



Short communication

Highly crystalline lithium–manganese spinel prepared by a hydrothermal process with co-solvent

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ABSTRACT

Lithium–manganese spinel is prepared by a hydrothermal process that uses ethanol as the co-solvent. The crystallinity, particle morphology and electrochemical performance of the spinel are examined and compared with those obtained without the co-solvent. The amount of co-solvent and reaction time are adjusted to control the properties. The addition of ethanol leads to uniform particle size and shape, as well as higher crystallinity, than for spinel prepared in pure water. The co-solvent also reduces the time required for synthesis. A prolonged reaction time is effective in obtaining high-purity Li–Mn spinel in pure water but more impurities form after a long reaction time in an ethanol-added solvent. A mechanism for this process is suggested. A report is given of the electrochemical performance of Li–Mn spinel, including the capacity, rate capability and cyclability, as well as the effects of the co-solvent on these properties.

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1. Introduction

Lithium–manganese spinel is a promising cathode material for large-format rechargeable lithium batteries owing to its good power capability and safety. The recent commercialization of hybrid electric vehicles powered by lithium-ion batteries has highlighted the potential use of Li–Mn spinel as a substitute for LiCoO₂ in the near future. A range of methods for the preparation of the spinel has been proposed, e.g., conventional solid-state synthesis [1], sol–gel [2] and spray-drying [3], but the resulting powders generally contain irregular particles with a broad size distribution.

The most serious problem with Li–Mn spinel is Mn dissolution into the electrolyte, which results in poor cycle-life performance at high temperatures [4]. Morphology control, the introduction of a dopant at the Mn-site and metal oxide coatings have all been suggested as a means to improve cycle-life [5–12]. A wet process, such as a hydrothermal or a precipitation method, is more advantageous in terms of morphology control and securing compositional uniformity than solid-state synthesis. Crystallinity is an equally important determinant of the electrochemical performance of a cathode material. Raja et al. [13] reported that highly crystalline Li–Mn spinel shows excellent reversibility of lithium insertion/de-

insertion, and a remarkable enhancement in capacity and rate capability.

In recent years, the hydrothermal method has been demonstrated to be an attractive low-temperature route for preparing crystalline Li–Mn spinel [14–20]. Jiang et al. [19] adopted a simple hydrothermal process to form well-crystallized nanocrystalline spinel Li–Mn spinel. Nevertheless, it usually takes considerable time to obtain a well-crystallized pure Li–Mn spinel phase using a hydrothermal process. Moreover, post-heat treatment is needed to improve the crystallinity of the material. This study reports a novel method to obtain Li–Mn spinel with high purity and crystallinity in a short time through the addition of ethanol using a hydrothermal process without a post-heat treatment.

2. Experimental

Li–Mn spinel was synthesized by means of a hydrothermal process. LiOH·H₂O and γ -MnO₂ served as the starting materials. LiOH·H₂O (1.5 mmol) was dissolved in 35 ml of distilled water and equimolar γ -MnO₂ was added to the solution with constant stirring. The resulting slurry was transferred to a Teflon-lined autoclave and kept at 200 °C for 1–10 days. To determine the effect of the co-solvent, the above procedure was repeated with the addition of ethanol to the slurry. The amount of ethanol was varied from 0 to 8.5 vol.%. The conditions for sample preparation are listed in Table 1. After the hydrothermal process, the resulting product was washed several times with distilled water, filtered and then dried at 70 °C in air. A reference Li–Mn spinel was synthesized by

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Table 1
Crystallite sizes and lattice constants of samples prepared under various preparation conditions.

Sample no.	Ethanol content (vol.%)	Reaction time (days)	Crystallite size (Å)	Lattice constant (Å)
1	0	2	165	8.15840
2	0	4	291	8.21121
3	0	6	295	8.21553
4	0	10	311	8.20887
5	1.4	2	605	8.23880
6	1.4	4	519	8.24156
7	2.9	4	418	8.23043
8	8.5	1	395	8.23069
9	8.5	2	472	8.22467
10	8.5	4	397	8.21182
11	8.5	6	354	8.20121

a solid-state process that involved calcination of a LiOH and MnO₂ mixture (LiOH:MnO₂ = 1:2) at 800 °C for 20 h in air to compare the electrochemical performance.

The crystal structure of the resulting powder was analyzed by powder X-ray diffraction (XRD, Rigaku D/Max-2500/PC, Japan) using a Cu K α radiation source. The particle size and shape of the samples were examined by field emission scanning microscopy (FE-SEM, S-800, Hitachi, Japan). The coating status of the sample was observed by transmission electron microscopy (TEM, JEM 2000EX, JEOL, Japan).

A coin-cell (CR2016) was employed to determine the electrochemical performance of the samples. A positive electrode was produced by coating a slurry of the active material, Super-P carbon black (MMM, Belgium) and a polyvinylidene fluoride (PVdF) binder (Kurea, Japan) at a weight ratio of 80:10:10 on an aluminum foil current-collector. The electrolyte was a 1.0 M LiPF₆ solution in ethylene carbonate/ethyl-methyl carbonate (EC/EMC) (1/1 vol.%) (Cheil Ind., Korea). Galvanostatic charge and discharge cycle tests of the cell were carried out at room temperature between 3.0 and 4.3 V.

3. Results and discussion

3.1. Effect of co-solvent

Fig. 1 shows XRD patterns of the hydrothermally prepared samples. The reaction time was set at 4 days. Li–Mn spinel is the major phase in all samples but some impurities are found. MnO₂, which is not converted to Li–Mn spinel, is present in the sample prepared without the co-solvent, and Mn₃O₄ is observed in the sample obtained with the co-solvent. He et al. [21] reported the reduction power of ethanol in their study of the synthesis of Mn₂O₃ via the reduction of MnO₂ by a solvo-thermal process in ethanol. Ethanol is believed to contribute to the formation of Mn₃O₄ by the reduction of manganese ions in Li–Mn spinel. The amount of Mn₃O₄ increases with increasing ethanol content in the solvent. Almost pure Li–Mn spinel with a trace of Mn₃O₄ is obtained in the solvent containing 1.4 vol.% ethanol. The crystallinity of the sample prepared in pure water was lower than that in the mixed solvents. The crystallite sizes from the (1 1 1) plane are listed in Table 1. The samples synthesized in the mixed solvents have higher crystallinity. The lattice constants of Li–Mn spinels are also given in Table 1. The lattice constants of the samples obtained in pure water are smaller than those prepared in the mixed solvents and indicates a contraction of the lattice due to excess lithium. This suggests that more lithium can be accommodated in Li–Mn spinel in pure water with the other conditions being the same.

The particle shape of the samples is shown in Fig. 2. As expected from the crystallinity, the particle size of the sample prepared in pure water is much smaller than that obtained in the mixed solvents

but the particles are densely aggregated. The addition of ethanol also produces well-dispersed uniform particles.

3.2. Effect of reaction time

X-ray diffraction patterns of samples prepared hydrothermally in pure water and a mixed solvent containing 8.5 vol.% ethanol are presented in Figs. 3 and 4, respectively. The reaction time is varied from 1 to 6 days. The amount of MnO₂ decreases gradually with reaction time, which means that a long reaction time is needed for the complete conversion of the reactant to Li–Mn spinel in pure water. By contrast, the amount of impurity (Mn₃O₄) increases with increasing reaction time in the presence of ethanol. Moreover, the crystallinity is not dependent on the reaction time. This means that a short reaction time is sufficient to obtain a pure and well-crystalline Li–Mn spinel, which can be one advantage of this synthetic process in a mixed solvent. Further study will be needed to determine the optimum reaction time to obtain pure Li–Mn spinel in a mixed solvent with a high ethanol content.

Scanning electron micrographs of the samples prepared in the ethanol-added solvent are given in Fig. 5. No significant changes in particle size and shape with the reaction time are observed for the samples, except for morphological changes due to a change in the level of impurities.

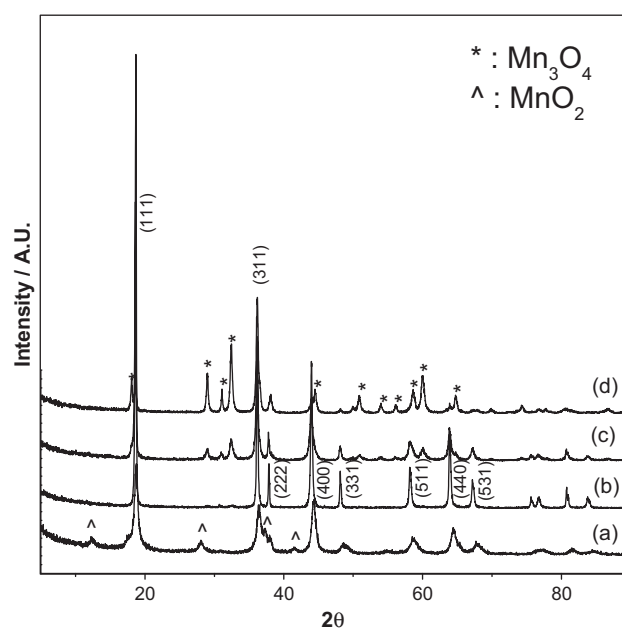


Fig. 1. XRD patterns of samples prepared in (a) pure water and solvent containing (b) 1.4 vol.%, (c) 2.9 vol.% and (d) 8.5 vol.% ethanol for 4 days.

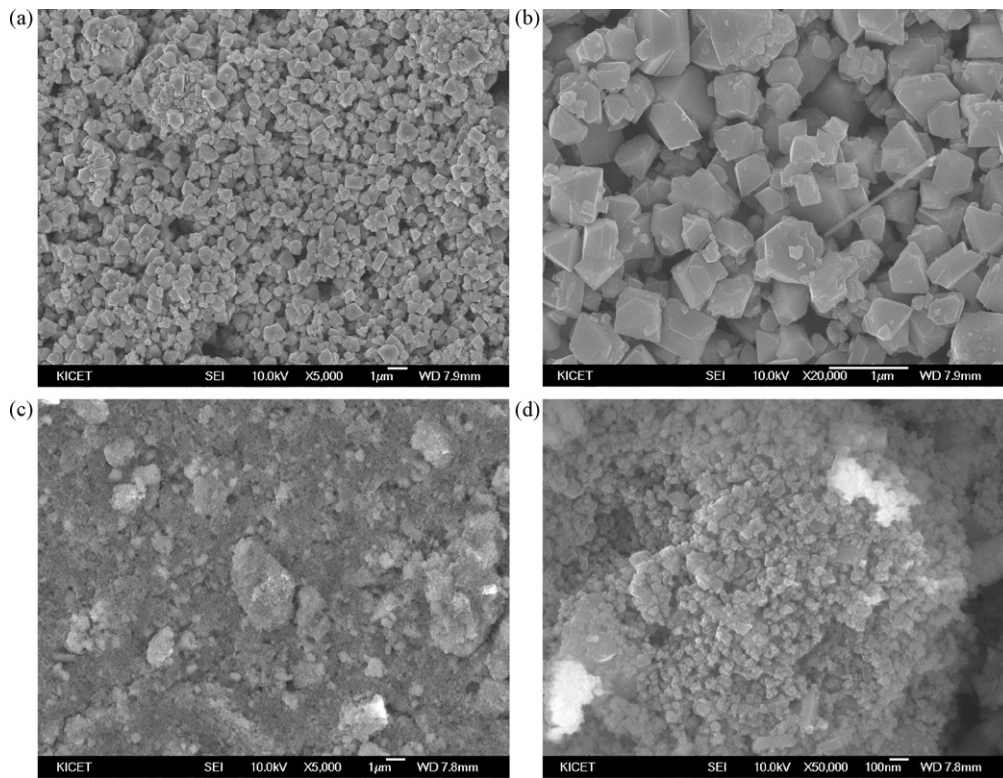


Fig. 2. SEM images of samples prepared in pure water ((a) 5000 \times and (b) 20,000 \times) and the solvent containing 1.4 vol.% ethanol for 4 days ((c) 5000 \times and (d) 50,000 \times).

3.3. Effect of amount of co-solvent

X-ray diffraction patterns of samples prepared hydrothermally with different amounts of ethanol in the solvent are shown in Fig. 1. As mentioned above, γ - MnO_2 is found in the sample prepared in pure water. The peaks for Mn_3O_4 , an impurity phase formed in the mixed solvent, become more intense with increasing amount of ethanol added. The crystallite sizes of the (1 1 1) plane listed in Table 1 show that the crystallite size of the Li–Mn spinel decreases

with increasing ethanol content that is caused by disorder in the atomic array of the crystals.

Scanning electron micrograph of the samples are presented in Fig. 6. The Li–Mn spinel particles are approximately 1 μm in size with an octahedral shape when the ethanol content in the solvent is 1.4 vol.%. Such a small amount of ethanol can dramatically alter the particle size and morphology. With the further addition of ethanol,

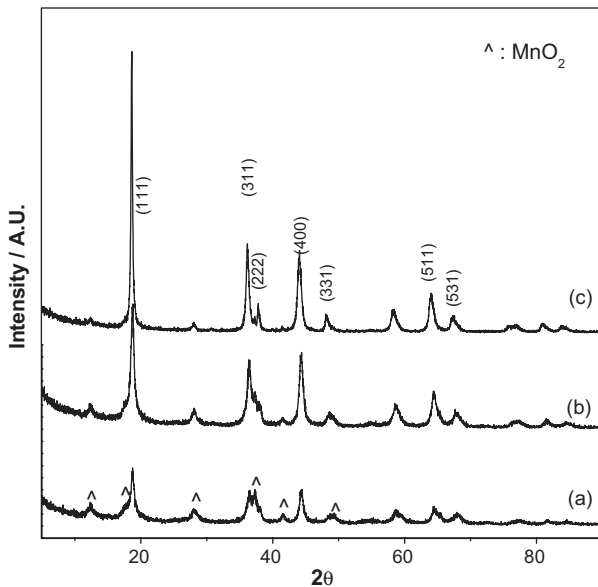


Fig. 3. XRD patterns of samples prepared in pure water for various reaction times (for (a) 2, (b) 4 and (c) 6 days).

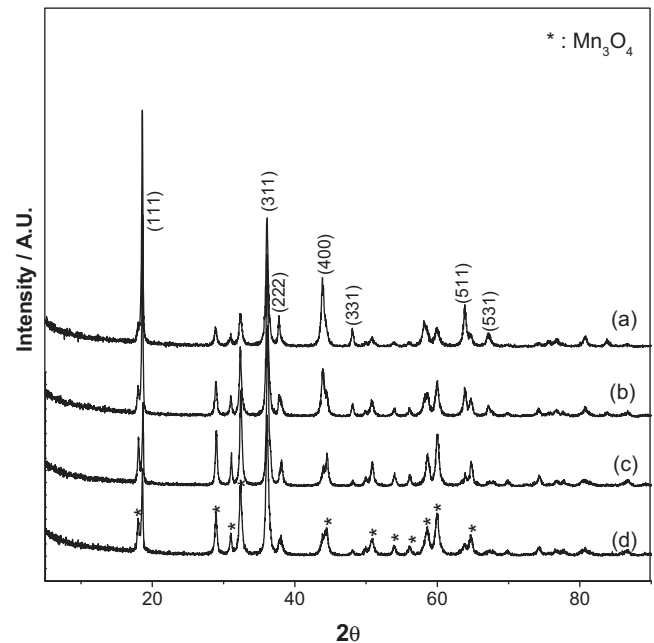


Fig. 4. XRD patterns of samples prepared in solvent containing 8.5 vol.% ethanol for various reaction times (for (a) 1, (b) 2, (c) 4 and (d) 6 days).

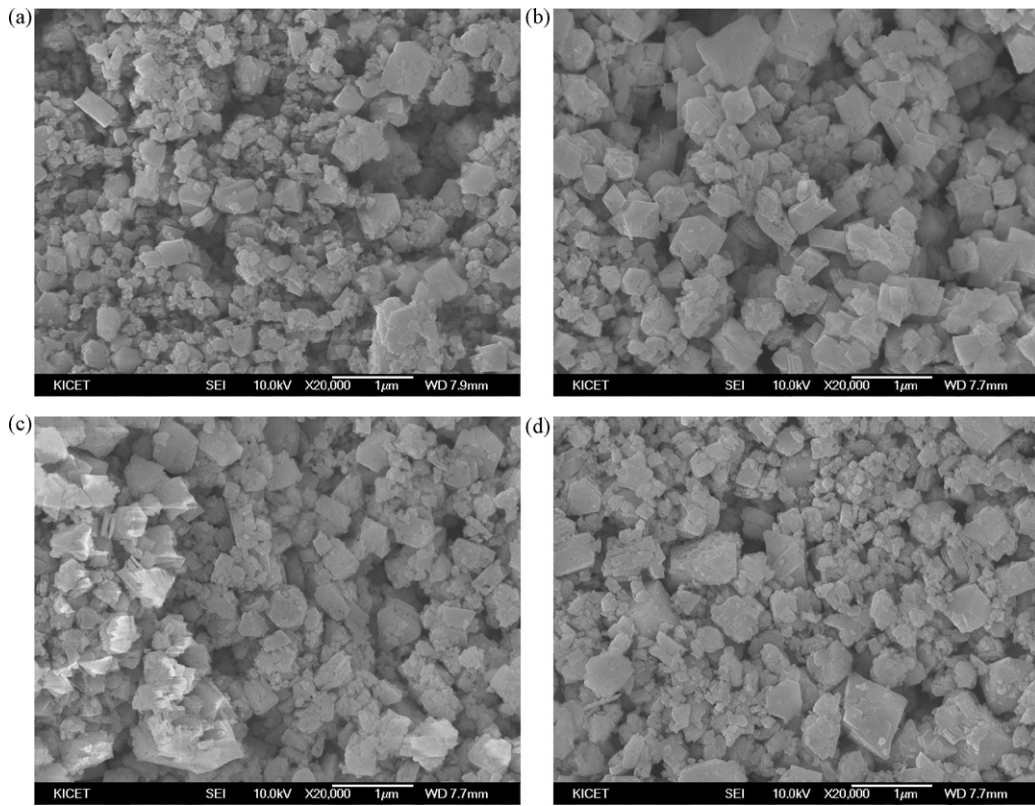


Fig. 5. SEM images of samples prepared in solvent containing 8.5 vol.% ethanol for various reaction times (for (a) 1, (b) 2, (c) 4 and (d) 6 days).

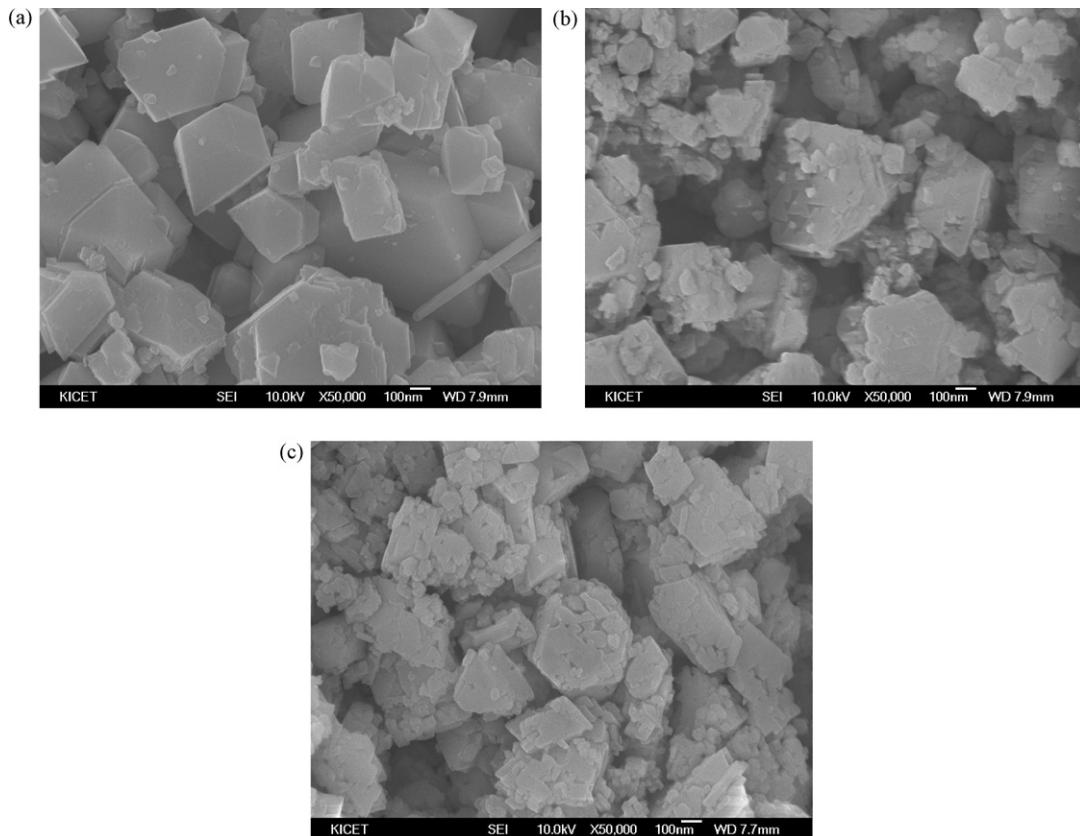


Fig. 6. SEM images of samples prepared in solvents containing different amounts of ethanol ((a) 1.4, (b) 2.9 and (c) 8.5 vol.%).

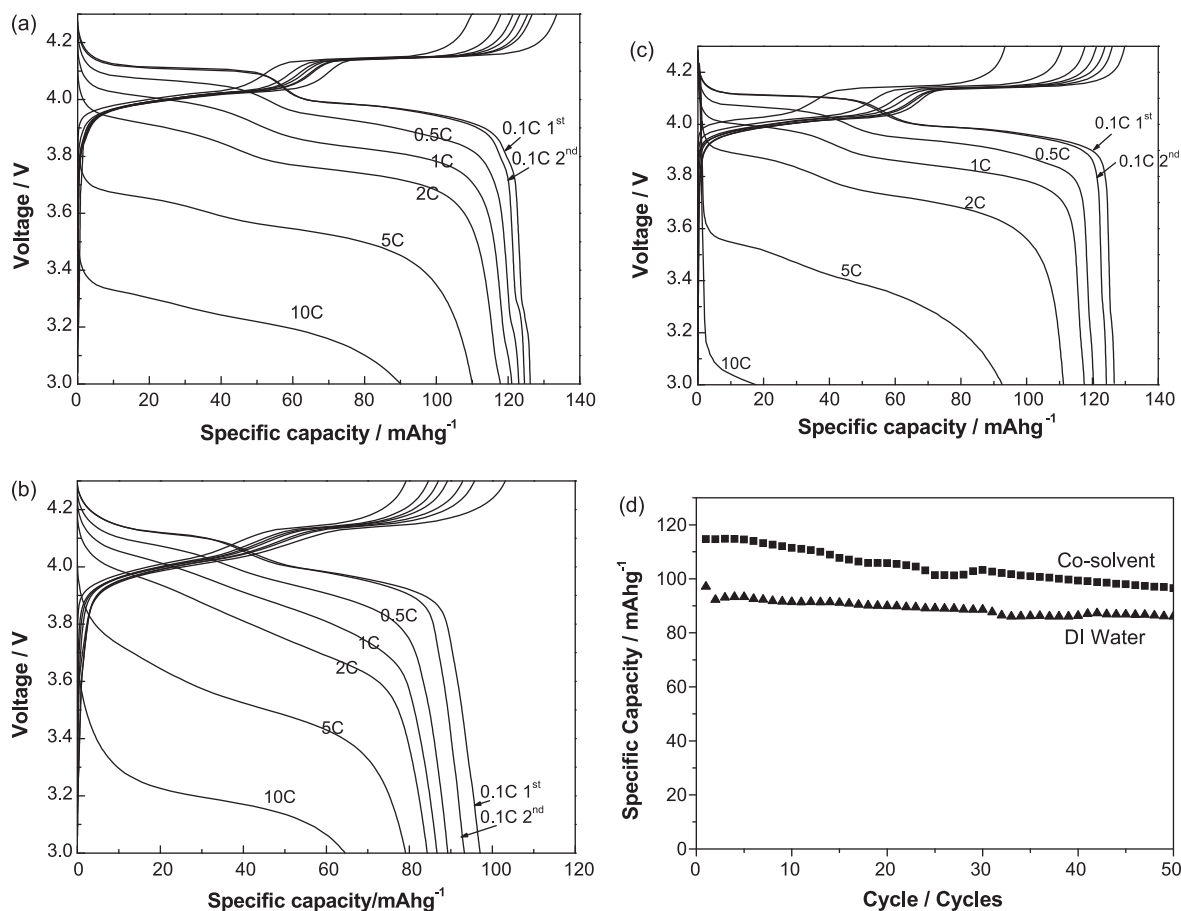


Fig. 7. Charge–discharge profile of Li–Mn spinel prepared in (a) solvent containing 1.4 vol.% ethanol, (b) pure water and (c) by a solid-state process. (d) cyclability of the Li–Mn spinel measured at a charge and discharge rate of 0.5 C.

the Li–Mn spinel particles change to aggregates of smaller primary particles, which can promote the conversion of Li–Mn spinel into Mn_3O_4 and thereby enhance contact and reactivity with ethanol.

3.4. Electrochemical performance of Li–Mn spinel

Fig. 7(a–c) shows a typical charge–discharge profile of the Li–Mn spinel prepared in the mixed solvent with an ethanol content of 1.4 vol.% (for 4 days), pure water (for 10 days) and by conventional solid-state process, respectively. These samples were selected because of their similar high purity, as confirmed by XRD. The profiles are typical of Li–Mn spinel with two distinct plateaus at approximately 4.0 V. In the case of Li–Mn spinel prepared in the mixed solvent, the capacity at a 0.1 C rate is approximately 127 mAh g^{-1} , whereas that prepared in pure water is $\sim 98 \text{ mAh g}^{-1}$. The lithium-rich composition in the latter sample, as inferred from the lattice constant (see Table 1), appears to be the reason for the low capacity. The retention of discharge capacity retention is approximately 70 and 64% at the 10.0 C rate vs. 0.1 C rate for the Li–Mn spinel prepared in the mixed solvent and pure water, respectively. By contrast, the Li–Mn spinel prepared by a solid-state process shows only 13% capacity retention at the 10.0 C rate.

Several studies have attempted to improve the rate capability of Li–Mn spinel and include preparing nanostructured materials using a template, composites with carbon, and cation or anion doping [22–25]. In general, they used a very complicated process or highly conducting materials (as much as 20 wt.% carbon) to achieve a high-rate capability. In this study, just adding a small amount of ethanol is sufficient to obtain high-rate performance as well as high capacity. A small particle size provides high-rate capability due to

the short diffusion length and large surface area. The particle size of Li–Mn spinel prepared in the mixed solvent is dependent on the amount of ethanol added. The primary particle is $< 1 \mu\text{m}$, and this results in high-rate performance. The Li–Mn spinel synthesized in pure water has a smaller primary particle size and poorer rate capability than those prepared in the mixed solvents. This can be explained by the dense aggregation of particles prepared in pure water, which restricts contact between the electrolyte and electrode material, and mitigates the effect of the small particle size. The cyclability of the Li–Mn spinel samples was measured at the 0.5 C rate in the charge and discharge cycles, and the results are reported in Fig. 7(c). 84 and 88% of the initial capacity is retained for a sample prepared in the mixed solvent and pure water after 50 cycles, respectively. This is not good performance at room temperature. To improve the cyclability, further optimization of the composition, e.g., Li-rich composition or doping with other metals, appears to be essential.

4. Conclusions

Li–Mn spinel is synthesized using a hydrothermal process with ethanol as the co-solvent. Submicron-sized Li–Mn spinel with high crystallinity and uniform particle morphology can be obtained in the presence of ethanol, whereas that prepared in pure water produces densely aggregated nano-particles. The kinetics and mechanism of the formation of Li–Mn spinel in pure water and ethanol-added water are different. In pure water, MnO_2 gradually converts to Li–Mn spinel via a reaction with LiOH but Li–Mn spinel is formed at the early stages and is converted gradually to Mn_3O_4 in

ethanol-added water. Ethanol helps reduce Li–Mn spinel to Mn_3O_4 . Pure Li–Mn spinel with high crystallinity can be obtained in a short time by adding small amounts of ethanol. Li–Mn spinel prepared in a mixed solvent shows high capacity and good rate capability due to its high purity and small particle size.

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References

- [1] M.M. Thackeray, P.J. Johnson, L.A. de Picciotto, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 19 (1984) 179.
- [2] Y.-S. Lee, Y.-K. Sun, K.-S. Nahm, *Solid State Ionics* 109 (1998) 285.
- [3] C. Wan, M. Wu, D. Wu, *Powder Technol.* 199 (2010) 154.
- [4] G. Amatucci, A.D. Pasquier, A. Blyr, T. Zheng, J.-M. Tarascon, *Electrochim. Acta* 45 (1999) 255.
- [5] Y. Xia, N. Kumada, M. Yoshio, *J. Power Sources* 90 (2000) 135.
- [6] W. Lu, I. Belharouak, S.H. Park, Y.K. Sun, K. Amine, *Electrochim. Acta* 52 (2007) 5837.
- [7] C.P. Fonseca, M.A. Bellei, F.A. Amaral, S.C. Canobre, S. Neves, *Energy Convers. Manage.* 50 (2009) 1556.
- [8] K. Amine, H. Tukamoto, H. Yasuda, Y. Fujita, *J. Power Sources* 68 (1997) 604.
- [9] Y.S. Hong, C.H. Han, K. Kim, C.W. Kwon, G. Campet, J.H. Choy, *Solid State Ionics* 139 (2001) 75.
- [10] G. Kumar, H. Schlorb, D. Rahner, *Mater. Chem. Phys.* 70 (2001) 117.
- [11] A. Eftekhari, *Solid State Ionics* 167 (2004) 237.
- [12] J.S. Gnanaraj, V.G. Pol, A. Gedanken, D. Aurbach, *Electrochem. Commun.* 5 (2003) 940.
- [13] M.W. Raja, S. Mahanty, R.N. Basu, *Solid State Ionics* 180 (2009) 1261.
- [14] Q. Feng, H. Kanoh, Y. Miyai, K. Ooi, *Chem. Mater.* 7 (1995) 1226.
- [15] S.H. Ye, J.K. Bo, C.Z. Li, J.S. Cao, Q.L. Sun, Y.L. Wang, *Electrochim. Acta* 55 (2010) 2972.
- [16] Y.C. Zhang, H. Wang, H.Y. Xu, B. Wang, H. Yan, A. Ahnizay, M. Yoshimura, *Solid State Ionics* 158 (2003) 113.
- [17] K. Kanamura, K. Dokko, T. Kaizawa, *J. Electrochem. Soc.* 152 (2005) A391.
- [18] H.M. Wu, J.P. Tu, Y.F. Yuan, X.T. Chen, J.Y. Xiang, X.B. Zhao, G.S. Cao, *J. Power Sources* 161 (2006) 1260.
- [19] C.H. Jiang, S.X. Dou, H.K. Liu, M. Ichihara, H.S. Zhou, *J. Power Sources* 172 (2007) 410.
- [20] H. Yue, X. Huang, D. Lv, Y. Yang, *Electrochim. Acta* 54 (2009) 5363.
- [21] W.L. He, Y.C. Zhang, X.X. Zhang, H. Wang, H. Yan, *J. Cryst. Growth* 252 (2003) 285.
- [22] J.-Y. Luo, Y.-G. Wang, H.-M. Xiong, Y.-Y. Xia, *Chem. Mater.* 19 (2007) 4791.
- [23] A.R. Han, T.W. Kim, D.H. Park, S.J. Hwang, J.H. Choy, *J. Phys. Chem. C* 111 (2007) 11347.
- [24] B. Deng, H. Nakamura, M. Yoshio, *J. Power Sources* 141 (2005) 116.
- [25] Y.-J. Kang, J.-H. Kim, Y.K. Sun, *J. Power Sources* 146 (2005) 237.