarkably improved cycle retention compared to the ZnMn₂O₄ electrode.



Fig. 8 Voltage profiles of the (a) $ZnMn_2O_4$ and (b) ZnO-MnO composite electrodes at a current rate of 0.1 C.

Figure 8 shows the first and second discharge-charge voltage profiles of the $ZnMn_2O_4$ and ZnO-MnO composite electrodes in the voltage range of 0.01 - 3.0 V at a current rate of 0.1 C. The general features of the discharge-charge profiles are consistent with other transition metal oxide anodes that

undergo conversion reactions.^{23,24} The initial discharge and charge capacities of the $ZnMn_2O_4$ electrode were 1275 and 699 mAh g⁻¹, respectively, corresponding to an initial coulombic efficiency of 54.7%. The initial capacities of the ZnO-MnO composite electrode were 1019 and 696 mAh g^{-1} , corresponding to an initial coulombic efficiency of 68.3%. The large irreversible capacity loss of the first cycle appeared to be attributed to the phenomenon of the formation of a solid electrolyte interphase (SEI) film and reduction of metal oxide to metal with Li₂O formation, which is commonly observed for various electrode materials.^{1,25-27} The first discharge capacity of the ZnO-MnO composite electrode was 1019 mAh g⁻¹, which is considerably larger than the calculated theoretical value of 828 mAh g⁻¹ expected according to the reduction of ZnO and MnO to Zn and Mn metal nanoparticles and Zn metal to LiZn alloy. The extra capacity of 191 mAh g⁻¹ observed in the experiment should be attributed to the formation of the solidelectrolyte interphase (SEI) due to the reaction of Li with the solvents.²⁸ It is also notable that the initial charge capacity of the ZnO-MnO composite electrode is 696 mAh g⁻¹, which is similar to that of the $ZnMn_2O_4$ electrode, 699 mAh g⁻¹. According to previous reports,^{17,18} the ZnMn₂O₄ was formed with a 4 mol Li₂O phase, which is reacted with 9 mol of lithium ions in the first discharge process. Meanwhile, the ZnO-MnO composite is expected to form 3 mol of Li₂O, which could react with 7 mol of lithium ions (vide infra). Its high coulombic efficiency may originate, at least partially, from the less formation of electrochemically inactive Li₂O phase.



Fig. 9 Cyclic voltammograms of the ZnO-MnO composite electrode at a scan rate of 0.1 mV $\mbox{s}^{-1}.$

Figure 9 shows the cyclic voltammetry (CV) curves of the ZnO-MnO composite electrode at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.01 - 3.0 V. The CV for the first cycle is different from those of the subsequent cycles. In the first cycle, an irreversible reduction peak was observed at ~0.15 V, which corresponds to the reduction of Zn²⁺ and Mn²⁺ to metallic Zn and Mn.^{29,30} The minor peak at ~0.75 V can be attributed to the reversible formation of an SEI film with the composition of the solvent in the electrolyte. This phenomenon has been reported in many previous studies, and it commonly exists in metal oxide anode material systems.³¹⁻³³ A somewhat broad oxidation peak occurred at 1.3 V vs. Li⁺/Li, ARTICLE

which is the potential required for $Zn^{2+} \rightarrow ZnO$ and $Mn^{2+} \rightarrow MnO$. In our previous work, two oxidation peaks appeared at $ZnMn_2O_4$.²¹ It might be caused by the configuration of Zn ions and Mn ions in electrode materials showing a broad peak. From the second cycle, the repeated reduction/oxidation of ZnO and MnO leads to redox peaks at ~1.3 V and ~0.45 V, respectively. In addition, the peak of the 10^{th} cycle is very close to the second one, which exhibits good reproducibility and similar shapes, revealing the good reversibility of the ZnO-MnO composite electrode. This presumably indicates that the formation of the SEI layer is almost completed on the ZnO-MnO composite, unlike the case of ZnMn₂O₄.



Fig. 10 Rate capabilities of the $\text{Zn}\text{Mn}_2\text{O}_4$ and ZnO-MnO composite electrodes at various current rates.

Because the rate performance is an important parameter for many applications of batteries, such as electric vehicles and portable power tools, which require fast discharge and/or charge rates, the capacity trend with cycle life for the ZnO-MnO composite electrode was also evaluated at various current rates (0.1 C ~ 10 C), as shown in Figure 10. The ZnO-MnO composite electrode exhibited good rate capability with average charge capacities of 736, 662, 574, 468, and 347 mAh g⁻¹ at current rates of 0.1, 0.2, 1, 5, and 10 C, respectively. Furthermore, the ZnO-MnO composite electrode still delivered a high reversible capacity of 694 mAh g⁻¹ when the current rate was reverted to 0.2 C.



Fig. 11 Ex situ XRD patterns of the ZnO-MnO composite electrodes after the 1st discharge-charge cycle.

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To clarify the discharge-charge mechanism of ZnO-MnO composite electrode, a structural investigation was performed using ex situ XRD and TEM. Figure 11 shows ex situ XRD patterns of the electrodes after the first discharge and charge, along with that of the pristine ZnO-MnO composite for comparison. The crystalline ZnO-MnO composite phase is completely decomposed after the first discharge, providing an amorphous phase, and it is not recovered after the charge. It is difficult to determine exact structural changes during charge and discharge processes; thus, an ex situ TEM analysis was performed. Figure 12 shows the HR-TEM images of the ZnO-MnO composite electrode and its SAED patterns. The ZnO-MnO composite phase is transformed to phases of Mn, LiZn, and Li₂O after the first discharge process due to the conversion reaction. The presence of weak and large rings in the SAED pattern (inset of Figure 12 (b)) for the fully discharged sample is evidence for the loss of sample crystallinity, which is consistent with the XRD data. This reaction mechanism is similar to the electrochemical process reported for ZnMn₂O₄ after the first cycle.²¹ Figure 12 (c) presents the image and SAED patterns of the ZnO-MnO composite after the first charge process followed by the 1st discharge, and the ZnO and MnO phase can be indexed, which is impossible to determine from the ex situ XRD analysis.



Fig. 12 HR-TEM images of ZnO-MnO composite and its SAED patterns depending on its electrochemical state: (a) pristine electrode, (b) after the 1st discharge process and (c) after the 1st cycle (discharge and charge).

Overall, we have enhanced the electrochemical performances of ZnMn₂O₄ not only through a carbonaceous coating but also by the phase transformation into a ZnO-MnO composite. Based on references and our results, the electrochemical reactions in the ZnO-MnO composite electrode could be described as follows:

$$\begin{aligned} \text{ZnO} + 2\text{MnO} + 7\text{Li}^{+} + 7\text{e}^{-} & \rightarrow 3\text{Li}_2\text{O} + \text{LiZn} + 2\text{Mn} \\ \text{LiZn} & \leftrightarrow \text{Zn} + \text{Li}^{+} + \text{e}^{-} \\ \text{Zn} + \text{Li}_2\text{O} & \leftrightarrow \text{ZnO} + 2\text{Li}^{+} + 2\text{e}^{-} \\ 2\text{Mn} + 2\text{Li}_2\text{O} & \leftrightarrow 2\text{MnO} + 4\text{Li}^{+} + 4\text{e}^{-} \end{aligned}$$

Conclusions

A ZnO-MnO composite was obtained incidentally from the carbon coating procedure of ZnMn₂O₄, and its electrochemical performances were evaluated. Under an atmosphere of Ar + H₂, the decomposition starts at 350 °C and finishes at 700 °C, forming ZnO + MnO. Above 700 °C, ZnO is evaporated. Its structural changes are in good agreement with the hightemperature XRD analysis under vacuum conditions. The initial

discharge and charge capacities of the ZnO-MnO composite electrode were 1019 and 696 mAh g⁻¹, respectively, corresponding to an initial coulombic efficiency of 68.3% compared to 54.7% for ZnMn₂O₄. It shows decent cycling performances (after 50 cycles, 90% of the initial capacity is maintained), which is remarkably higher than 49% for ZnMn₂O₄. During the charge and discharge processes, the crystal structure of the ZnO-MnO composite was transformed to Mn, LiZn, and Li₂O after the first discharge process. Its original structure was partially restored after the first cycle (discharge-charge process) followed by the first discharge, and the ZnO and MnO phases can be indexed.

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