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SYNTHESIS OF Fe DOPED $LiMn_2O_4$ CATHODE MATERIALS FOR Li BATTERY BY SOLID STATE REACTION

SYNTEZA MATERIAŁU KATODOWEGO $LiMn_2O_4$ DOMIESZKOWANEGO Fe METODĄ REAKCJI W FAZIE STAŁEJ DO ZASTOSOWANIA W BATERIACH Li

$LiFe_{0.1}Mn_{1.9}O_4$ is expected as a cathode material for the rechargeable lithium-ion batteries. $LiMn_2O_4$ has been received attention because this has advantages such as low cost and low toxicity compared with other cathode materials of $LiCoO_2$ and $LiNiO_2$. However, $LiMn_2O_4$ has some problems such as small capacity and no long life. $LiMn_2O_4$ is phase transformation at around human life temperature. One of the methods to overcome this problem is to stabilize the spinel structure by substituting Mn site ion in $LiMn_2O_4$ with transition metals (Al, Mg, Ti, Ni, Fe, etc.). $LiFe_{0.1}Mn_{1.9}O_4$ spinel was synthesized from Li_2CO_3, Fe_2O_3 and MnO_2 powder. The purpose of this study is to report the optimal condition of Fe doped $LiFe_{0.1}Mn_{1.9}O_4$. Li_2CO_3, Fe_2O_3, and MnO_2 mixture powder was heated up to 1173 K by TG-DTA. Li_2CO_3 was thermal decomposed, and CO_2 gas evolved, and formed Li_2O at about 800 K. $LiFe_{0.1}Mn_{1.9}O_4$ was synthesized from a consecutive reaction Li_2O, Fe_2O_3 and MnO_2 at 723 ~1023 K. Active energy is calculated to 178 kJmol^{-1} at 723 ~1023 K. The X-ray powder diffraction pattern of the $LiFe_{0.1}Mn_{1.9}O_4$ heated mixture powder at 1023 K for 32 h in air flow was observed.

Keywords: Doped $LiMn_2O_4$, Lthium ion battery, cathode material, solid state reaction

$LiFe_{0,1}Mn_{1,9}O_4$ jest obiecującym materiałem katodowym do zastosowania w bateriach litowo-jonowych z możliwością wielokrotnego ładowania. $LiMn_2O_4$ cieszy się dużym zainteresowaniem z powodu niskiego kosztu otrzymywania oraz niskiej toksyczności w porównaniu z innymi materiałami katodowymi typu $LiCoO_2$ czy $LiNiO_2$. Jednak $LiMn_2O_4$ posiada również wady: niską pojemność i krótką żywotność. Dodatkowo, przemiana fazowa $LiMn_2O_4$ zachodzi w temperaturze pokojowej. Jedną z metod rozwiązania tego problemu jest stabilizacja struktury spinelu poprzez podstawienie jonu Mn w sieci $LiMn_2O_4$ metalami przejściowymi (Al, Mg, Ti, Ni, Fe, itp.). Spinel $LiFe_{0,1}Mn_{1,9}O_4$ syntezowano z proszków Li_2CO_3, Fe_2O_3 i MnO_2. Celem badań było znalezienie optymalnych warunków syntezy spinelu $LiFe_{0,1}Mn_{1,9}O_4$ domieszkowanego Fe. Mieszaninę proszków Li_2CO_3, Fe_2O_3 i MnO_2 poddano analizie TG-DTA. W temperaturze 800 K Li_2CO_3 uległ rozkładowi termicznemu, w wyniku czego powstało CO_2 i Li_2O. $LiFe_{0,1}Mn_{1,9}O_4$ zsyntezowano w wyniku reakcji następczej pomiędzy Li_2O, Fe_2O_3 i MnO_2 w temperaturze 723 ~1023 K. Energię aktywacji oszacowano na 178 kJmol^{-1} w zakresie temperatur 723 ~1023 K. Przeprowadzono także analizę XRD proszku $LiFe_{0,1}Mn_{1,9}O_4$ wygrzewanego w 1023 K przez 32 godz. w warunkach przepływu powietrza.

1. Introduction

In recent years, lithium-ion batteries (LIB) have been used as power sources for cells of phone, computer, camera, hybrid electric vehicle (HEV) and electric vehicle (EV) [1-3]. Particularly, practical application of automotive LIB is a great deal of attention because it can contribute to global warming by suppressing the emission of CO_2 and depletion problem of oil. Energy density is most important in the performance of the rechargeble battery. Energy density of nickel-cadmium battery and lead-acid battery is about 40-50 W h kg^{-1} although LIB is about 140 W h kg^{-1} [2]. In the future, improvement of safety in use and thorough reduction of production cost is required in order to expand the demand. $LiMn_2O_4$ is a promising material for the cathode material for LIB because this has several advantages such as low cost, low toxicity, rich resource and high safety compared with other cathode materials such as $LiCoO_2$ and $LiNiO_2$ [4]. However, the major problem with $LiMn_2O_4$ is low capacity and low life with phase transformation at around room temperature [5]. One of the methods to overcome this problem is to stabilize the spinel structure by substituting Mn in $LiMn_2O_4$ with transition metals (Al, Mg, Ti, Ni, Fe etc.) [6-11]. Also, improving synthesis process is important in order to reducing manufacturing cost. Controlling atmosphere, heating temperature and heating time in the solid state reaction is a factor that contribute to the cost reduction [12]. In this study, we report the solid state reaction method that is easiest synthesis method. The purpose of this study is to report optimal synthesis condition of Fe doped $LiFe_{0.1}Mn_{1.9}O_4$.

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2. Experimental

Li_2CO_3, Fe_2O_3 and MnO_2 powder were used as starting materials to synthesize $LiFe_{0.1}Mn_{1.9}O_4$. Those powder weighed at a predetermined molar rate (Li:Fe:Mn = 1 : 0.1 : 1.9), and mixed for 1 h in a mortar with pestle.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed to analyze the weight loss temperature in a TG-DTA system (2000s,NETZCH JAPAN) at a heating rate of 5 K min^{-1} from 25 K to 1173 K with air flow rate of 100 ml min^{-1}. We decided the heat treatment temperature of the mixed powder from TG-DTA measurements. Mixture powder was heated at several temperatures for 8 h in furnace.

We carried out TG analysis at a heating rate of 20 K min^{-1} with Air flow rate of 25-150 ml min^{-1} in order to investigate the effect of gas flow rate on the thermal decomposition of Li_2CO_3. Li_2CO_3 and $Mn_{1.9}Fe_{0.1}O_3$ powder weighed at a predetermined molar rate (Li_2CO_3:$Mn_{1.9}Fe_{0.1}O_3$ = 1:2) for starting material.

The crystal structure of the samples was characterized by X-ray powder diffraction (XRD-6100 Shimazu).

3. Results and discussion

The TG-DTA curve of the Li_2CO_3-Fe_2O_3-MnO_2 mixture powder at 5 K min^{-1} heating rate was shown in Fig. 1. On the TG curves, a weight loss can be observed from 298 K to 973 K. It can be estimated to be a CO_2 was released by thermal decomposition of Li_2CO_3 and a O_2 was released by the synthesis of $LiFe_{0.1}Mn_{1.9}O_4$. Mixture powder was heated at 600-1023 K for 8 h from this result of measurements.

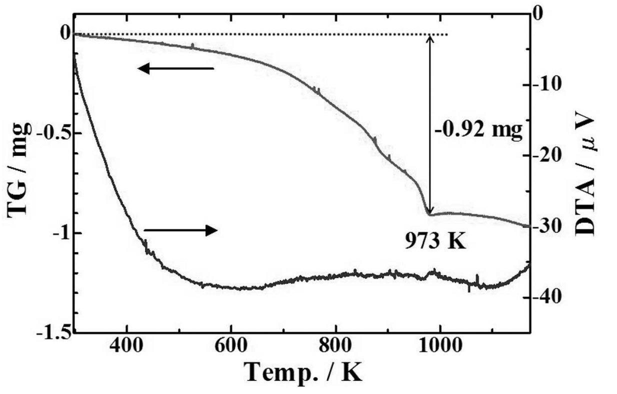

Fig. 1. TG-DTA curves of Li_2CO_3-Fe_2O_3-MnO_2 powder at 5 K min^{-1} heating rate

The XRD patterns of the (a) mixture powder, (b) heated at 600 K, (c) 873 K, (d) 923 K, (e) 973 K and (f) 1023 K are shown Fig. 2. Fig. 2(b) can be confirmed peaks of the same starting materials in Fig. 2(a). Fig. 2(c) can be observed peaks of starting materials, intermediate phase $Mn_{1.9}Fe_{0.1}O_3$ and final phase $LiFe_{0.1}Mn_{1.9}O_4$. Furthermore, with the increasing of heat treatments temperature, decrease of impurity peaks and increase of $LiFe_{0.1}Mn_{1.9}O_4$ peak can be confirmed. However, the peak of $Mn_{1.9}Fe_{0.1}O_4$ at 2θ = 44.8° in (f) was slightly confirmed, it was not possible to obtain a single phase of $LiFe_{0.1}Mn_{1.9}O_4$ finally.

Next, we changed heat treatment time for 1-32 h at 1023 K in order to investigate the influence of heat treatment time. Fig. 3 shows XRD patterns of heated mixture powder at 1023 K for (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, (e) 16 h and (f) 32 h. Fig. 3(a) indicated peaks of intermediate phase $Mn_{1.9}Fe_{0.1}O_3$ and finally phase $LiFe_{0.1}Mn_{1.9}O_4$. With the increasing of heat treatments time, decrease of intermediate phase peak and increase of $LiFe_{0.1}Mn_{1.9}O_4$ peak can be confirmed. Finally, as a result of the mixture powder heated at 1023 K for 32h, impurity peaks were disappeared and a single phase of $LiFe_{0.1}Mn_{1.9}O_4$ was obtained. The lattice parameters was calculated to 8.247, 8.234(3), 8.231(2) and 8.225(8) Å for $LiMn_2O_4$ (ICDD 88-1030) and Fig. 3(d)-(f), respectively. The lattice parameter decreases from 8.247 to 8.225(8) Å by Fe doped. It is considered that this small difference in lattice parameter is due to difference of the ion radius of Mn and Fe.

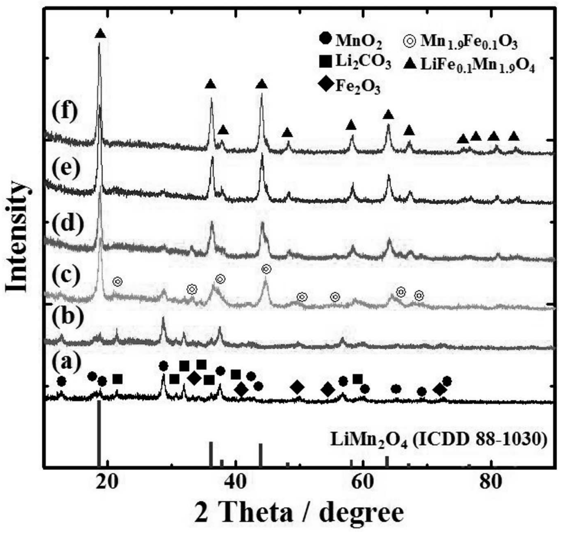

Fig. 2. XRD patterns of the heated Li_2CO_3-Fe_2O_3-MnO_2 powder at several temperatures for 8 h. (a) mixture powder, (b) 600 K, (c) 873 K, (d) 923 K, (e) 973 K ,(f) 1023 K

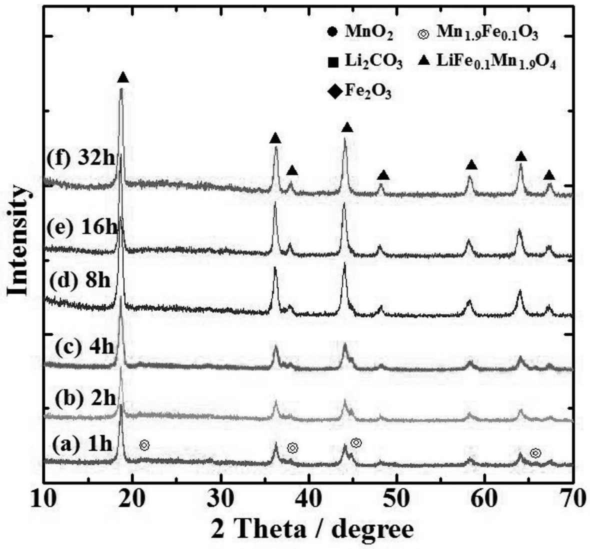

Fig. 3. XRD patterns of heated Li_2CO_3-Fe_2O_3-MnO_2 powder at different time; (a) 1 h,(b) 2 h,(c) 4 h,(d) 8 h,(e) 16 h,(f) 32 h at 1023 K

Fig. 4 shows TG curves of the Li_2CO_3-$Mn_{1.9}Fe_{0.1}O_3$ mixture powder at a heating rate of 20 K min^{-1} with Air flow rate of (a) 25 ml min^{-1}, (b) 50 ml min^{-1}, (c) 100 ml min^{-1} and (d) 150 ml min^{-1}. It can be seen reach more quickly of theoretical decrement of CO_2 (0.99 mg) with increasing of Air flow rate. However, it can't be confirmed difference in Fig. 4(c) and (d). Therefore, the optimal gas flow rate is 100 ml min^{-1} in this study. In addition, the activation energy was 178 kJ mol^{-1} at air flow rate 100 ml min^{-1}.

In summary, the optimal condition to achieve reduction of synthesis cost of $LiFe_{0.1}Mn_{1.9}O_4$ was determined, that is heat treatment at 1023 K for 32 h in Air flow rate 100 ml min^{-1}.

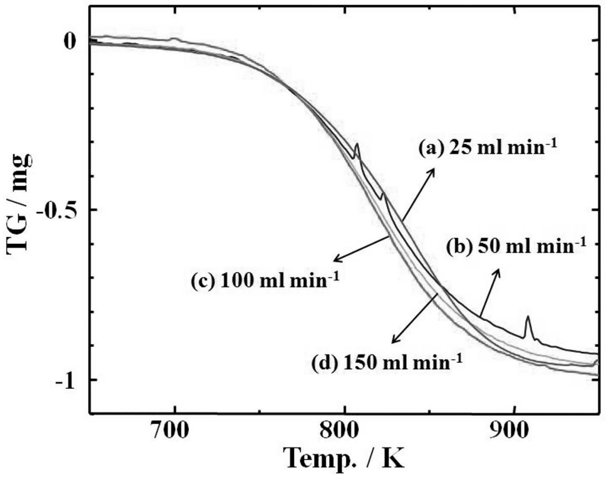

Fig. 4. TG curves of Li_2CO_3-$Mn_{1.9}Fe_{0.1}O_3$ powder up to 1173K at 20 K min^{-1} in several gas flow rate; (a) 25 ml min^{-1}, (b) 50 ml min^{-1}, (c) 100 ml min^{-1}, (d) 150 ml min^{-1}

4. Conclusions

The weight loss during synthesis progress of $LiFe_{0.1}Mn_{1.9}O_4$ was due to thermal decomposition of Li_2CO3, formation of intermediate phase $Mn_{1.9}Fe_{0.1}O_3$ and formation of $LiFe_{0.1}Mn_{1.9}O_4$ spinel.

The XRD pattern of the Li2CO3-Fe2O3-MnO2 mixture powder heated at 1023 K for 8 h was observed intermediate phase Mn1.9Fe0.1O3 at $2\theta = 44.8°$, it was disappear when heated at 1023 K for 32h.

It could not be confirmed difference of weight loss speed when Air gas flow rate was increased more than 100 ml min^{-1}.

Therefore, the optimal condition during synthesise of Fe doped $LiFe_{0.1}Mn_{1.9}O_4$ spinel cathode material by solid state reaction is heated at 1023 K for 32 h in Air flow rate 100 ml min^{-1}.

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