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Electrochemical properties of $Li_2Mn_{1-x}V_xO_3$ ($0 \le x \le 0.018$) as cathode materials for secondary lithium batteries

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 $Li_2Mn_{1-x}V_xO_3$ ($0 \le x \le 0.018$) samples were synthesized at low temperature by solid-state reaction using precipitated products of Mn and V. $Li_2Mn_{1-x}V_xO_3$ samples had a single phase of monoclinic layered structure with a space group of C2/m, and the solubility limit of V was 1.8%. Compared to Li_2MnO_3 sample, V-doped samples exhibited improved electrochemical properties. The initial charge and discharge capacities of $Li_{1.682}Mn_{0.982}V_{0.018}O_3$ sample were 353 and 248 mAh/g, respectively.

Key words: Lithium-ion batteries, Cathode material, Li2MnO3, Crystal structure, Electrochemical properties.

Introduction

Recently, secondary lithium batteries are widely used in consumer electronics as well as in hybrid electric vehicles (HEV). O₃-type layered oxides with various compositions have been investigated for the cathode materials of lithium-ion batteries [1]. Various electrochemical behaviors depend on the composition of metal ions in LiMO₂-type cathodes. In spite of the high intercalation reversibility of LiMO₂-type cathodes in the adequate potential range, theoretical capacities are limited. In an attempt to develop an enhanced energy density of cell, layered compounds with a higher lithium content have been pursued with much attention [2-4]. Although the theoretical capacity of Li_2MnO_3 is 478 mAh/g, an inferior intercalation reaction was observed because the further oxidation of Mn4+ is not easy and Li[Li_{1/3}Mn_{2/3}]O₂ has a low electrical conductivity due to the mixing of lithium ions in MnO₆ octahedra layers [5-9]. According to the recent research, Li₂MnO₃ synthesized at low temperature and composite phases result from the substitution of metal ions give improved electrochemical behaviors [10-13]. It is known that the properties of Li₂MnO₃-type materials depend on the synthesis conditions of precursors, heating condition, and doping of transition metal ions [14]. In this regard, the substitution of pentavalent metal ions in Li₂MnO₃ is challenging as the possible formation of $Mn^{3+/4+}$ couples in the compound. In this study, the doping of V using new precursors was systematically investigated because the V substitution was not possible by solidstate reaction.

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Experimental

For the synthesis of Mn precursor, 0.5 M $Mn(SO_4)$. 5H₂O aqueous solution and 1 M NaOH aqueous solutions were prepared. After adding 1 M NaOH solution into the NH₄OH solution to fix the pH value of 11, 0.5 M $Mn(SO_4) \cdot 5H_2O$ solution was added slowly using a burette under constant stirring. A constant pH of 11 was kept for the precipitation reaction by adding NaOH solution. In the case of V precursor, 3 g of V₂O₅ was dissolved in 0.25 M of 100 ml aqueous solution of $LiOH \cdot H_2O$. 0.5 M of 100 ml aqueous solution of LiOH \cdot H₂O and KBH₄ with a ratio of 1:2 was prepared for the reduction reaction. 0.5 M of KBH₄ solution was slowly added in the vanadium solution at a constant pH of 4. Obtained products were washed with deionized water followed by drying at 80 °C for 24 hrs. For the synthesis of $Li_2Mn_{1-x}V_xO_3$ ($0 \le x \le 0.2$), adequate amounts of Li2CO3 and prepared precursors were mixed in a mortar for 30 min. Heat treatment was carried out in an oxygen atmosphere. Pellet forms of mixed powders were heated at 500 °C for 12 hrs and then heated at 550 °C for 16 hrs. The flow rate of oxygen and heating rate were 200 ml/min and 5 °C/ min, respectively. Synthesized powders were washed with deionized water to remove impurities on the powder surface. The products were heated again at 300 °C for 5 hrs to remove any water in the sample.

X-ray powder diffraction (PANalytical, Model: X'pert pro MPD) was used to characterize the crystal structures of synthesized powders and electrodes. The morphologies of the powder samples were observed by scanning electron microscopy (SEM, S-4200, Hitachi, Japan). Quantitative composition and specific surface area were evaluated by ICP (Inductively Coupled Plasma, Model: Optima7300DV, Perkin Elmer) and BET (Model: Autosorb1-c, Quntachrome), respectively. The electrochemical properties were evaluated by using 2032-type

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coin cells. The slurries were prepared by mixing of 80 wt% cathode material, 10 wt% Super P carbon as a conducting additive, 10 wt% polyvinylidene fluoride (PVDF) as a binder, and N-methyl pyrrolidone (NMP) as a solvent. Prepared slurries were coated onto Al foil of 10 μ m in thickness followed by drying in an oven at 120 °C and cold pressing. For electrolytes, 1 M LiPF₆ was dissolved in the mixed solution of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with the ratio of 1 : 2. Lithium metal was used as the counter electrode and the coin cells were assembled in an Ar-filled glove box. The charge/discharge tests were performed by a constant current of 10 mA/g between 1.5 and 4.8 V.

Results and Discussion

As shown in Fig. 1, for the obtained precursors of V and Mn after the reactions were amorphous and Mn₃O₄, respectively. XRD results of Li₂Mn_{1-x}V_xO₃ ($0 \le x \le 0.2$) after the heat treatment are shown in Fig. 2.



Fig. 1. XRD patterns after (a) reduction reaction of vanadium solution and (b) precipitation reaction of manganese solution.



Fig. 2. XRD patterns of unwashed $\text{Li}_2\text{Mn}_{1,x}\text{V}_x\text{O}_3$ with (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15, and (e) x = 0.2.

Li₃VO₄ impurity was found in the sample of $x \ge 0.10$. It is reported that the well-developed monoclinic system with the distinct formation of (135) and (060) planes was observed above the heating temperature of 700 °C of heating temperature [15]. In the case of the synthesis with new precursors, the formation of (135) and (060) planes become conspicuous with the increase of V contents in Li₂Mn_{1-x}V_xO₃ at 500 °C of heating temperature.

In order to remove Li₃VO₄ impurities in the samples, powders were washed with deionized water. The results of ICP measurement after washing are summarized in Table 1. The removal of Li in the samples increased with the increase of V doping, ~ 2% of V was substituted in the final compound. The XRD results of the samples after washing and heat treating at 300 °C are shown in Fig. 3. A single phase of a monoclinc layer structure with a space group of C2/m was obtained in the sample of $x \le 0.018$ in Li₂Mn_{1-x}V_xO₃. The best crystallinity was found in the sample composition with x = 0.018, and Li₄Mn₅O₁₂ impurity was found in the sample with x = 0.022 in Li₂Mn_{1-x}V_xO₃.

To investigate the influence of Li/Mn ratios on the formation of Li_2MnO_3 structure (C2/m), various Li/Mn ratios of 0.5-2.0 were prepared using Li_2CO_3 and Mn precursor, and the results of XRD are shown in Fig. 4. While Li/Mn ratio of 0.5-0.75 give $Li_4Mn_5O_{12}$ phase, Li/

Table 1. ICP data and final composition after washing of $Li_2Mn_{1\text{-}x}V_xO_3.$

Reaction	ICP data			Final composition
condition of Li_2 [$Mn_{1-x}V_x$] O_3	Mn	V	Li/ (Mn+V) ratio	after washing
x = 0.00	1.000	0.000	1.897	$Li_{1.897}MnO_3$
x = 0.05	0.995	0.005	1.834	Li _{1.834} Mn _{0.995} V _{0.005} O ₃
x = 0.10	0.990	0.010	1.756	$Li_{1.756}Mn_{0.99}V_{0.01}O_{3}$
x = 0.15	0.982	0.018	1.628	Li _{1.628} Mn _{0.982} V _{0.018} O ₃
x = 0.20	0.978	0.022	1.398	Li _{1.398} Mn _{0.978} V _{0.022} O ₃



Fig. 3. XRD patterns of various $\text{Li}_2\text{Mn}_{1,x}\text{V}_x\text{O}_3$ samples after washing with (a) x = 0, (b) x = 0.005, (c) x = 0.01, (d) x = 0.018, and (e) x = 0.022.



Fig. 4. XRD patterns of the samples with various Li/Mn ratios.



Fig. 5. SEM images of various $\text{Li}_2\text{Mn}_{1-x}V_xO_3$ samples after washing with (a) x = 0, (b) x = 0.005, (c) x = 0.01, (d) x = 0.018, and (e) x = 0.022.

Mn ratio of 1.75-2.0 samples have Li₂MnO₃ structure with a typical disordered region (20-23 °) and peak separation (64-66 °). Li/Mn ratio of 1.0-1.5 give a twophase mixture of Li₂MnO₃ and Li₄Mn₅O₁₂, this is similar with the previously reported result [16]. Fig. 2(e) and ICP result show Li₃VO₄ impurities in the as-prepared sample are removed during washing process and the final Li/M ratio is 1.398. As shown in Fig. 4, Li₄Mn₅O₁₂ starts to form at Li/Mn ratio < 1.5. The condition of single phase Li₂MnO₃ was Li/M ratio > 1.5. The solubility limit of V in Li₂Mn_{1-x}V_xO₃ was found at x = 0.018. Lattice constants and unit cell volume of



Fig. 6. Specific surface area of various $Li_2Mn_{1-x}V_xO_3$ samples after washing.



Fig. 7. Electrochemical properties of $Li_2Mn_{1-x}V_xO_3$ (x = 0 and 0.018) samples after washing.

 Li_2MnO_3 were a-axis = 4.937 Å, b-axis = 8.533 Å, caxis = 5.028 Å, β = 109.204 °, and 200.021 Å³, respectively. In the case of $Li_{1.682}Mn_{0.982}V_{0.018}O_3$, lattice constants and unit cell volume were increased to a-axis = 4.946 Å, b-axis = 8.547 Å, c-axis = 5.037 Å, β = 109.212°, and 201.06 Å³, respectively. S.E.M. results of various samples are shown in Fig. 5, similar morphologies are observed in the various V-substituted samples. The size of primary particle is 50-100 nm, and agglomeration behaviors are observed. As shown in Fig. 6, the specific surface area was slightly decreased with V content in the sample; this can be explained by the slightly increased agglomeration of primary particles. Fig. 7 shows charge and discharge profiles of $Li_{1.682}Mn_{0.982}V_{0.018}O_3$ with a constant current of 10 mA/ g in the potential range of 1.5-4.8 V vs. Li. In the case of Li₂MnO₃, a plateau region appears at 4.58 V during the initial charge process. It is known that oxygens released from the lattice after the initial charge [17]. The initial charge behavior up to 4.4 V of $Li_{1.682}Mn_{0.982}V_{0.018}O_3$ is different from that of Li_2MnO_3 . V-substituted sample exhibits relatively easier delithiation behavior below 4.4 V for the initial charge



Fig. 8. XRD results of $Li_{1.628}Mn_{0.0982}V_{0.018}O_3$ electrodes at various potentials (a) OCV, (b) 4.5 V, (c) 4.8 V, (d) 2.7 V, and (e) 1.5 V.



Fig. 9. Cyclabilities of various $Li_2Mn_{1-x}V_xO_3$ samples after washing with (a) x = 0, (b) x = 0.005, (c) x = 0.01, (d) x = 0.018, and (e) x = 0.022.

process. Initial charge and discharge capacities of $Li_{1.682}Mn_{0.982}V_{0.018}O_3$ were 353 and 248 mAh/g, respectively. V-doped sample has a lower charge potential and higher discharge potential than those of undoped one during the subsequent cycles, and these result in the improved electrochemical behaviors. To investigate the phase transition behaviors for Li insertion/extraction in the structure XRD measurements are carried out at various potentials of the cells. As shown in Fig. 8(c), the disordered region ($2\theta = 20-23^{\circ}$) disappeared during the initial charge at 4.8 V and a small amount of $Li_{1.x}Mn_2O_4$ phase was detected in the major phase. After discharge at 1.5 V, the peaks of the major phase were broadened and unknown peaks were observed.

Cyclabilities of the various $Li_2Mn_{1-x}V_xO_3$ are shown in Fig. 9. $Li_{1.682}Mn_{0.982}V_{0.018}O_3$ exhibits a better initial discharge capacity and capacity retention.

Conclusions

Single phase of Li₂Mn_{1-x}V_xO₃ samples were successfully synthesized using new V and Mn precursors at low temperature. After washing and heat treatment process Li₂Mn_{1-x}V_xO₃ (x \leq 0.018) have a monoclinic layer structure with a space group C2/m. The initial charge and discharge capacities of Li_{1.682}Mn_{0.982}V_{0.018}O₃ are 353 mAh/g and 248 mAh/g, respectively. Investigations on the further increase in V substitution amount in the compound and enhanced electrochemical properties are highly anticipated.

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