

Enhancing the elevated temperature performance of Li/LiMn₂O₄ cells by reducing LiMn₂O₄ surface area

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Abstract

Lithium-rich spinels were obtained with the same structure but different surface area by two different synthesis routes, namely the “once-annealed” and the “twice-annealed” methods. The elevated temperature performance of Li/Li_{1+x}Mn₂O₄ cell is significantly improved using a spinel cathode with a small surface area: the cell at 50°C lost 5% of the initial capacity over the first 100 cycles based on a spinel cathode with the small surface area of 1.2 m²/g compared to 8% based on a large one of 6.2 m²/g. Also the mechanism responsible for the reaction of LiMn₂O₄ with LiOH to form lithium-rich spinel has been investigated. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In view of the economic and environmental advantages, spinel Li_xMn₂O₄ has been demonstrated to be the most promising positive electrode material for lithium-ion batteries because they are cheaper, less toxic, and easier to prepare than their alternatives (LiCoO₂ and LiNiO₂). An important problem prohibiting them from wider use as a cathode for lithium-ion batteries is the capacity fading on cycling at elevated temperatures. Recently, we have demonstrated the failure mechanism in detail [1]. The major factors responsible for the capacity loss at elevated temperatures are ascribed to the following: (i) the transformation of an unstable two-phase on the high-voltage region to a more stable one-phase structure, accompanied by the loss of MnO; (ii) direct dissolution of Mn₂O₃ in the electrolyte solution; and (iii) the decomposition of electrolyte solution on the electrode. Accordingly, we have succeeded in improving the elevated temperature performance of Li/LiMn₂O₄ by using the lithium-rich or transition metal-ion doped spinels [2] because either lithium or

transition metal ions presented in the 16d octahedral sites stabilized the structure, thereby allowing a homogenous lithium insertion and extraction over the entire 4-V intercalated region [3]. However, the capacity fading was still observed on cycling, this is most likely due to the catalytic activity of the spinel towards electrolyte oxidation and dissolution of Mn₂O₃, which is expected to scale with the specific surface area of the spinel particles. Amatucci et al. [4,5] have also done numerous works to reduce the surface area of spinel or surface reaction with electrolyte by preparing a coated spinel with Li₂O · B₂O₃. In the present work we report two synthesis routes to prepare the lithium-rich spinels with the same structure but different surface area, then concentrate on investigation of the effect of the surface area on the cycle life of Li/1 M LiPF₆-EC/DMC (1:2)/LiMn₂O₄ cell at the elevated temperature.

2. Experimental

Stoichiometric spinel LiMn₂O₄ (sample A) was obtained from the reaction of a stoichiometric mixture of LiOH and Mn₂O₃ (Li/Mn = 0.50 in molar ratio). The mixture was preheated at 470°C for 5 h, with further heating at 530°C for 5 h under an O₂ flow, and a final heating at 700°C for 20 h in air, then cooled for 3 h in air.

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Two different synthesis routes obtained the lithium-rich compounds (samples B and C), the detailed synthesis conditions will be given in the following section.

The chemical composition of each examined compound was determined by chemical analysis [6]. The specific surface area for each as-prepared compound was analyzed in a Micromeritics Gemini 2375 (USA) by the Brunauer, Emmett, and Teller (BET) method in which N_2 gas adsorption was employed. Each compound was heated to 200°C for 20 min to remove the adsorbed water before measurement. The scanning electron microscopy (SEM) picture was taken in a JSM-5300E Scanning Microscope (Japan).

For thermogravimetric analysis (TGA) and differential thermal analysis (DTA), powders of $LiMn_2O_4$ and $LiOH$ (10:1 in molar ratio) were mixed and thoroughly ground. Approximately 25 mg samples were used for the thermal analysis. The experiments were conducted on a TG-8110 thermal analyzer system (TAS100 system, Rigaku, Japan) at a heating rate of 2°C/min with 30 ml/min air flow rate.

The electrochemical cell we used was the same as that described previously [7]. The cathode consisted of 20 mg active material and 12 mg conducting binder (acetylene black-polytetrafluoroethylene composite). The electrolyte solution used here was 1 M $LiPF_6$ -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 in volume). The cycling tests for the $Li/LiMn_2O_4$ cell were performed in a CR2032-type button cell. Cells were cycled between the voltages limits of 3.0 and 4.3 V; the typical charge and discharge current rate was C/3 (40 mA/g), except where otherwise specified.

3. Results and discussion

In our previous works we have reported that the elevated temperature performance of $Li/LiMn_2O_4$ was significantly improved by using the lithium-rich spinels because of the existence of a one-phase structure over the 4 V entire intercalated region, thus arresting the loss of MnO caused by the unstable two-phase structure change during cycling compared with stoichiometric spinel $LiMn_2O_4$ [2]. We thus select lithium-rich compound to investigate the effect of the surface area on the elevated temperature performance of $Li/LiMn_2O_4$ cell.

The lithium-rich spinel is usually prepared by heating a stoichiometric mixture of manganese oxides with excess of lithium salt (Li/Mn over 0.5 in molar ratio) at definite temperature; herein it is termed the “once-annealed” method. Sample B was prepared by the same procedure as that for stoichiometric spinel $LiMn_2O_4$, which was described in the experimental section: lithium-rich spinel $Li_{1.1}Mn_2O_4$ was obtained from the reaction of $LiOH$ with Mn_3O_4 ($Li/Mn = 0.55$) preheated at 470°C for 5 h, followed by heating at 530°C for 5 h under an O_2 flow, and a final heating at 700°C for 20 h in air, then cooled for 3 h in

air. Chemical analysis and surface area measurement show sample B has a chemical composition of $Li_{1.1}Mn_2O_{4.19}$ and specific surface area of 6.2 m^2/g .

The classic way to decrease the surface area is to prepare stoichiometric spinel at a high temperature over 850°C. The other way is that $LiMn_2O_4$ can be easily obtained with the small specific surface area, e.g., ca. 1 m^2/g , by annealing at a high temperature, even as high as 900°C under O_2 flow [10].

However, it is absolutely avoided to fire at high temperature for lithium-rich spinel because of a tendency of formation of an oxygen-deficient spinel. As a consequence, the resulting compound exhibits a poor battery performance [8,9]. It is well known that the surface area of the resulting compound is critically dependent on that of the starting material. An alternative method is thereby to select the react precursor with a small gravimetric surface area; however, this method may work well up to limits only by selecting small surface MnO_2 such as EMD (electrochemically prepared manganese dioxide).

If the stoichiometric spinel $LiMn_2O_4$ could react with $LiOH$ and the temperature to form lithium-rich spinel could be lower than the decomposition temperature at which lithium-rich spinel lose oxygen to form oxygen-deficient spinel, then it is possible to reduce the surface area by only using stoichiometric spinel $LiMn_2O_4$ as a reaction precursor.

To clarify the above mechanism, the reaction of $LiMn_2O_4$ and $LiOH$ was studied by TGA and DTA. This was performed in air for a mixture of $LiMn_2O_4$ and $LiOH$ in a 10:1 molar ratio, where $LiMn_2O_4$ was obtained by the same preparing procedure as that of sample A but at a final heating temperature of 800°C, having a surface area of 1.1 m^2/g . The TGA and DTA traces are displayed in Fig. 1. The TGA plot shows the mass increase occurs at the temperature ranging from 260°C to 400°C; this is attributed to combination with O_2 to form oxygen-rich spinel. On further heating, oxygen is lost. In correspondence to it, a broad exothermic peak was observable on DTA curve

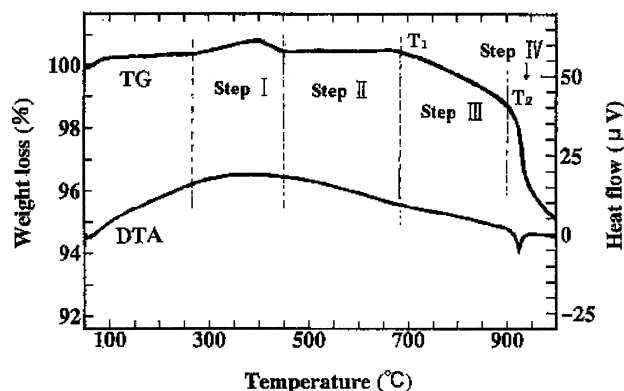


Fig. 1. TGA and DTA traces for the reaction of $LiMn_2O_4$ and $LiOH$ in air. The heating rate is 2°C/min.

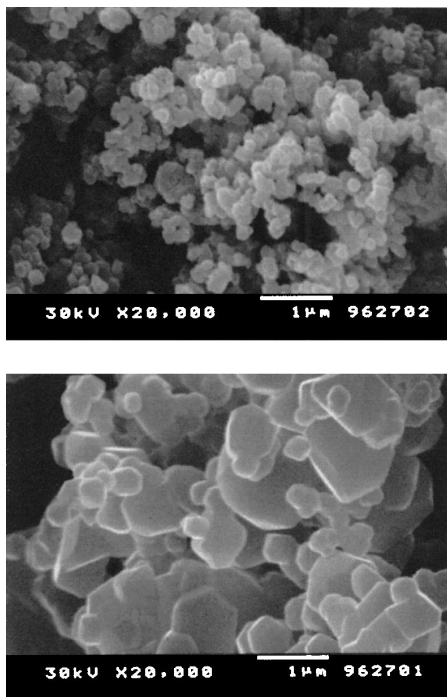
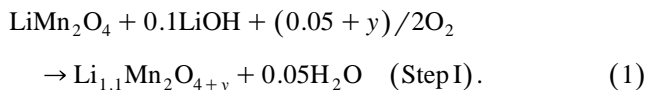
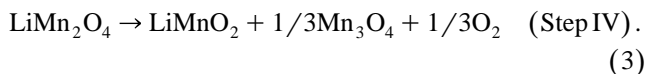
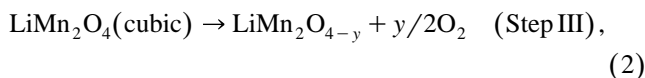


Fig. 2. SEM micrographs of samples B (top) with $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.19}$ ($6.3 \text{ m}^2/\text{g}$) and C (bottom) with $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.17}$ ($1.2 \text{ m}^2/\text{g}$).

between 260°C and 450°C , which is associated with the formation of a wide range lithium-rich spinel $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4+y}$ ($0.13 < y < 0.55$). Thus



The lithium-rich spinel, $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.13}$, can stably exist up to T_1 of 700°C (Step II), then lose oxygen to form oxygen-deficient spinel, further to LiMnO_2 at T_2 of 900°C , which corresponds to the following reaction:



We thus suggest that optimal synthesis conditions for a lithium-rich spinel involve preheating the mixture of LiMn_2O_4 and LiOH at 450°C , in this process LiOH is melted and reacted with LiMn_2O_4 . This is then followed by heating at T_1 in which T_1 should be dependent on the lithium content, it becomes lower as the lithium content in the starting material is increased [9], e.g., for $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, T_1 is 700°C . Herein we define this as the “twice-annealed” method.

Gao and Dahn [9] usually prepared lithium-rich spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ with various x values via the above type

method by annealing LiMn_2O_4 with excess Li_2CO_3 . Herein we emphasized that the present attempt is to obtain lithium-rich spinel with various surface areas only by controlling the surface area of LiMn_2O_4 rather than lithium-rich spinel with different lithium content.

An attempt was made to synthesize the lithium-rich spinel $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ (sample C) according to this description. This is prepared by preheating a mixture of LiMn_2O_4 and LiOH in a 10:1 molar ratio at 450°C for 5 h under an O_2 flow and thereafter heated at 700°C in air for 20 h, cooled for 3 h in air. Chemical analysis shows sample C has a chemical composition of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.17}$, which is very close to that of sample B. The heating process of both samples is similar but different in the final heating process. Therefore, the oxygen content in the resulting compound should be determined by the final heating process [11]. The measured specific surface area is $1.2 \text{ m}^2/\text{g}$. The SEM micrographs of samples B and C shown in Fig. 2 reveals that samples B and C have mean particle size of 0.2 and $1.0 \mu\text{m}$ in diameter, respectively. From all the above, we comment that the lithium-rich spinel with the same composition but different surface area can be easily obtained by either the “once-annealed” or “twice-annealed” methods in which the synthesis condition of the final step process is strictly controlled, i.e., annealed temperature, cool rate, and atmosphere. In particular, the later is most recommend for preparing lithium-rich spinel with a small surface area. Both of the above routes may overcome the disadvantage of the common method to obtain different surface areas by ball-mil, i.e., grinding may result in some structural changes due to its longtime mechanical treatment [12].

Now that two compounds (sample B and C) having the same composition but different surface area are obtained, then $\text{Li}/1 \text{ M LiPF}_6\text{-EC:DMC}/\text{Li}_x\text{Mn}_2\text{O}_4$ coin-type cells based on these two cathode are compared in terms of the elevated temperature performance. The capacity loss upon cycling for each sample is plotted in Fig. 3 as a function of

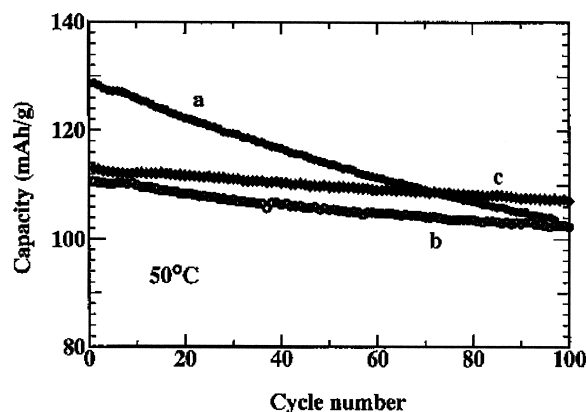


Fig. 3. Capacity as a function of cycle number for $\text{Li}/1 \text{ M LiPF}_6\text{-EC/DME (1:2 in volume)}/\text{LiMn}_2\text{O}_4$ cells at 50°C based on spinel electrodes with various surface area. (a) LiMn_2O_4 ($3.0 \text{ m}^2/\text{g}$), (b) $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.19}$ ($6.3 \text{ m}^2/\text{g}$), and (c) $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4.17}$ ($1.2 \text{ m}^2/\text{g}$). Cells were cycled at a current rate of $C/3$ between 3.0 and 4.3 V.

cycle number. The sample B loses about 8% of the initial capacity over the 100 cycles at 50°C, while the sample C loses only 5% of the initial capacity. This may be interpreted in terms of the decrease of the spinel–electrolyte interface area, thus reducing the electrolyte oxidation and dissolution of Mn_2O_3 . We are pursuing further work to clarify the mechanism.

Summarizing, we speculate that a large surface area is also expected to be effective to the high rate cycleability of lithium-ion batteries, this is similar to manganese dioxides required for use in primary batteries where the surface areas are maximized for optimum performance. However, a large surface area will prompt $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell to lose capacity at the elevated temperature. Therefore, the spinel with a small surface area, for example about $1\text{m}^2/\text{g}$, is recommended for use as a cathode for $\text{Li}/\text{LiMn}_2\text{O}_4$ lithium-ion batteries. Indeed, the surface area of LiCoO_2 cathode is always less than $1\text{m}^2/\text{g}$ in the presently commercialized liquid-electrolyte LiCoO_2/C lithium-ion batteries.

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