O U R N A L O F

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Electrochemical behavior of prelithiated ZnMn₂O₄ anode for Lithium ion batteries

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A partial prelithiation process has been employed in order to compensate the irreversible capacity loss of the $ZnMn_2O_4$ anode material during the first cycle. The partial prelithiation is carried out by depositing a lithium metal film onto a $ZnMn_2O_4$ electrode, and then allowing the film to react with the $ZnMn_2O_4$ when electrolyte is added to the cell. The first cycle irreversibility was simply compensated by a controlled partial prelithiation. The structural change during the prelithiation process is confirmed by an ex situ XRD analysis of the pristine and lithium metal deposited electrodes after being impregnated with electrolyte. The irreversible capacity loss is studied as a function of the degree of prelithiation.

Key words: Zinc-manganate, Prelithiation process, Lithium metal film deposition, Anode material, Lithium-ion battery.

Introduction

Rechargeable lithium-ion batteries are the most promising power sources for portable electronic devices and automotive applications due to their high energy density, but there is still a growing interest in developing low-cost alternative electrode materials with a high-energy density. Accordingly, extensive studies have been conducted on alternatives to carbon as anode materials in lithium-ion batteries, because the theoretical capacity of commercial graphite is limited to 372 mAh g^{-1} .

Recently, spinel binary oxides such as $ZnCo_2O_4$ [1], ZnFe₂O₄, [2-5] and ZnMn₂O₄ [6-8] have been proposed as promising anode materials, due to their high lithium storage capacity and stable capacity retention during charge-discharge cycling. Among these, ZnMn₂O₄, consisting of cheap and non-toxic Zn and Mn ions, is particularly interesting [6-8].

However, it appears that the major drawback of $ZnMn_2O_4$ as an anode material is large irreversible capacity loss during the first discharge cycle. This loss is due to the solid electrolyte interphase (SEI) formation, and the irreversible reduction of $ZnMn_2O_4$, with the concomitant crystal structure destruction, to form metallic nanograins (Zn and Mn) which are dispersed into the amorphous Li₂O matrix [7]. On the other hand, the irreversible capacity loss of the $ZnMn_2O_4$ anode material during the first cycle can be compensated by a partial prelithiation. A prelithiated $ZnMn_2O_4$ electrode can be fabricated by depositing a lithium metal film onto a $ZnMn_2O_4$ electrode, which then reacts when electrolyte is added to the cell, producing an SEI layer and causing an irreversible reaction. In this work, the preparation of a

prelithiated $ZnMn_2O_4$ anode and its electrochemical performance were studied.

Experimental

ZnMn₂O₄ was prepared by ball-milling a mixture of ZnO (99.9%, Aldrich) and Mn₂O₃ (99.9%, Aldrich) powders, followed by annealing at 600 °C for 2 hrs in air. The preparation of ZnMn₂O₄ was carried out according to the procedure described in the previous study [9]. Structural properties were studied by X-ray diffraction (XRD) using Cu K α radiation. The particle size and morphology were analyzed by scanning electron microscopy (SEM).

The electrodes were prepared by pasting a slurry, containing 70 wt.% $ZnMn_2O_4$ active material, 20 wt.% carbon black, and 10 wt.% polyvinyldene fluoride (PVDF) as a binder, dissolved in N-methyl-2-pyrrolidone (NMP) onto a copper foil. The electrodes were then dried at 120 °C overnight in a vacuum, and then pressed to a thickness of 10 μ m. The lithium metal films were deposited onto the $ZnMn_2O_4$ composite electrodes under a vacuum from a thermal evaporation source. The film thickness was controlled by the evaporation time, and was checked during the deposition by a quartz-crystal thickness monitor.

Coin-type half cells were assembled, both with and without lithium metal film deposition on the $ZnMn_2O_4$ composite electrodes. A solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume, provided by PANAX ETEC Co., Ltd, Korea) was used as an electrolyte to evaluate the electrochemical performance of the coated and uncoated electrodes. The cells were charged (lithiation) and discharged (delithiation) in galvanostatic mode at a constant current of 100 mA \cdot mg⁻¹ in the voltage range 0.01 - 3.0 V.

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Results and Discussion

Fig. 1 shows the XRD patterns of the as-milled powders and the annealed sample after being milled for 40 min. The XRD pattern for the ball-milled powder (Fig. 1(a)) displays characteristic peaks corresponding to a tetragonal ZnMn₂O₄ structure, although it is extremely broad owing to the fine particle sizes, lattice strains, and crystal defects. Annealing at 600 °C for 2 hrs in air leads to a well-crystallized ZnMn₂O₄ phase (Fig. 1(b)). The well-crystallized ZnMn₂O₄ powders were used in the electrodes for the evaluation of electrochemical performance. The SEM micrograph of the annealed sample shows the agglomerate structure of primary particles with submicron size. (Not shown here). These are consistent with previous findings [9].

Two types of $ZnMn_2O_4$ composite electrodes, one pristine and one modified with lithium metal deposited on its surface, were fabricated.

The lithium metal film was deposited at three different thicknesses, of around 0.5, 0.75, and 1.0 µm. In order to confirm the structural change during the prelithiation process, an ex situ XRD analysis of the pristine and lithium metal film deposited electrodes was performed after impregnation with electrolyte for 12 hrs, as illustrated in Fig. 2. The crystalline ZnMn₂O₄ phase is destroyed with increasing the thickness of lithium metal film, especially when a 1.0 µm thick film is deposited, as no obvious diffraction peaks can be detected. Notably, the reflection peak at around $2\theta =$ 43 ° appears which are nearly overlapping with that of the Cu substrate. To confirm what it is, the XRD pattern of the 1.0 µm thick lithium film deposited electrode when removed from the Cu substrate is compared with that of a pristine electrode in the inset of Fig. 2. A broad peak at around $2\theta = 43^{\circ}$ is detected in the prelithiated electrode, while it is absent in the pristine one. At this point, it is worth noting that the phase transition mechanism of ZnMn₂O₄ during the initial charge process, proposed by Xiao et al [7].



50

40

60

30

20

ntensity(a.u)

ZnMn,O

 $[1^{s} charge] ZnMn_{2}O_{4} + 9Li^{+} + 9e^{-} \rightarrow LiZn + 2Mn + 4Li_{2}O(1)$

 $[charge/discharge] Zn + Li^{+} + e^{-} \leftrightarrow LiZn$ (2)

[charge/discharge] $2Mn + 2Li_2O \leftrightarrow 2MnO + 4Li^+ + 4e^-(3)$

[charge/discharge] $Zn + Li_2O \leftrightarrow ZnO + 2Li^+ + 2e^-$ (4)

In addition to this, it has recently suggested that the following oxidation step can be occurring [8].

$$2MnO + 2/3 Li_2O \leftrightarrow 2/3 Mn_3O_4 + 4/3Li + 4/3 e^{-1}$$
 (5)

 $ZnMn_2O_4$ is reduced during the first discharge to form a nanocomposite of Zn, Mn and Li₂O according to Eq. (1). After the first cycle, reversible electrode reactions take place according to Eqs. (2-4). Therefore, the broad peak shown in the inset of Fig. 2 is attributed to nanocrysyalline Mn and Zn phases formed by a reduction reaction (Eq. (1)) during the partial lithiation process.

The charge-discharge curves for the pristine and lithium modified electrodes over the first two cycles are given in Fig. 3. Fig. 3(a) presents the 1^{st} and 2^{nd} charge-discharge curves of pristine $ZnMn_2O_4$ electrode cycled between 0.01 and 3 V at a constant current density of 100 mA g⁻¹. The first charge / discharge capacities and the initial coulombic efficiency for the pristine electrode are 1,093 / 704 mAh g⁻¹ and 64%, respectively.

Fig. 3(b-d) shows the charge-discharge curves of the lithium metal deposited electrodes for the initial two cycles. It can be seen that the initial voltage of lithium metal film deposited electrodes is lower than that of the pristine electrode, and decreases as the deposited lithium metal thickness increases. This indicates that a prelithiation reaction has occurred in the modified electrodes. As a result of this prelithiation, the initial charge capacity decreases. In addition, the voltage profile, ranging from 1.25 to 0.5 V during charge, mainly due to the formation of the SEI layers [7], disappears. Fig. 4 shows the initial coulombic efficiency of the pristine and



Fig. 2. XRD analysis of the pristine and the lithium metal film deposited $ZnMn_2O_4$ electrodes; (a) pristine, (b) 0.5 μ m, (c) 0.75 μ m and (d) 1 μ m.



Fig. 3. Charge-discharge profiles for the first two cycles of pristine and lithium metal film deposited $ZnMn_2O_4$ electrodes: (a) pristine, (b) 0.5 μ m, (c) 0.75 μ m and (d) 1 μ m.



Fig. 4. The initial coulombic efficiency of the pristine and lithium metal film deposited electrodes.

Li deposited electrodes. The initial coulombic efficiency was significantly improved by the prelithiation process, and reached around 99 % for the electrode with the 1.0 µm thick lithium film. In order to reveal the features of irreversible reactions more clearly, differential capacity curves (dQ/dV versus potential) for the first and second charges and discharges of each cell are plotted in Fig. 5. Two peaks, located near 1.25 and 0.75 V, are observed in the first charge curve of the pristine electrode. However, these peaks are less apparent for the lithium metal film-deposited electrodes, and are absent in the electrode with a 1.0 µm thick lithium film. Nevertheless, the initial discharge capacity and voltage profiles for the subsequent cycles were similar for the pristine and modified electrodes. Based on the dQ/dV plot, initial charge capacity can be divided into 3 distinct voltage regions as illustrated in Figs. 3(a) and 5(a). The capacity of the pristine and the lithium metal film deposited electrodes in each voltage region during the 1st charge reaction is given in Fig. 6. The capacity in voltage range of Region I and Region II decreases with increasing the amount of pre-deposited



Fig. 5. The differential capacity vs voltage (dQ/dV) curves for the first two cycles of pristine and lithium deposited $ZnMn_2O_4$ electrodes; (a) pristine, (b) 0.5 µm, (c) 0.75 µm and (d) 1 µm.



Fig. 6. The charged capacity of the pristine and the lithium metal film deposited $ZnMn_2O_4$ electrodes in each voltage range during the 1st charge reaction. The voltage ranges as illustrated in Fig. 3(a) and 5(a) were used.



Fig. 7. Cycle performances of the pristine and the lithium metal film deposited $ZnMn_2O_4$ electrodes; (a) pristine, (b) 0.5 μ m, (c) 0.75 μ m and (d) 1 μ m.

lithium metal, while the capacity in Region III appears to be nearly the same for all the electrodes. Considering the coulombic efficiency of 1 μ m thick Li deposited electrode, most of the irreversible reaction of the pristine electrode appears to occur in regions I and II. The irreversible capacity in Region I of the pristine $ZnMn_2O_4$ electrode is attributed to the formation of the SEI layers. The extra irreversible capacity in Region II should be ascribed to irreversible reactions related to the formation of the nanocomposite of Zn, Mn and Li₂O, probably based on Eqs. (1-4). Presumably, when first charged to the potential corresponding to the lower voltage limit of the region II, the phase transitions according to Eqs. (1-4) proceeds during which most irreversible capacity loss related reactions occur. The cycle performances of cells with pristine and prelithiated electrodes are very similar to each other, and their capacity retention appears to be stable as shown in Fig. 7.

Conclusions

A partial prelithiation method was applied in order to compensate the irreversible capacity loss of the $ZnMn_2O_4$ anode material during the first cycle. The partial prelithiation was performed by depositing a lithium metal film onto a $ZnMn_2O_4$ electrode, and allowing the modified electrodes to be impregnated with electrolyte in a cell. The first cycle irreversibility was simply compensated by a controlled partial prelithiation. The resulting prelithiated electrode exhibits a good cycle performance, similar to a pristine electrode.

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