

Synthesis of LiMn_2O_4 by modified Pechini method and characterization as a cathode for rechargeable Li/ LiMn_2O_4 cells

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Abstract

The Pechini process to produce LiMn_2O_4 powder is modified such that precursors are pre-ignited in open air followed by calcining in the range of 600°C–800°C for 4 h. The molar ratio (R) of ethylene glycol (EG) to citric acid (CA) is 0, 1, 2 or 4. The effect of EG content on powder characteristics and electrochemical performance is evaluated. With increasing R , the homogeneity and the specific surface area of the powder are increased. Lithium is evaporated during ignition (and/or the charring reaction) and calcination because of the inhomogeneous mixing and exothermic heat of decomposition of polymer. Samples calcined at 800°C for 4 h yield maximum specific capacity for both charge and discharge (130.7 and 126.7 mA h g⁻¹). The cycleability of the powder increases with increasing R . The effect of the EG content on the homogeneity is discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium manganese spinel; Cathode Pechini method; Ethylene glycol; Cycleability; Secondary battery

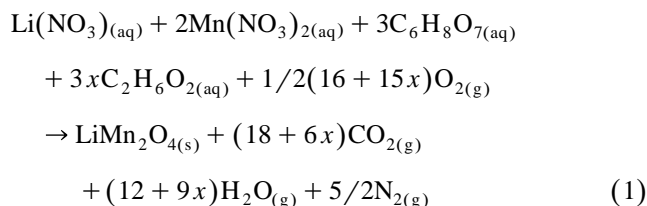
1. Introduction

Lithium manganese spinel is a candidate electrode material for lithium-ion batteries [1] because manganese oxides offer advantages in terms of specific energy, toxicity and cost [2]. The capacity loss of the lithium spinel during cycling has become an area of interest to both electrochemists and ceramicists. Several attempts have been made to solve this problem by, for example, new preparation methods and partial substitution of manganese in LiMn_2O_4 .

When scaling-up for commercialization, the solid-state reaction takes more than 24 h with excessive lithium [3]. Solution methods such as the Pechini process [4] and the solgel method [5] can, within several hours, produce a capacity above 130 mA h g⁻¹ together with excellent cycling behaviour.

In our preliminary experiments with the Pechini process, it was found that lithium evaporation could occur during the synthesis. Therefore, excessive lithium is required to maintain stoichiometry. This observation can be understood in terms of the finding of Sun [5], namely, if too much polymer is added, it can have a negative effect

by raising the temperature too high in a short period of time and by decreasing the partial pressure of oxygen near the oxide due to an increased amount of CO or CO₂ through decomposition of the polymers. It can also be explained in terms of the ‘Fuel-Oxidizer Concept’ proposed by Jain et al. [6], viz., NO₃ can act as an oxidant and the polymers as a fuel in the Pechini process. Therefore, the following reaction can be assumed for the decomposition reaction of the polymers:



where x is equal to the ratio of ethylene glycol (EG) to citric acid (CA). Consequently, as more EG is added, more oxygen is required to burn out all the polymers.

In this work, the Pechini process used to produce LiMn_2O_4 powder has been modified such that the precursors are pre-ignited in open space before calcination in order to supply sufficient oxygen to the sample. The powder characteristics and electrochemical performance we evaluated for varying amounts of EG.

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2. Experimental

2.1. Powder preparation

Reagents of MnO_2 (Aldrich Chemicals; 99%), LiCO_3 (Anderson Physics Lab.; 99.99%), CA (Aldrich Chemicals; 99.5%), EG (Junsei Chemicals; extra pure) and nitric acid (Oriental Chemicals; 60%) were used as starting materials. MnO_2 was dissolved in dilute nitric acid with several drops of hydrogen peroxide (Junsei Chemicals; 30%) until a clear solution was obtained. Stoichiometric amounts of LiCO_3 were then added to the solution.

Pre-dissolved solutions of CA and EG with a molar ratio (R) of EG to CA 0, 1, 2 and 4, were added to the clear cation solutions. The mixed solutions were stirred on a hot plate, which allowed the temperature to be controlled below 180°C , until the solutions become a dark-brown gel. This was followed by drying in vacuum to evaporate the residual water (from 120°C to 170°C step by step) and, finally, a puffed char was obtained. The puffed precursors were transferred to a stainless steel tray and auto-ignition was initiated by the flame of a gas lighter. The ignited powders were calcined in a furnace at 600°C , 700°C and 800°C for 4 h in air.

The thermal decomposition behaviour of the dried precursors before ignition was examined by means of thermogravimetry (TG) and differential scanning calorimeter (DSC) at a heating rate of $5^\circ\text{C}/\text{min}$ with a STA409 instrument from Netzch. Phase analysis was carried out by powder X-ray diffraction (XRD) with Cu K α radiation in a Rigaku X-ray diffractometer. Scanning electron micrographs (SEM) were obtained to examine the morphology of the powder. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method using N_2 gas.

Induction-coupled plasma (ICP) was used to determine the lithium content of each sample.

2.2. Electrochemical measurements

A cathode electrode was prepared by mixing LiMn_2O_4 powder with 10 wt.% carbon black (Vulcan, XC-72) and 10 wt.% PVDF (polyvinylidene fluoride) in NMP (*n*-methyl pyrrolidinone) solution. The stirred mixture was spread on a 316 stainless-steel ex-met. The electrode specimens were dried under vacuum at 120°C .

A three-electrode cell was constructed for charge–discharge experiments. Lithium foil (Foote Mineral, 99.9%) was used as the reference and counter-electrodes, and a 1 M LiClO_4 –PC solution (pre-mixed at Mitsubishi Chemicals) was used as the electrolyte. Galvanostatic charge–discharge experiments were conducted using a potentiostat/galvanostat (EG&G PARC Model 263 or 273). The cut-off voltages were set at 4.5 and 3.0 V for charge and discharge, respectively, at a current rate of 0.5 C.

3. Results and discussion

3.1. Preparation of powders

During evaporating the water from the mixed solution, precipitates of polymer, which have a light-brown colour, were observed with low addition of EG ($R = 0, 1$). With no addition of EG ($R = 0$), the esterification and polymerization reactions [4] did not occur, because of the absence of the hydroxyl groups of EG. A solid with a brown colour was obtained instead of a polymeric gel.

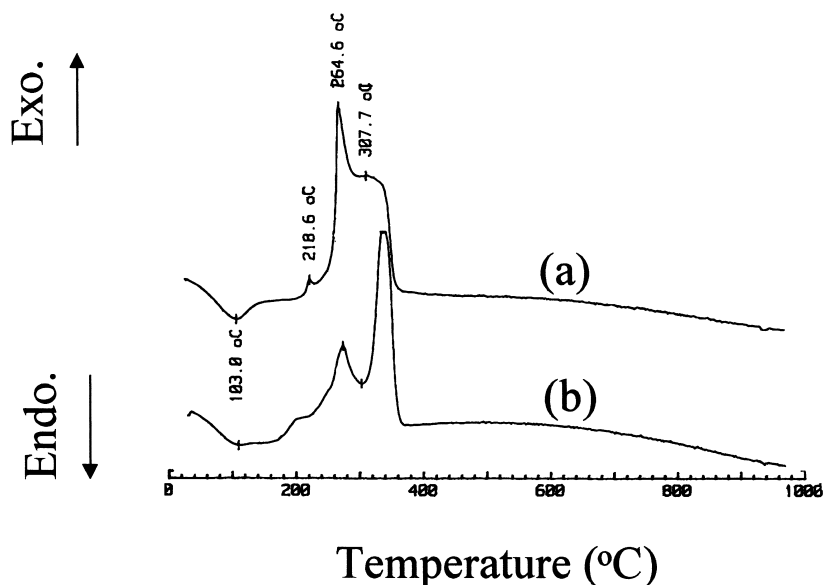


Fig. 1. DSC curves of precursors after vacuum drying from solutions with (a) $R = 1$; (b) $R = 4$.

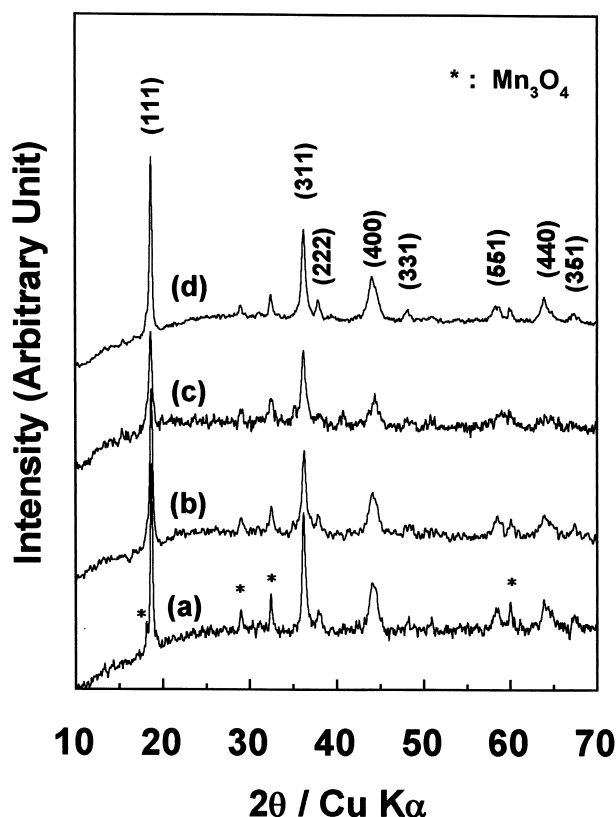


Fig. 2. XRD patterns of ignited precursors with different EG addition: (a) $R = 0$; (b) $R = 1$; (c) $R = 2$; (d) $R = 4$.

With the addition of a mole of EG, a little precipitation occurred during drying. The vacuum dried precursors took the form of a sponge-like black solid (char). The apparent volume of the precursor was greater for an addition of 4 mol of EG.

Tai and Lessing [7] have reported that an optimal gelling condition is achieved near a ratio of EG to CA of 1:1, and the resultant resins had the largest apparent volumes among the samples. The reason why our experiment did not consistent with the condition proposed by Tai and Lessing, is thought to be due to the fact that sufficient reaction could not occur because the polymerization could only take place for several hours during the drying process.

The thermal decomposition behaviour of vacuum-dried precursors for $R = 1$ and $R = 4$, is presented in Fig. 1. The endothermic peaks at 103°C in both curves represent the evaporation of residual water which is probably produced by the polymerization reaction. There are two major exothermic peaks near 260°C and 330°C which end below 360°C . It is concluded that most of the organic substances in the precursors are burned out at this temperature.

The small flame of a cigarette lighter could initiate auto-ignition of the char at room temperature in air, except for the sample with $R = 0$ which had to be subjected to additional heating on a hot plate. Ignition was completed within 10 min.

Table 1

Equilibrium partial pressure of oxygen for reduction of Mn_2O_3 at a given temperature. Calculated from Ref. [13] for reaction: $3\text{Mn}_2\text{O}_3 \leftrightarrow 2\text{Mn}_3\text{O}_4 + 1/2\text{O}_2$

Temperature ($^\circ\text{C}$)	P_{O_2}
300	$1.026\text{E} - 10$
400	$6.70\text{E} - 8$
500	$6.73\text{E} - 6$
600	$2.30\text{E} - 4$
700	$3.73\text{E} - 3$
800	$3.54\text{E} - 2$
900	$2.25\text{E} - 1$

The XRD patterns of the ignited powder is given in Fig. 2. It is found that the LiMn_2O_4 phase is crystallized within a few minutes during ignition. The existence of the Mn_3O_4 phase shows that the oxygen partial pressure in the ignition condition is very low in open air [8]. The equilibrium partial pressure of oxygen determined from thermodynamic data [9] is given in Table 1. The equilibrium partial pressure near the oxide should be below $6.7\text{E} - 8$ at 400°C , $2.3\text{E} - 3$ at 600°C and $2.25\text{E} - 1$ at 900°C . Aruna et al. [10] have reported that the temperature of the flame during auto-ignition is $900 \pm 50^\circ\text{C}$. Therefore, under a partial pressure of oxygen close to that in air, Mn_3O_4 can be sufficiently stable at this temperature.

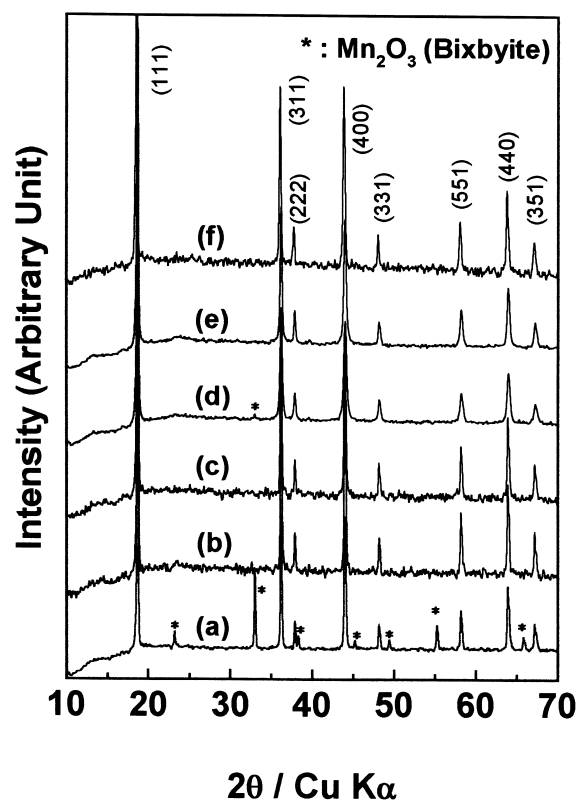


Fig. 3. XRD patterns of LiMn_2O_4 powders calcined at 800°C for 4 h with molar ratio of (a) $R = 0$; (b) $R = 1$; (c) $R = 2$; and calcined at (d) 600°C , (e) 700°C and (f) 800°C for 4 h with $R = 4$.

The XRD patterns of calcined powder are presented in Fig. 3. When no EG ($R = 0$) is added to the solution, a large amount of Mn_2O_3 instead of the Mn_3O_4 is produced (Fig. 3(a)). A trace of Mn_2O_3 is also detected in the powder calcined at 600°C for 4 h, which was prepared with $R = 4$ (Fig. 3(d)) and further heating resulted in a single-phase spinel (Fig. 3(e) and (f)). The relative lithium contents of lithium manganite powders before and after calcination for each EG content are given in Fig. 4. Before calcination, the lithium content of a powder with $R = 4$ was the lowest. After calcination, the lowest lithium content was obtained at $R = 0$.

The following conclusions are drawn. For $R = 0$, the lumps of lithium which segregated out (non-homogeneous gel) during drying of the solution became an amorphous phase (this was partly due to insufficient heating during ignition [11]) and were then evaporated during calcination. The homogeneity of the metal cation was therefore increased when lithium evaporation was decreased by increasing the EG content. If excessive EG was added ($R = 4$), however, the explosive gas and exothermic heat of the auto-decomposition reaction also promoted the evaporation of lithium during ignition (and/or charring).

The dependence of the $LiMn_2O_4$ lattice parameter upon EG content and calcination temperature is shown in Fig. 5. Both the molar ratio of EG to CA and the calcination temperature influenced the lattice parameter. Sun [5] has reported similar results in that the lattice parameter of $LiMn_2O_4$ is increased with increasing amounts of chelate polymers. As mentioned above, the powder prepared with a large amount of EG ($R = 4$) is closed to the optimal gelling conditions in which there is a more extended three-dimensional network, i.e., more homogeneous mixing of the cation and less tendency for segregation during charring [12]. Therefore, it is found that increasing R increases the homogeneity of the sample and, hence, the crystallinity of the $LiMn_2O_4$ powder.

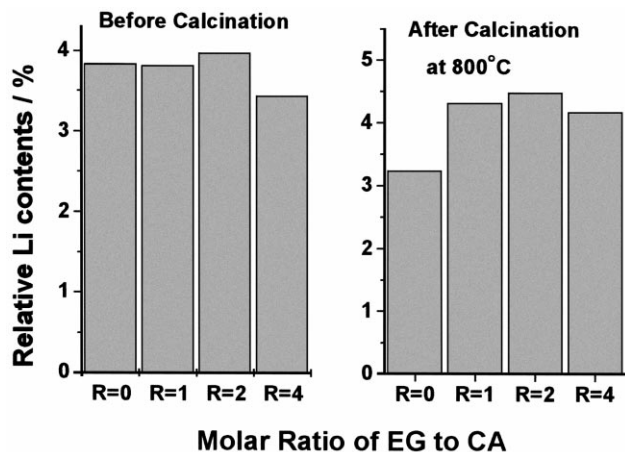


Fig. 4. Relative lithium contents of lithium manganite powders according to R value.

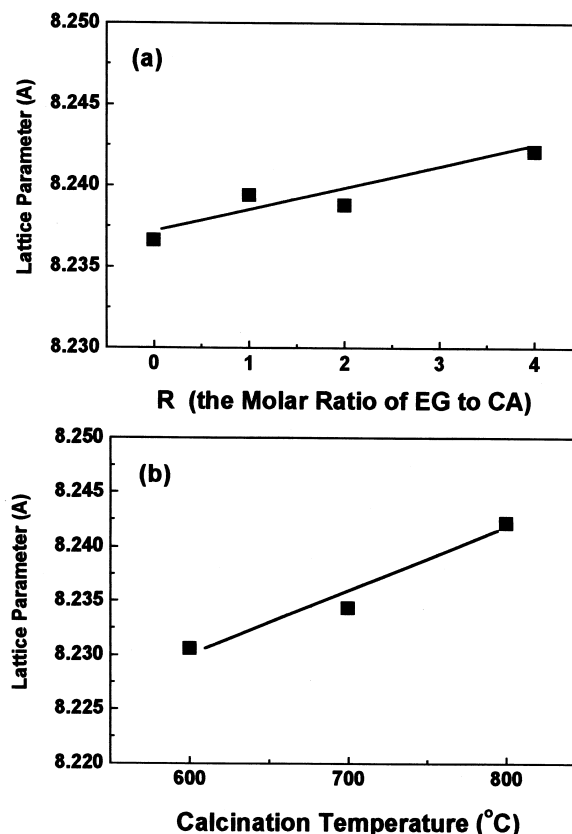


Fig. 5. Dependence of lattice parameter of $LiMn_2O_4$ powder upon (a) R value, (b) calcination temperature.

The final morphology of the calcined powder and the dependence of specific surface area of $LiMn_2O_4$ powder on the ratio of EG to CA, are given in Figs. 6 and 7. It is clear that the mean particle size decreases with increasing R . With a low addition of EG ($R = 0, 1$), there are abnormally coarsened particles (marked by arrows in Fig. 5(a) and (b)). As mentioned above, the drying of solutions for $R = 0$ and $R = 1$ produces precipitates Monchilov et al. [13] have reported that Mn_2O_3 has a considerably greater tendency for crystal growth by a solid-state reaction than $LiMn_2O_4$. Therefore, the dependence of the surface area of calcined powder on the molar ratio can be partly explained by the Mn-rich phase promoting the growth of particles.

3.2. Electrochemical characterization

Charge–discharge curves for $LiMn_2O_4$ samples, calcined at different temperatures, in $Li/1\text{ M }LiClO_4\text{-PC}$ solution/ $LiMn_2O_4$ cells are shown in Fig. 8. All the charge/discharge curves exhibit plateaux of about 100 mV. The samples calcined at 800°C for 4 h yielded the highest specific capacity for both of charge and discharge. As the calcination temperature is decreased, the capacities decrease. This result is consistent with previous reports [4,14]. It is found that the decrease in the discharge

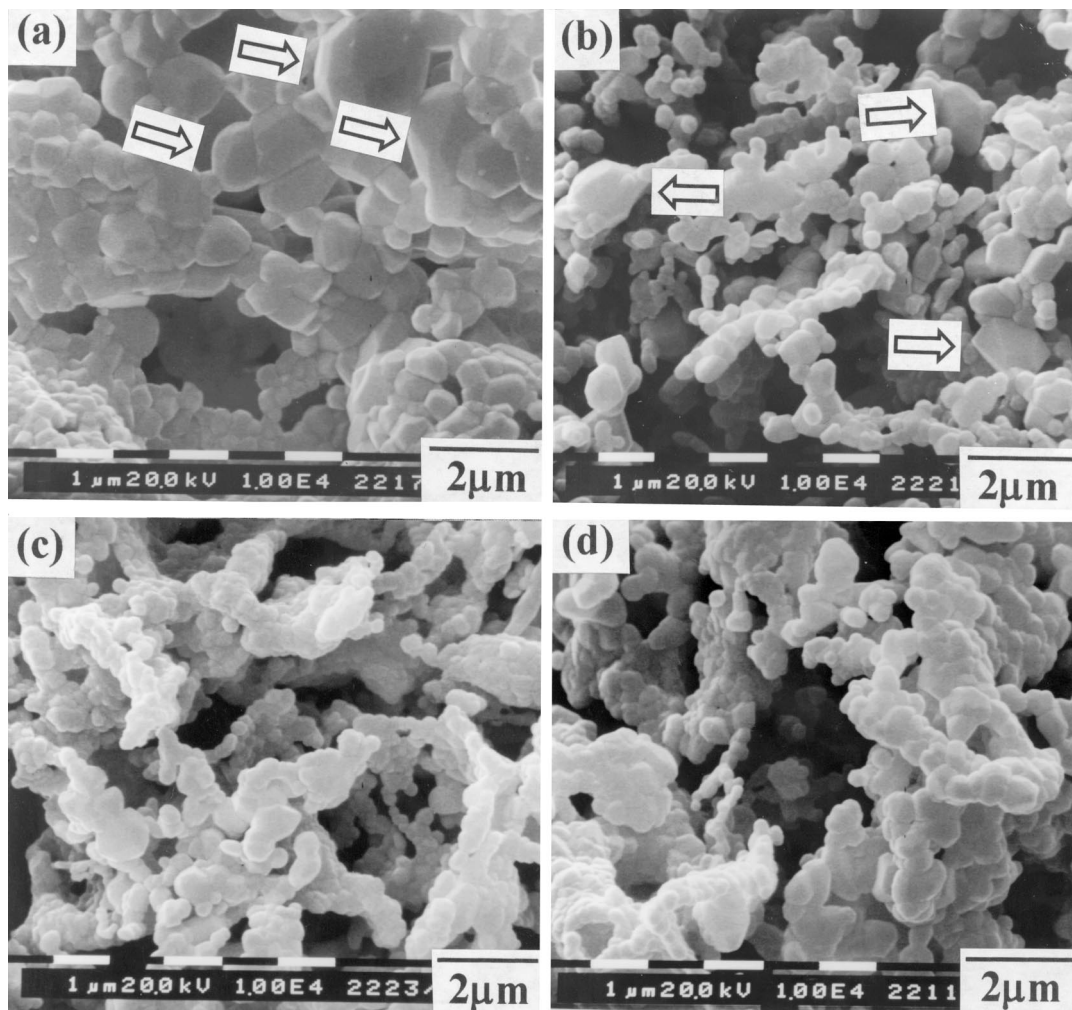


Fig. 6. Electron micrographs of calcined powder at 800°C for 4 h from the solutions with (a) $R = 0$, (b) $R = 1$, (c) $R = 2$, (d) $R = 4$.

capacity from 800°C to 700°C is mainly associated with the lower plateau, while that from 700°C to 600°C is associated with from upper plateau.

The initial charge–discharge curves of LiMn_2O_4 samples, prepared from solutions with various molar ratios (R) of to EG to CA and calcined at 800°C for 4 h in Li/1 M

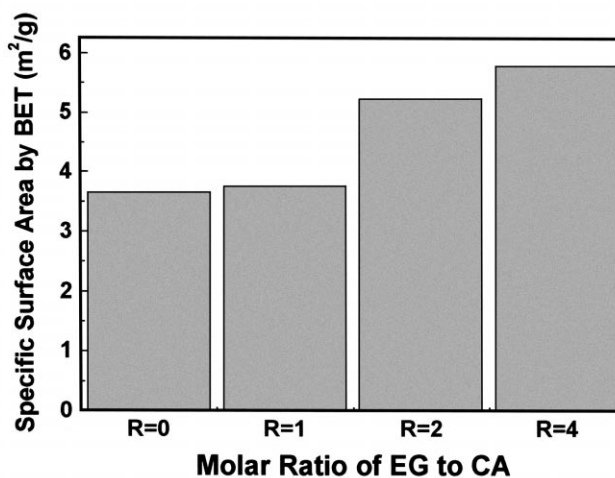


Fig. 7. Dependence of specific surface area of LiMn_2O_4 powder calcined at 800°C for 4 h upon R value.

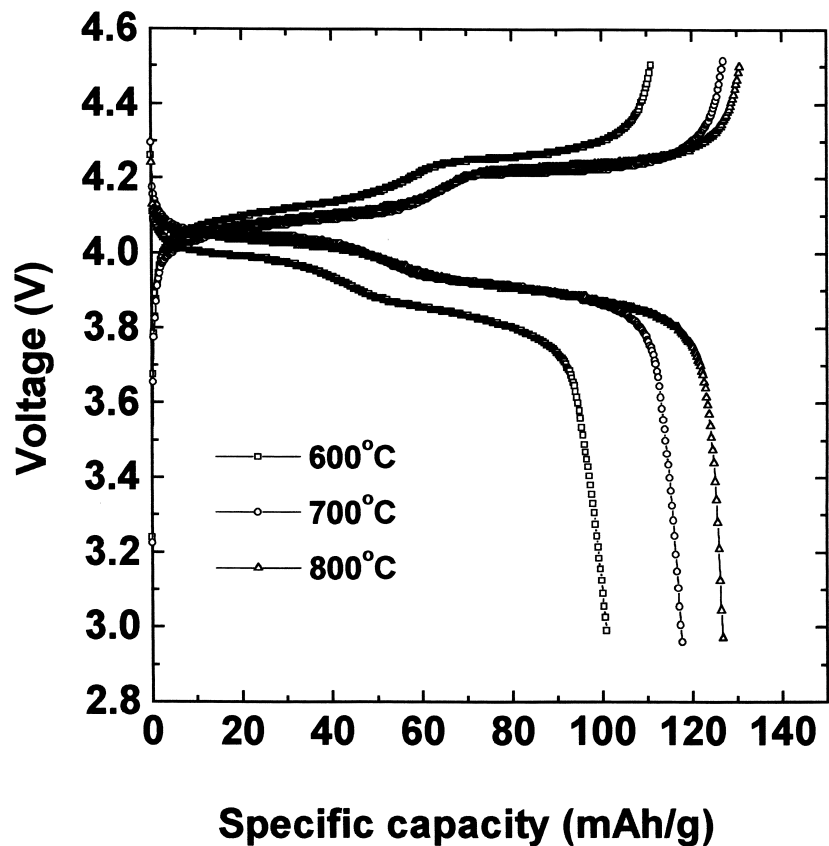


Fig. 8. Initial charge–discharge behaviour of LiMn_2O_4 samples, calcined at various conditions, in $\text{Li}/1 \text{ M LiClO}_4\text{-PC}$ solution/ LiMn_2O_4 cells.

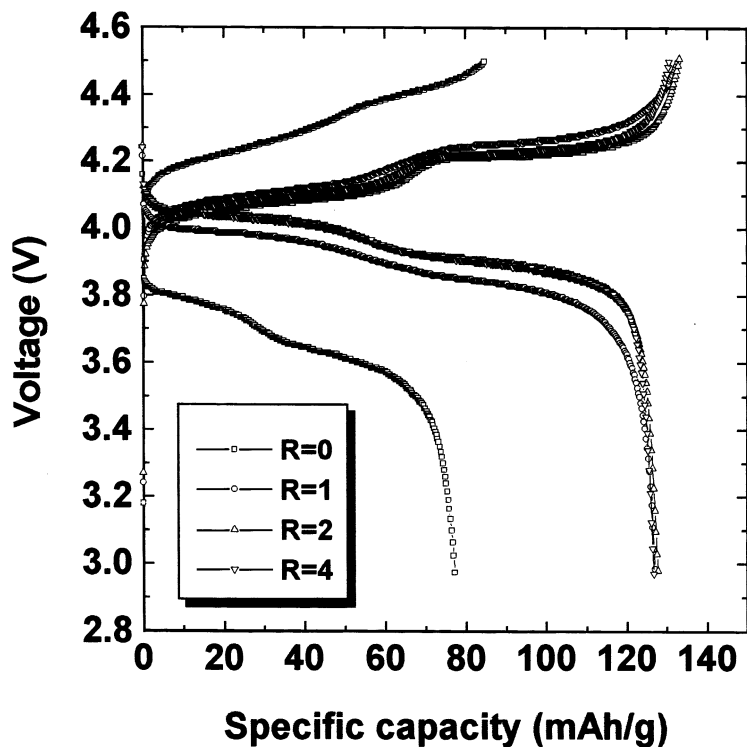


Fig. 9. Initial charge–discharge behaviour of LiMn_2O_4 samples, prepared from solutions with various R values and calcined at 800°C 4 h in $\text{Li}/1 \text{ M LiClO}_4\text{-PC}$ solution/ LiMn_2O_4 cells.

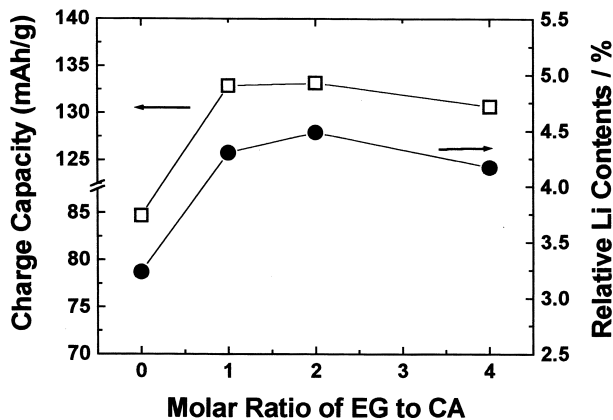


Fig. 10. Relationship between lithium content and specific charge capacity with respect to R value. Samples calcined at 800°C for 4 h.

$\text{LiClO}_4\text{-PC}$ solution/ LiMn_2O_4 cells are given in Fig. 9. The samples prepared from the solution with non EG

($R = 0$) yield very small charge and discharge capacities. This is mainly the result of the low specific surface area as well as the large amount of second phase (Mn_2O_3). The discharge capacities for $R = 1, 2,$ and 4 are about 127 mA h g^{-1} , i.e., there was no dependence on the value of R . There is a similar influence of R on the lithium content. (Fig. 10).

The cycling performance for each condition of powder preparation is shown in Fig. 11. The cycleability of the cathode is improved by increasing the calcination temperature, Fig. 11(a). This result differs from that of Liu et al. [4]. The homogeneity and crystallinity (lattice parameter) of the powder increases with increasing temperature and, hence, the cycleability increases. In addition, dissolution of manganese can decrease on increasing the temperature because the surface area of the powder should also decrease with increasing temperature; this would also affect the cycleability [14].

The capacity on the 10th cycle for $R = 4, 2, 1, 0$ was 94.9%, 91.2%, 88.8% and 79.7% of the initial cycle,

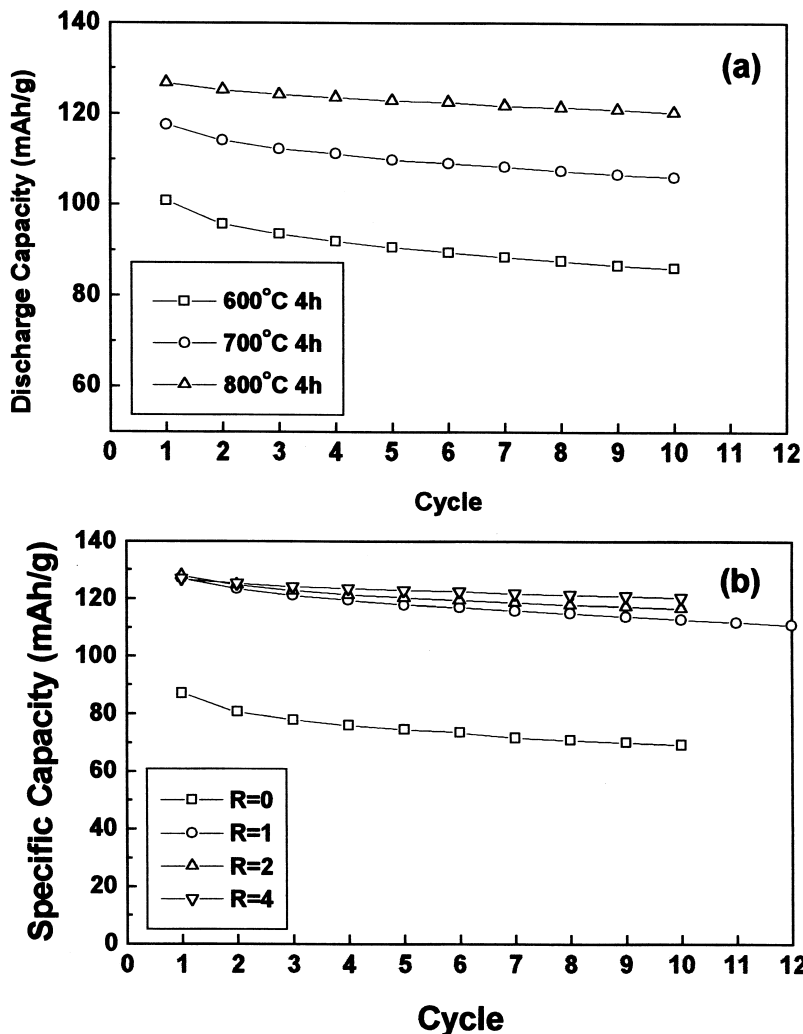


Fig. 11. Discharge capacity of $\text{Li}/\text{LiMn}_2\text{O}_4$ cell according to: (a) calcination temperature of powder from solution of $R = 4$; (b) R value followed by calcining at 800°C for 4 h.

respectively (Fig. 11(b)). Thus, the cycleability is improved with increasing R . There are three parameters which are affected by the R value, namely, specific surface area, lithium content and homogeneity. We note the following. First, even though the surface area of the powder increases with increasing R (Fig. 7), the cycleability increases. Consequently, the dissolution of manganese does not affect the cycleability. Second, the lithium content and the charge capacity have a maximum values for $R = 2$ (Fig. 10). Therefore, the powder $R = 4$ might be lithium deficient and indicates the best reversibility. This result is not consistent with previous studies [3]. Consequently, the homogeneity of the powder is thought to exert a dominant effect on cycleability.

4. Conclusions

With increasing EG content in the Pechini process, the homogeneity of LiMn_2O_4 powder is increased and the particle size is decreased. Lithium evaporation during ignition (and/or charring reaction) and calcination is facilitated by the inhomogeneous mixing and exothermic heat of decomposition of the polymer. Samples calcined at 800°C for 4 h yield the highest specific capacity for both charge and discharge (130.7 and $126.7 \text{ mA h g}^{-1}$). Cycleability decreases with decreasing R . The capacities on

the 10th cycle for $R = 4, 2, 1, 0$ are 94.9%, 91.2%, 88.8% and 79.7% of the initial cycle, respectively. The homogeneity of the powder has the most claimant effects on cycleability.

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