Ionics (2009) 15:779–784
DOI 10.1007/s11581-009-0373-x

REVIEW

A review of recent developments in the surface modification of $LiMn_2O_4$ as cathode material of power lithium-ion battery

Ting-Feng Yi · Yan-Rong Zhu · Xiao-Dong Zhu ·
J. Shu · Cai-Bo Yue · An-Na Zhou

Received: 1 April 2009 / Revised: 6 April 2009 / Accepted: 28 July 2009 /

Abstract $LiMn_2O_4$ (LMO) is a very attractive choice as cathode material for power lithium-ion batteries due to its economical and environmental advantages. However, $LiMn_2O_4$ in the 4-V region suffers from a poor cycling behavior. Recent research results confirm that modification by coating is an important method to achieve improved electrochemical performance of LMO, and the latest progress was reviewed in the paper. The surface treatment of LMO by coating oxides and nonoxide systems could decrease the surface area to retard the side reactions between the electrode and electrolyte and to further diminish the Mn dissolution during cycling test. At present, $LiMn_2O_4$ is the mainstreaming cathode material of power lithium-ion battery, and, especially the modified LMO, is the trend of development of power lithium-ion battery cathode material in the long term.

Keywords Power lithium-ion battery · Cathode material · $LiMn_2O_4$ · Surface modification

T.-F. Yi (✉) · Y.-R. Zhu · C.-B. Yue · A.-N. Zhou
School of Chemistry and Chemical Engineering,
Anhui University of Technology,
No 59 Hudong Road,
Maanshan 243002, People's Republic of China
e-mail: tfyihit@163.com

X.-D. Zhu (✉)
Science Research Center, Academy of Fundamental
and Interdisciplinary Sciences, Harbin Institute of Technology,
Harbin, Heilongjiang 150001, People's Republic of China
e-mail: zxd9863@163.com

J. Shu
College of Materials Science and Chemical Engineering,
Ningbo University,
Ningbo, Zhejiang 315211, People's Republic of China

Introduction

Lithium-ion batteries are regarded as promising new power sources for hybrid electric vehicles as well as for portable electronic devices due to their long cycle life and high energy density. Spinel $LiMn_2O_4$ is one of the most promising cathodes because of its low material cost, high natural abundance, environmental harmlessness, and good safety compared with the $LiCoO_2$ used in current batteries [1–10]. Unfortunately, $LiMn_2O_4$ shows fast capacity fading during cycling, which has been an obstacle to its commercialization. The capacity fading has been ascribed to the following possible factors: (1) dissolution of Mn^{2+} [2], (2) Jahn–Teller distortion of Mn^{3+} ions [3], and (3) decomposition of electrolyte solution on the electrode [4]. Of the above factors, dissolution of manganese into the electrolyte during cycling is believed to be the main one. To solve these problems, many researchers have studied the mechanism of capacity fading and have put forward some method to overcome capacity fading by doping the spinel with several cations, such as Al [5], Mg [6], transition metal ions [7–10], etc., to enhance the structural stability. However, Mn dissolution resulted from some side reactions that occurred at the interface between the electrode and the electrolyte during the charge/discharge process [11]. As the cathode electrode contacted with the Li-based electrolyte directly in Li-ion batteries, Mn dissolution was induced by the generation of acids like hydrogen fluoride (HF), which was resulted from the reactions of fluorinated anions with the manufacture of instable Li-based salt [12] and solvent oxidation [13]. In order to solve this problem, surface modification of the cathode electrode is an effective way to reduce the side reactions. By coating oxides and nonoxide systems, the surface treatment of spinel $LiMn_2O_4$ could decrease the surface area to retard the side reactions between the electrode and electrolyte and to further diminish the Mn dissolution during cycling test. Here, we reviewed the recent progress on this aspect, and future directions were pointed out.

LMO coated by oxides systems

Oxides coating over $LiMn_2O_4$ (LMO) can suppress the dissolution reaction of manganese ions at elevated temperature and clearly improve the cycleability of the spinel $LiMn_2O_4$ cathode materials. The coated oxides include nano-SiO_2 [14], MgO [15, 16], ZnO [17–20], CeO_2 [21], ZrO_2 [22, 23], Al_2O_3 [23, 24], and Co–Al mixed metal oxide [25]. The schematic diagram of the metal oxide coating LMO procedure can be shown in Fig. 1 [15]. The synthesis methods and the electrochemical performance of LMO coated by oxides are shown in Table 1.

It can be concluded that the surface coating of LMO with metal oxides could be an effective way to improve its electrochemical performance at elevated temperatures in practical batteries.

LMO coated by nonoxide systems

The nonoxide systems include metal phosphates, metal, other electrode materials, carbon, fluoride, or other novel materials.

Metal phosphates

It has been reported that the $AlPO_4$ coating exhibited better thermal stability than the metal oxide coating for lithium-ion battery [26, 27]. Hence, it can be expected that $AlPO_4$-coated LMO has an improved electrochemical performance. $AlPO_4$-coated LMO was synthesized as follows [28]: LMO powders (prepared by solid-state method) were slowly dispersed into the $AlPO_4$ solution under constant stirring for 5 h, and then the mixed slurry was dried in an oven for 2 h at 100 °C and subsequently annealed at 700 °C under air for 3 h in a furnace. The uncoated LiMO showed 17.9% and 32.9% capacity loss in 50 cycles at 30 °C and 55 °C, respectively; the $AlPO_4$-coated LMO only exhibited the capacity loss of 2.6% and 7.6% at 30 °C and 55 °C, respectively. The improvement of cycleability is ascribed to the $AlPO_4$ film, minimizing the contact area of $LiMn_2O_4$/electrolyte interface, thus, suppressing the dissolution of Mn effectively [28].

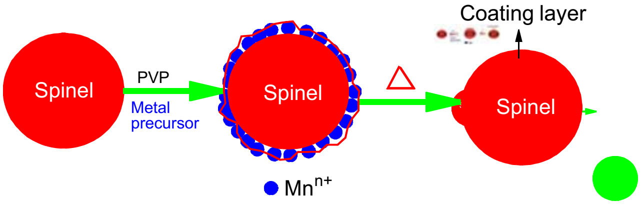

Fig.1 Schematic diagram of the metal oxide coating LMO procedure from [15]

Metal

It is well known that gold and silver belong to the lowest-resistance metals; hence, they can be expected to enhance electron conduction of coated LMO and then improve its electrochemical performance. Tu et al. [29] have reported that a nano-gold film-coated LMO by ion sputtering method shows better capacity retention at room temperature than that of uncoated LMO, which is attributed to reduce contact area of electrode/electrolyte interface and suppressed dissolution of manganese during electrochemical cycling. Zhou et al. [30] reported that the initial discharge capacity was decreased with increasing the amount of Ag coating, but Ag (0.1)/LMO exhibits the highest discharge capacity after 40 cycles 108 mAh g^{-1} among all samples. Son et al. [31] also reported that the silver-coated nanoparticle LMO (3.2 wt.% Ag) shows excellent cycleability at 2 C galvanostatic conditions. It can be concluded that the improved cycleability of metal coating LMO can be attributed to enhanced electron conduction between LMO particles because of the low resistance of silver and gold.

Electrode materials

The LMO surface coated with other electrode materials can probably be an effective way to improve the electrochemical performance at room temperature and elevated temperature. The reason for the improved elevated temperature properties of LMO coated by other electrode materials is that the surface coating reduces the dissolution of Mn, which results from the suppression of the electrolyte decomposition. The coated electrode materials include $LiCoO_2$ performed by sol–gel methods [32–34] and microemulsion method [35], $LiNi_{0.8}Co_{0.2}O_2$ [36], $Li_4Ti_5O_{12}$ [37, 38], $LiNi_{0.05}Mn_{1.95}O_4$ [39], and $LiCu_xMn_{2-x}O_4$ [40]. The synthesis methods and the electrochemical performance of coating by other electrode materials are plotted in Table 2.

Carbon materials

Carbon coating has been known to be effective not only in enhancing the electrical conductivity of metal oxides but also in increasing their absorbing ability against organic molecules. In addition, a coated carbon layer would protect the metal oxides from chemical corrosion. Han et al. reported that [41] the coated carbon layer composed of disordered amorphous carbon and polycyclic aromatic

Table 1 Synthesis methods and the electrochemical performance of LMO coated by metal oxide

Coated oxides and references	Synthesis	Electrochemical performances
Nano-SiO_2 [14]	LMO powder was prepared by the sol–gel method calcinated at 850 °C for 15 h. SiO_2-coated LMO were synthesized by polymeric process at the calculation of 1.0, 2.0, and 3.0 wt.% by using silicic acid as the coating of raw materials.	2.0 wt.% of SiO_2-coated LMO has significantly improved the capacity retention and excellent cycleability for 30 °C and 60 °C compared with the uncoated LMO because the formation of a passive layer film during electrochemical cycling is controlled.
MgO [16]	LMO powder was obtained from Merck KGaA (highly pure, Li battery grade). MgO-coated LMO was synthesized as follows: the mixed solution of LMO and $(CH_3COO)_2$ Mg·$4H_2O$ is added with aqueous ammonia, then centrifuged, and washed. The formed product was further dried at 450 °C under air for 4 h.	The capacity fading of MgO-coated LMO electrodes at elevated temperatures is much smaller compared to regular LMO electrodes.
ZnO [17]	LMO was synthesized by a solid-state method. LMO was added into the mixed solution of zinc acetate and triethanolamine and evaporated at 80 °C until a black gel formed. The gel was dried at 100 °C for 2 h and calcined for 6 h at 500 °C to obtain the ZnO-coated LMO.	Uncoated LMO delivered an average capacity loss of 0.81% per cycle in 50 cycles; the 1 wt.%, 2 wt.%, and 5 wt.% ZnO-coated LMO only showed the average capacity loss of 0.54%, 0.19%, and 0.14% per cycle, respectively, under a current rate of C/2 at 55 °C between 3.4 and 4.3 V.
CeO_2 [21]	LMO was synthesized by a solid-state method. For preparing CeO_2-coated LMO powder by using a polymeric precursor based on the Pechini method.	The initial discharge capacity was decreased with the increased amount of CeO_2 coating, and 2% CeO_2-coated LMO exhibits a slight decrease in its original specific capacity of 107 mAh g^{-1} and excellent capacity retention (more than 82% of its initial capacity).
ZrO_2 [22]	LMO was from Sedema(Belgium). For making the Zr oxide coating layer, Zr butoxide was mixed with 1-butanol in a volume ratio of alkoxide/alcohol = 1:4 under ultrasonic agitation for 30 min. LMO powder was then dispersed into the coating solution, followed by settling under vacuum. The dispersion solution was then evaporated. Finally, the coated powder was calcined at 400 °C, ground, and sieved.	5 wt % ZrO_2-coated LMO shows tremendous enhancement in cycling stability at CD rates up to 10 C, and the coated spinel electrode exhibits a lower cubic-tetragonal transition potential, a smaller charge-transfer impedance by 4- to 5-fold, and it profoundly reduces lattice contraction by 66% upon charge.
Al_2O_3 [24]	A sol precursor for coating was prepared by mixing ethyl alcohol and $AlCl_3·6H_2O$ (Junsei, Japan) and then $LiMn_{2-x}M_xO4$ (Nikki, Japan, M = Zr, reversible capacity: 100 mAh g^{-1}) was immersed in sol precursor. After drying at 80 °C, the powder obtained was calcinated at 500 °C for 3 h.	The initial capacity of Al_2O_3-coated LMO is higher than that of the bare LMO, and the cell performance was enhanced with the Al_2O_3 coating. Al_2O_3-coated samples have improved interfacial properties between the electrolyte and electrode.
Co–Al mixed metal oxide [25]	LMO powder was provided by Shijiazhuang Best BatteryMaterial Co., Ltd. (China). The mixed solution of LMO, $Co(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$ is added with $LiOH·H_2O$ solution to maintain the mixture at pH 10.5 with vigorous agitation for 3 h, and then filtered and dried at 120 °C for 12 h, and subsequently heat-treated in a furnace at different temperatures for 5 h in air. The amount of Co in the coating solution was varied from 2 to 4 wt.% (based on LMO) while the amount of Al in the coating solution was fixed at 0.5 wt.% (based on LMO).	The CoAl-MMO-coated (3 wt.% Co and 0.5 wt.% Al based on LMO) LMO after heat treatment at 400 °C shows the best cycling stability with a specific discharge capacity of 100 mAh g^{-1} and 92.2 $mAhg^{-1}$ after 50 cycles at 25 °C and 55 °C, respectively. This is much higher than that of the pristine LMO (97.4 and 73.7 $mAhg^{-1}$ at 25 °C and 55 °C, respectively).

Table 2 Synthesis methods and the electrochemical performance coated by other electrode materials

Other electrode coating materials [references]	Synthesis	Electrochemical performances
$LiCoO_2$ [33]	Stoichiometric amounts of lithium acetate and cobalt acetate were dissolved in distilled water. An aqueous glycolic acid water solution was then added to this mixture solution to produce a gel-type solution, and the pH value was controlled at 6.5–7.0. The resultant solution was evaporated until its concentration reached about 1 mol/l. The commercial LMO powder was then added to this resultant coating solution while stirring, and then screened with a centrifuge. The screened powder was dried in a vacuum oven and calcined for 6 h at 800 °C.	$LiCoO_2$-coated LMO showed a higher discharge capacity of 120 mAh/g than $LiMn_2O_4$ (115 mAh/g). LMO maintained only 50% of its maximum capacity at a 20-C rate (2400 mA/g); the $LiCoO_2$-coated LMO maintained more than 80% of maximum capacity. $LiCoO_2$-coated LMO with 3 wt.% conducting agent (acetylene black) showed the higher rate capability than as-received LMO with 20 wt.% conducting agent.
$LiNi_{0.8}Co_{0.2}O_2$ [36]	Stoichiometric amounts of acetate and glycolic acid were mixed in distilled water according to priority, and the pH was controlled 6.5–7.0. The resultant solution concentration of was controlled at 0.7–1 mol/l. Commercial LMO was then added to this coating solution with a constant stirring. The powder in the coating solution was screened with a centrifuge to remove the remaining coating solution. The screened powder was dried in a vacuum oven and was calcined for 6 h at 750 °C in oxygen atmosphere.	The coated LMO showed an excellent capacity retention at 65 °C compared with pure LMO. The capacity of pure LMO decreased drastically with cycling at 65 °C, and $LiNi_{0.8}Co_{0.2}O_2$-coated LMO shows lower 0.08% per cycle loss. $LiNi_{0.8}Co_{0.2}O_2$-coating is a very effective in improving the elevated temperature properties.
$Li_4Ti_5O_{12}$ [37]	LMO was prepared by a citric acid-assisted sol–gel method. Tetrabutyltitanate, lithium acetate, and acetic acid were dissolved in a mixed solution containing ethanol and distilled water according to priority. And then, the as-prepared LMO was added to the previously mentioned sol under stirring. The gelatin so formed was dried at 100 °C for 1 h and fired at 800 °C for 1 h to obtain the final powders.	The LMO delivered a discharge capacity of 116 mAh g^{-1} at the first cycle and remained only 71.4 mAh g^{-1} after 45 cycles. The capacity loss was about 0.99% at 55 °C. However, 0.62% and 0.45% capacity loss per cycle were found for 2 and 5 mol% LTO-coated LMO. The improvement of electrochemical performance is attributed to the suppression of electrolyte decomposition on the surface of LMO.
$LiNi_{0.05}Mn_{1.95}O_4$ [39]	By a tartaric acid gel method	In comparison with the unmodified LMO, the $LiNi_{0.05}Mn_{1.95}O_4$-modified LMO exhibited excellent electrochemical characteristics, the same initial discharge capacity of 125 mAh g^{-1}, high charging–discharging efficiency, and good cycle stability.
$LiCu_xMn_{2-x}O_4$ [40]	The precursor of LMO was calcined at 600 °C for 10 h and mixed with $Cu(CH_3COO)_2$ in deionized water. The mixture powders were then calcined at 870 °C for 10 h to synthesize $LiCu_xMn_{2-x}O_4$-coated LMO composite.	$LiCu_xMn_{2-x}O_4$-coated LMO composite cathode material exhibited better electrochemical performance than the base LMO, especially at high C rates.

hydrocarbons can modify the cubic spinel-type atomic arrangement of lithium manganate, and that the carbon coating can improve the electrode performance of spinel lithium manganate because of the increase of grain connectivity and/or the protection of manganese oxide from chemical corrosion. Patey et al. [42] reported that LMO/carbon nanocomposites had a considerably higher specific galvanostatic discharge capacity at a 5-C rate or greater than the electrode with powder of pure LMO, and the specific energy of a thin-layer lithium-ion battery containing the flame-made LMO/carbon nanocomposite as positive electrode and LiC_6 as negative electrode (78 Wh kg^{-1} at 50-C rate).

Fluoride

Fluoride is also used to coat LMO to improve its cycleability because it is very stable even in HF. Li et al. [43] reported that the discharge capacity of LMO decreases slightly with increasing the amount of the coated SrF_2 to 2.0%, but the cycleability of LMO at elevated temperature is improved obviously. LMO remains only 79% of its initial capacity after 20 cycles, whereas the 2.0% (molar fraction) coated LMO shows 97% of its initial capacity retention cycle at 55 °C. Lee et al. [44] reported that the BiOF-coated spinel $Li_{1.1}Al_{0.05}Mn_{1.85}O_4$ electrode had excellent capacity retention at 55 °C, maintaining its initial discharge capacity of 96.1% after 100 cycles while that of the pristine material was only 84.4% compared with the initial discharge capacity.

Novel materials

It is well known that molten $Li_2O–2B_2O_3$ (LBO) compositions exhibit a combination of good wetting properties and relatively low viscosity in the molten state and also exhibit good ionic conductivity [45, 46]; LBO materials also are stable against the high oxidation potentials of the 4-V positive electrode materials used in Li-ion batteries. The side reaction and Mn dissolution between the interface of the cathode electrode and electrolyte was reduced significantly by surface modification of LBO glass in the LMO. Chan et al. [47] have reported that LMO cathode materials coated with LBO via solid-state method exhibited relatively good cycling performance, but the capacity fade was still 2.63% after 10 cycles at a current rate of 0.1 C. Şahan et al. [48] reported that the capacity retention of LBO-coated LMO via solid-state method is 7.5% after 30 cycles, and LBO-coated LMO electrode via solution method has an excellent cycling behavior without any capacity loss even after 30 cycles at room temperature and a 1-C rate as plotted in Fig. 2. Chan et al. [49] have also reported that $Li_{1.08}Mn_2O_4$ cathode materials coated with LBO have a better high-temperature performance than that of $Li_{1.08}Mn_2O_4$. The LBO-coated cathode powder with the fading rate of only 7% after 25 cycles showed better cycleability than the base one with the fading rate of 17% after 25 cycles at higher temperature.

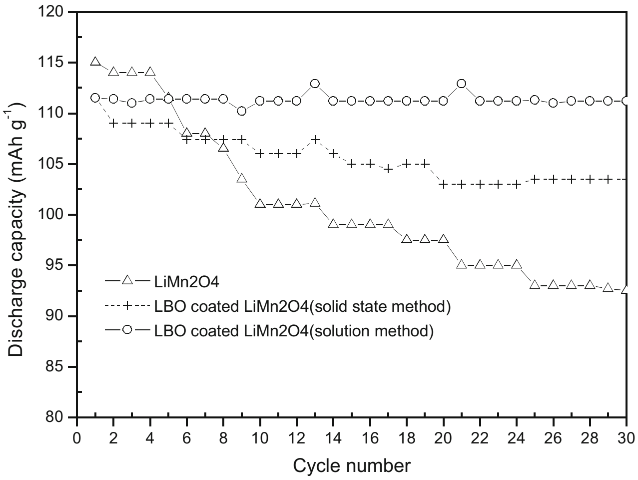

Fig. 2 Cycleability of all LMO materials at1-C discharge rate at room temperature from [48]

The polymer possesses the antioxidative capability, and slowly expands instead of dissolving while dipping it in the electrolyte for a long time. As a result, the modified LMO-based cathode displays an improved stability during repeated charge/discharge in organic electrolyte at an elevated temperature [50, 51]. Hu et al. [50] reported that the electrochemical storage properties of the spinel at 55 °C based on the LMO film surface decorated with the functional polymer was improved, and the 45th discharge capacity was improved at 55 °C from 56.8 to 81.4 mAh g^{-1} on the LMO electrode. Arbizzani et al. [51] reported that poly(3,4-ethylenedioxy) thiophene (pEDOT) can function as an electronic conductor and substitute the carbon usually mixed with the inorganic oxide-based electrodes to improve the electronic conductivity of nonstoichiometric $Li_{1.03}Mn_{1.97}O_4$ spinel, and the reversible capacity and capacity retention are increased.

Prospect

From the above illustrations, it can be concluded that coated LMO is one of the promising cathode materials for power lithium-ion batteries for electric vehicles since they show excellent performances, such as high capacity, good cycleability, high rate capability, high thermal stability, and high-temperature performance. Surface coatings such as metal oxide and other compounds/composites on LMO can prevent the direct contact of electrolyte solutions with cathode materials, reduce the generation of acids like HF, improve structural stability, and suppress phase transitions. It is sure that the surface coating of LMO cathode materials will play, more and more, an important role in improving its electrochemical performance. Better and/or cheaper LMO cathode materials from surface modification will come up in the near future [52–55]. At present, LMO is the mainstreaming cathode material of power lithium-ion battery, and, especially the modified LMO, is the trend of development of power lithium-ion battery cathode material in the long term.

References

1. Thackeray MM, Johnson PJ, de Picciotto LA, Bruce PG, Goodenough JB (1984) Mater Res Bull 19:179
2. Amatucci GG, Schmutz CN, Blyr A, Sigala C, Gozdz AS, Larcher D, Tarascon JM (1997) J Power Sources 69:11
3. Wohlfahrt-Mehrens M, Vogler C, Garche J (2004) J Power Sources 127:58
4. Xia Y, Zhou Y, Yoshio M (1997) J Electrochem Soc 144:2593
5. Xia Y, Zhang Q, Wang H, Nakamura H, Noguchi H, Yoshio M (2007) Electrochim Acta 52:4708
6. Jeong I-S, Kim J-U, Gu H-B (2001) J Power Sources 102:55
7. Sun Y-K, Hong K-J, Prakash J, Amine K (2002) Electrochem Commun 4:344
8. Ein-Eli Y, Vaughey JT, Thackeray MM, Mukerjee S, Yang XQ, McBreen J (1999) J Electrochem Soc 146:908
9. Molenda J, Marzec J, Świerczek K, Pałubiak D, Ojczyk W, Ziemnicki M (2004) Solid State Ionics 175:297
10. Yi TF, Hu XG, Huo HB, Gao K (2006) Rare Metal Mat Eng 35:1350
11. Arora P, White RE, Doyle M (1998) J Electrochem Soc 145:3647
12. Aubarch D, Zaban A, Schlecter A, Ein-Eli Y, Zinigrad E, Markowsky B (1995) J Electrochem Soc 142:2873
13. Jang DH, Oh SM (1997) J Electrochem Soc 144:3342
14. Arumugam D, Kalaignan GP (2008) J Electroanal Chem 624:197–204
15. Lim S, Cho J (2008) Chem Commun 37:4472–4474
16. Gnanaraj JS, Pol VG, Gedanken A, Aurbach D (2003) Electrochem Commun 5:940–945
17. Liu D, Liu X, He Z (2007) J Alloys Compd 436:387–391
18. Tu J, Zhao XB, Xie J, Cao GS, Zhuang DG, Zhu TJ, Tu JP (2007) J Alloys Compd 432:313–317
19. Liu H, Cheng C, Hu Z, Zhang K (2007) Mater Chem Phys 101:276–279
20. Liu H, Cheng C, Hu Z, Zhang K (2005) J Mater Sci 40:5767–5769
21. Ha H-W, Yun NJ, Kim K (2007) Electrochim Acta 52:3236–3241
22. Lin Y-M, Wu H-C, Yen Y-C, Guo Z-Z, Yang M-H, Chen H-M, Sheu H-S, Wu N-L (2005) J Electrochem Soc 152:A1526–A1532
23. Kim J-S, Johnson CS, Vaughey JT, Hackney SA, Walz KA, Zeltner WA, Anderson MA, Thackeray MM (2004) J Electrochem Soc 151:A1755–A1761
24. Lee S-W, Kim K-S, Moon H-S, Kim H-J, Cho B-W, Cho W-I, Ju J-B, Park J-W (2004) J Power Sources 126:150–155
25. Yang Z, Yang W, Evans DG, Zhao Y, Wei X (2009) J Power Sources 189:1147–1153
26. Cho J, Kim Y-W, Kim B, Lee J-G, Park B (2003) Angew Chem Int Ed 42:1618
27. Cho J, Lee J-G, Kim B, Park B (2003) Chem Mater 15:3190
28. Liu DQ, He ZZ, Liu XQ (2007) Mater Lett 25:4703
29. Tu J, Zhao XB, Cao GS, Tu JP, Zhu TJ (2006) Mater Lett 60:3251–3254
30. Zhou W-J, He B-L, Li HL (2008) Mater Res Bull 43:2285
31. Son JT, Park KS, Kim HG, Chung HT (2004) J Power Sources 126:182
32. Kannan AM, Manthiram A (2002) Electrochem Solid State Lett 5:A167
33. Park SC, Kim YM, Kang YM, Kim KT, Lee PS, Lee JY (2001) J Power Sources 103:86
34. Park SC, Han YS, Kang YS, Lee PS, Ahn S, Lee HM, Lee JY (2001) J Electrochem Soc 148:A680
35. Liu Z, Wang H, Fang L, Lee JY, Gan LM (2002) J Power Sources 104:101
36. Park S-C, Kim Y-M, Han S-C, Ahn S, Ku C-H, Lee J-Y (2002) J Power Sources 107:42
37. Liu D-Q, Liu X-Q, He Z-Z (2007) Mater Chem Phys 105:362–366
38. Liu D-Q, Yu J, Sun Y-H, He Z-Z, Liu X-Q (2007) Chin J Inorg Chem 23:41
39. Yuan YF, Wu HM, Guo SY, Wu JB, Yang JL, Wang XL, Tu JP (2008) Appl Surf Sci 255:2225
40. Chan H-W, Duh J-G, Sheu H-S (2006) J Electrochem Soc 153:A1533
41. Han AR, Kim TW, Park DH, Hwang S-J, Choy J-H (2007) J Phys Chem C 111:11347
42. Patey TJ, Büchel R, Ng SH, Krumeich F, Pratsinis SE, Novák P (2009) J Power Sources 189:149
43. Li JG, He XM, Zhao RS (2007) Trans Nonferrous Met Soc China (English Edition) 17:1324
44. Lee K-S, Myung S-T, Amine K, Yashiro H, Sun Y-K (2009) J Mater Chem 19:1995
45. Eddrief M, Dzwonkowski P, Julien C, Balkanski M (1991) Solid State Ionics 45:77
46. Soppe W, Aldenkamp F, den Hartog HW (1987) J Non-Cryst Solids 91:351
47. Chan H-W, Duh J-G, Sheen S-R (2004) Surf Coat Technol 188–189:116
48. Şahan H, Göktepe H, Patat Ş, Ülgen A (2008) Solid State Ionics 178:1837
49. Chan HW, Duh JG, Sheen SR (2006) Electrochim Acta 51:3645
50. Hu G, Wang X, Chen F, Zhou J, Li R, Deng Z (2005) Electrochem Commun 7:383
51. Arbizzani C, Mastragostino M, Rossi M (2002) Electrochem Commun 4:545
52. Li C, Zhang HP, Fu LJ, Liu H, Wu YP, Rahm E, Holze R, Wu HQ (2006) Electrochim Acta 51:3872–3883
53. Hung F-Y, Lui T-S, Liao H-C (2007) Appl Surf Sci 253:7443
54. Vidu R, Stroeve P (2004) Ind Eng Chem Res 43:3314
55. Sugita M, Noguchi H, Soejima Y, Yoshio M (2000) Electrochemistry 68:587