

Short communication

Improvement of capacity fading resistance of LiMn_2O_4 by amphoteric oxides

Sung Bin Park^a, Ho Chul Shin^{a,b}, Wan-Gyu Lee^a, Won Il Cho^b, Ho Jang^{a,*}

^a Department of Materials Science & Engineering, College of Engineering, Korea University, 5-1 Anam-dong, Seongbuk-gu, Seoul 136-713, South Korea

^b Eco-Nano Research Center, Korea Institute of Science and Technology 39-1, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, South Korea

Received 2 October 2007; received in revised form 3 December 2007; accepted 17 January 2008

Available online 6 February 2008

Abstract

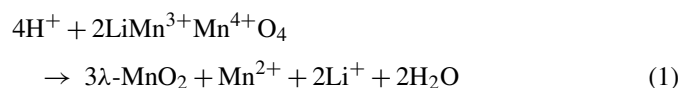
The capacity fading of LiMn_2O_4 is improved by adding amphoteric oxides such as Al_2O_3 , ZnO , SnO_2 , and ZrO_2 to the cathode slurry. The effectiveness of the amphoteric oxides on the fade resistance of LiMn_2O_4 is compared by measuring the capability of scavenging hydrofluoric acid (HF) in the electrolyte by the oxides using a pH meter and by BET surface analysis. Results suggest that the capacity fading is determined by the reactivity of oxides with HF and the effective surface-area of the oxide particles when they were mixed in the slurry. Zinc oxide is the most effective of the oxides in scavenging HF.

© 2008 Elsevier B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Coating; Amphoteric oxide; Lithium-ion battery; Capacity fading hydrofluoric acid scavenging

1. Introduction

Lithium manganese oxide (LiMn_2O_4) has attracted much attention as a cathode material for lithium-ion batteries due to its non-toxic nature and cost effectiveness. The LiMn_2O_4 cathode, however, suffers from poor cycleability and structural instability due to secondary phase formation and Jahn–Teller distortion in the voltage range of 3–4 V [1]. It has been reported [2] that LiMn_2O_4 dissolution occurs when lithium hexafluorophosphate (LiPF_6) reacts with H_2O to produce hydrofluoric acid (HF) in the electrolyte. The loss of capacity by Mn dissolution can be understood in terms of Hunter's reaction [3], i.e.,



and it has been proposed that excessive capacity fading of LiMn_2O_4 at elevated temperatures is due to the dissolution of MnO_2 and Li_2O into the electrolyte [4–7].

Various approaches have been carried out to overcome the shortcomings of LiMn_2O_4 [8–13]. Several research groups have reported that the substitution of mono, di or trivalent cations in LiMn_2O_4 decreases Mn^{3+} ions that cause ion dissolution [8–11]. Liu et al. [12] reported that a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating on a LiMn_2O_4 cathode improves the cycle properties by preventing electrolyte decomposition on the electrode surface. Improvement of the fade resistance of cathodes by adding dimethyl acetamide (DMAC) to the electrolyte was also communicated by Li and Lucht [13]. They suggested that DMAC suppresses the reaction of LiPF_6 with water impurity in the cell and decreases capacity fading. Coating of LiMn_2O_4 particles using amphoteric oxides such as ZrO_2 , ZnO , Al_2O_3 and SiO_2 [4,5] was also investigated because the oxides scavenge HF and reduce the degree of Mn dissolution. Recently, an alternative method to scavenge HF has been introduced by adding an amphoteric oxide to the slurry used to produce a LiMn_2O_4 cathode [14]. It was reported that the new approach offers easier fabrication together with effects similar to those obtained with other coating methods.

In this study, we investigate the mechanism of the fade resistance of LiMn_2O_4 after mixing amphoteric oxides such as Al_2O_3 , ZrO_2 , SnO_2 or ZnO into the cathode slurry.

The effectiveness of the oxides on improving the fade resistance is evaluated by measuring the pH change of an HF solution

* Corresponding author at: Department of Advanced Materials Engineering, College of Engineering, Korea University, 5-1 Anam-dong, Seongbuk-gu, Seoul 136-713, South Korea. Tel.: +82 2 3290 3276; fax: +82 2 928 3584.

E-mail addresses: cuterat@korea.ac.kr (S.B. Park), lead@korea.ac.kr (H.C. Shin), wonica@kist.re.kr (W.I. Cho), hojang@korea.ac.kr (H. Jang).

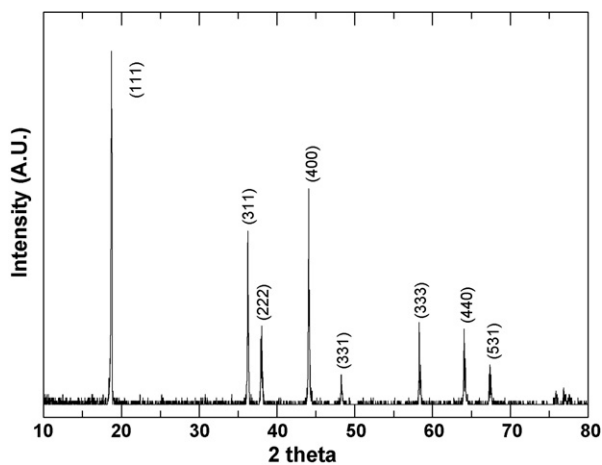


Fig. 1. X-ray diffraction patterns obtained from LiMn_2O_4 .

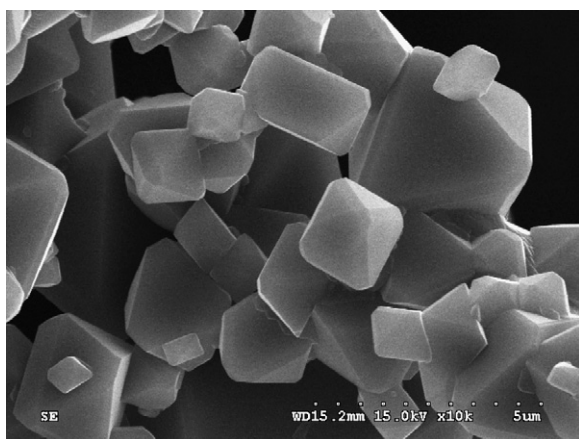


Fig. 2. Scanning electron micrograph of LiMn_2O_4 showing well-developed facets.

on addition of the amphoteric oxides and by considering particle size effects.

2. Experimental

The cathode was prepared by combining LiMn_2O_4 , polyvinylidene difluoride (PVdF) [8 wt.% in NMP (1-methyl-2-pyrrolinone)] and carbon (85:5:10 in wt.%). The amount of amphoteric oxide in the slurry was set at 2.0 wt.% of the LiMn_2O_4 used to produce the cathode. Due to their different densities, the vol.% of the oxides was 0.57, 0.34, 0.29 and 0.36 for Al_2O_3 , ZrO_2 , SnO_2 , and ZnO , respectively. Acetone was added to enhance homogenization of the mixture at 5000 rpm. The cathode was fabricated by the doctor blade method on Al

Table 1

pH changes of HF solutions on reaction with Al_2O_3 , ZrO_2 , SnO_2 and ZnO

	pH (average)	vol.%	wt.%
HF solution	2.84 ± 0	N/A	N/A
Al_2O_3	5.09	0.57	2
ZrO_2	3.36	0.34	2
SnO_2	2.92	0.29	2
ZnO	5.67	0.36	2

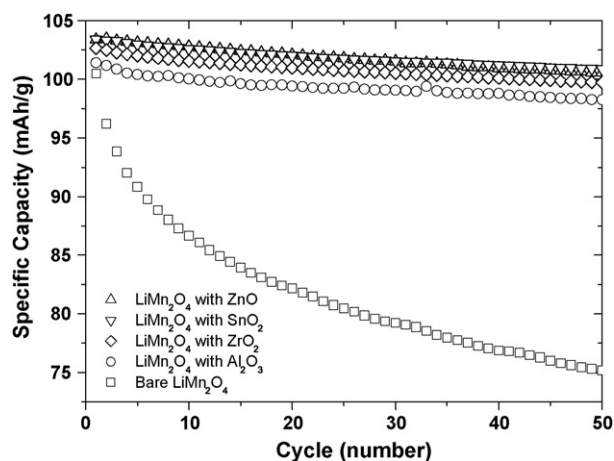


Fig. 3. Cycle stability of bare LiMn_2O_4 and LiMn_2O_4 with 2 wt.% of amphoteric oxides (Al_2O_3 , ZnO , SnO_2 and ZrO_2) at room temperature at 0.5 °C rate.

foil, followed by roll pressing and drying in a vacuum oven for 24 h at 80 °C.

The electrochemical properties of LiMn_2O_4 were examined in coin cells that used lithium foil as a negative electrode. The electrolyte was 1 M of high-purity LiPF_6 dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (1:1:1 volume ratio). The cells were assembled in a dry room and polypropylene (PP) was used as a separator. Charge–discharge and cycle experiments were carried out with a battery cycler (Maccor4000, Maccor). Charge–discharge was conducted at the 0.5 C rate and carried out for 50 cycles with cut-off voltages in the range of 3.5–4.5 V.

The crystal structure of LiMn_2O_4 (Dong-woo fine chem., Korea) was examined by X-ray diffraction (D/MAX-II A) with $\text{Cu K}\alpha$ in a scan range of 10–80° (2θ). The morphology of the LiMn_2O_4 particle was examined by means of an SEM (Hitachi, S-4300, Japan) and the specific surface-area of the oxides (Al_2O_3 , ZrO_2 , SnO_2 , ZnO) was measured by a BET (Brunauer–Emmett–Teller) surface-area analyzer (Micromeritics, ASAP2010). The pH change of the HF solution after mixing

Table 2
pH changes/specific area of HF solutions containing Al_2O_3 , ZrO_2 , SnO_2 and ZnO

	Specific area ($\text{m}^2 \text{g}^{-1}$)	ΔpH (average pH change)	$\Delta\text{pH}/\text{specific area}$ (wt.%)	$\Delta\text{pH}/\text{specific area}$ (vol.%)
Al_2O_3	36.99	2.25	0.061	0.0347
ZrO_2	42.05	0.52	0.012	0.0042
SnO_2	16.50	0.08	0.005	0.0014
ZnO	11.35	2.83	0.249	0.0898

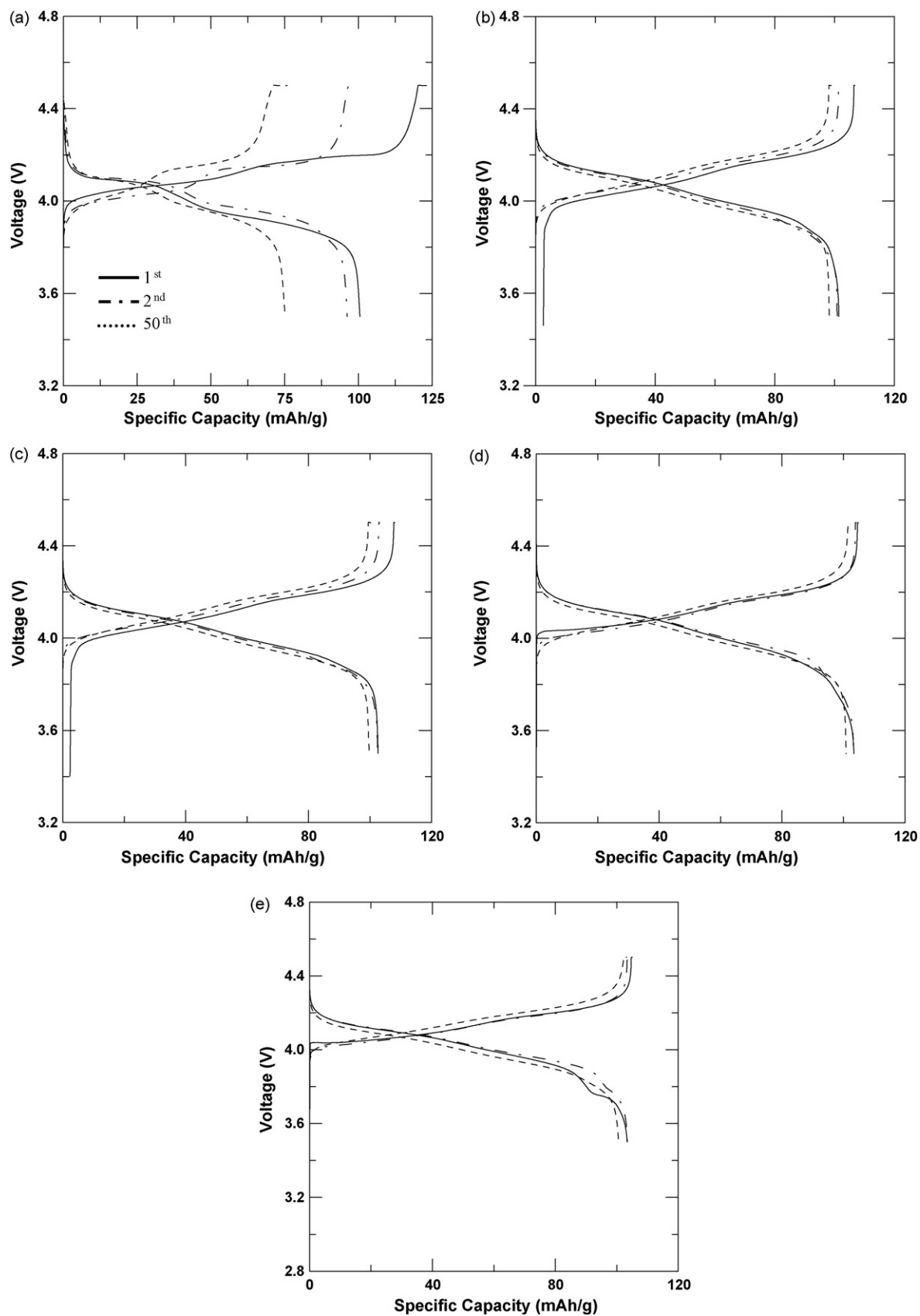


Fig. 4. Charge–discharge curves from cathodes at room temperature using (a) bare LiMn_2O_4 , (b) LiMn_2O_4 with 2 wt.% Al_2O_3 , (c) LiMn_2O_4 with 2 wt.% ZrO_2 , (d) LiMn_2O_4 with 2 wt.% SnO_2 and (e) LiMn_2O_4 with 2 wt.% ZnO .

with Al_2O_3 , ZrO_2 , SnO_2 , or ZnO was measured with a pH meter (Fisher, AR20).

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD pattern of a typical spinel structure, which indicates that the LiMn_2O_4 particles used in this study do not contain any secondary phases [15]. The particle size is in the range of 2–5 μm in diameter, which is larger than that of previous work [14]. In addition, the particles are well faceted (Fig. 2). The larger LiMn_2O_4 particles used in this study suggest the possibility of a lower specific capacity in electrochemical tests compared with our previous work. This is based on the fact that large particles tended to have low specific capacity with better capacity retention, whereas small particles tend to exhibit poor capacity retention with high specific capacity due to the influence of specific surface-area [16–18].

3.2. Chemical reactivity of amphoteric oxides with HF

Four amphoteric oxides were submerged in an HF solution (pH 2.84) to investigate their reactivity by measuring the resulting change in pH. The type of oxide significantly affects the pH change of the solution after oxide addition, as shown in Table 1. The data show that ZnO and Al_2O_3 are effective HF scavengers. The reactivity of the oxide, however, has to be normalized by the specific surface-area of the particles since the particle size and specific gravity of the oxides used in this study are different.

The specific surface areas of the oxide particles added to the HF solution are listed in Table 2. ZrO_2 has the largest specific surface-area (42.05 $\text{m}^2 \text{g}^{-1}$) due to its small particle size while coarse ZnO particles have the smallest area (11.35 $\text{m}^2 \text{g}^{-1}$). Thus the fine ZrO_2 particles used in this work appear to be more effective for HF scavenging than the large ZnO particles when the same amount of oxide is used. This is consistent with the report [19] that LiMn_2O_4 coated with small oxide particles exhibits better fade resistance.

To evaluate the effectiveness of the amphoteric oxide in scavenging HF in the solution, normalization of the pH change was carried out by the measuring the effective surface-area. The normalized pH changes are listed in Table 2. The normalization procedure comprises the conversion of the amount of oxide from wt.% to vol.% since the effective area is associated with the vol.% of the oxides. The results show that ZnO is the most efficient oxide in scavenging HF assuming the same surface-area. The normalized reactivity of the oxides in Table 2 also suggests that SnO_2 and ZrO_2 are not effective HF scavengers and that is necessary to expand their surface by using finer particles to obtain a pronounced improvement in fade resistance.

3.3. Electrochemical properties

The cycle performance of the cathodes was examined at room temperature at the 0.5 C rate. Fig. 3 shows that the cathode with bare LiMn_2O_4 retains 75% of capacity after 50 cycles,

whereas the addition of amphoteric oxides produces about 97% of capacity retention. The specific capacity of the bare LiMn_2O_4 decreases rapidly during the first 15 cycles and then decreases linearly. On the other hand, LiMn_2O_4 with amphoteric oxides displays much improved capacity retention. Thus the amphoteric oxides protect LiMn_2O_4 from HF attack. The initial capacities of the four modified specimens are similar to that of the bare cathode. This is a salient result because cathodes have usually given a lower initial capacity than the bare cathode when they are coated by amphoteric oxides [19,20].

Kim et al. [19] found that coating with fine ZrO_2 particles is more effective than coating with coarse ZrO_2 particles. This was because the large specific surface-area from the small ZrO_2 particles provided a larger surface-area to react with HF in the electrolyte. The authors also found that the initial capacity was decreased on coating LiMn_2O_4 with ZrO_2 particles since the coated layer provides resistance to the mobility of Li ions. On the other hand, the present method of mixing the amphoteric oxides in the slurry circumvents the resistance by the coat layer while they efficiently remove HF from the electrolyte. These results suggest that the root cause of the capacity fading of LiMn_2O_4 is mainly HF attack rather than structural instability during the phase transition. It also concluded that the 2 wt.% of oxides used in this study is sufficient to remove HF in the electrolyte.

The charge–discharge characteristics of the specimens, are presented in Fig. 4. All the specimens display two plateaux that are attributed to orderly and disorderly intercalation of lithium ions in the tetrahedral (8a) sites at 4.1 and 3.9 V, respectively [21]. The solid line in the figure indicates the first charge–discharge curve, whereas the dotted line indicates the 50th charge–discharge curve. Therefore, the large gap between the first solid line and the 50th dashed line indicates poor capacity retention. In particular, the charge–discharge curve exhibits a shortened second plateau when bare LiMn_2O_4 is used to produce a cathode. This suggests that the disorderly intercalating lithium ions have limited mobility due to the dissolution of LiMn_2O_4 from the surface. On the other hand, the specimens mixed with the amphoteric oxides do not show shortening of the second plateau, which indicates that the LiMn_2O_4 surface is protected from HF attack during charge–discharge reactions.

4. Conclusions

The effect of amphoteric oxides on the electrochemical properties of LiMn_2O_4 has been studied using electrochemical tests and several analytical methods such as XRD, SEM and BET surface-area analysis. The results from this work can be summarized as follows.

- (i) Hydrofluoric acid is the most important determinant of the capacity fading of LiMn_2O_4 . Enhanced capacity retention can be achieved by efficient removal of HF in the electrolyte. The capacity retention of a bare cathode is 75%, whereas cathodes with amphoteric oxides mixed in the slurry maintain 97% of the initial capacity after 50 cycles.

- (ii) The reactivity of amphoteric oxides with HF is highly dependent on particle size and effective surface-area, as well as to the inherent chemical reactivity.
- (iii) The normalized reactivity of the amphoteric oxides with HF, based on effective surface-area, is highest for ZnO followed by Al₂O₃, ZrO₂ and SnO₂.
- (iv) Cathodes containing amphoteric oxides in the slurry do not exhibit initial capacity loss.

Acknowledgement

This work was financially supported by a grant from the Ministry of Commerce, Industry and Energy of Korea (research grant code #: M10428010002-04L2801-00210).

References

- [1] Q. Zhong, A. Bonakadarpour, M. Zhang, Y. Gao, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 205.
- [2] R. Alcantara, M. Jaraba, P. Lavela, J.L. Tirado, J. Electroanal. Chem. 566 (2004) 187.
- [3] J.M. Tarascon, W.R. McKinnon, F. Coowar, T.N. Bowmer, G. Amatucci, D. Guyomard, J. Electrochem. Soc. 141 (1994) 1421.
- [4] J.C. Hunter, J. Solid State Chem. 39 (1981) 142.
- [5] A. Blyr, C. Sigala, G.G. Amatucci, D. Guyomard, Y. Chabres, J.M. Tarascon, J. Electrochem. Soc. 145 (1998) 194.
- [6] A.D. Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gerand, J.M. Tarascon, J. Electrochem. Soc. 146 (1999) 428.
- [7] Y. Matsuo, R. Kostecki, F. McLarnon, J. Electrochem. Soc. 148 (2001) A687.
- [8] S.T. Myoung, S. Komaba, N. Kumagai, H. Yashiro, H.T. Chung, T.H. Cho, Electrochim. Acta 47 (2002) 2543.
- [9] D. Song, T. Uchida, M. Wakihara, Solid State Ionics 117 (1999) 151.
- [10] M.M. Thackeray, C.S. Johnson, J.-S. Kim, K.C. Lauzze, J.T. Vaughey, Electrochem. Commun. 5 (2003) 752–758.
- [11] Ali Eftekhari, Solid State Ionics 167 (2004) 237–242.
- [12] D.Q. Liu, X. Liu, Z. He, Mater. Chem. Phys. 105 (2007) 362.
- [13] W. Li, B.L. Lucht, Electrochem. Solid-State Lett. 10 (2007) A115.
- [14] S.B. Park, S.M. Lee, H.C. Shin, W.I. Cho, H. Jang, J. Power Sources 166 (2007) 219.
- [15] X. Wu, S.B. Kim, J. Power Sources 109 (2002) 53.
- [16] Y. Tingfeng, W. Dianlong, G. Kun, H. Xinguo, Rare Metals 26 (2007) 30.
- [17] C. Tsang, A. Manthiram, Solid State Ionics 89 (1996) 305.
- [18] G.A. Nazri, G. Pistoia, Lithium Batteries: Science and Technology, Kluwer Academic Publishers, New York, 2003, pp. 321–324.
- [19] J.-S. Kim, C.S. Johnson, J.T. Vaughey, S.A. Hackney, K.A. Walz, M.A. Anderson, M.M. Thackeray, J. Electrochem. Soc. 151 (2004) A1755.
- [20] Z. Zheng, Z. Tang, Z. Zhang, W. Shen, Y. Lin, Solid State Ionics 148 (2002) 317.
- [21] X. He, J. Li, Y. Wang, J. Ying, C. Jiang, C. Wan, J. Power Sources 150 (2005) 216.