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$LiMn_2O_4$ CATHODES FOR SOLID STATE LITHIUM-ION BATTERIES - ENERGY STORAGE AND CONVERSION

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Thermoelectric devices for power generation and solid-state refrigeration represent an important technology that could potentially offer long term solid-state solutions for increased energy efficiency. Lithium manganese oxide with cubic spinel structure has attracted a great deal of attention due to its advantages like low cost, abundance of manganese in earth crust, environmental harmlessness and high theoretical lithiation capacity. The electrochemical studies of $LiMn_2O_4$ have been carried out with a composite electrode which consists of powdered electro active materials an organic binder such as polyvinylidene fluoride and a conductive additive. $LiMn_2O_4$ is a leading positive electrode material alternative to $LiCoO_2$ due to its lower cost, slightly higher electrochemical potential vs. graphite and its improved thermal stability. High power applications such as electric vehicles require that Li-ion batteries have a high specific power and energy. One route to increase specific power is to significantly increase the interfacial area between electrochemically active material and electrolyte, thereby increasing the charge and discharge rates. This opportunity has led many groups to develop nano-structured and nanosized $LiMn_2O_4$ particles with promising results. This paper deals with the detailed technological aspects of properties, structures of $LiMn_2O_4$ as candidate cathode material for solid state lithium ion batteries with wide applications.

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1. Introduction

Thermoelectric devices for power generation and solid-state refrigeration represent an important technology that could potentially offer long term solid-state solutions for increased energy efficiency and address environmental concerns. However, the efficiency of existing thermoelectric materials, limited temperature stability and potential scarcity of key elements, such as Tellurium, have motivated researchers to consider oxides as thermoelectric materials. Lithium manganese oxide is one among the prominent electrode materials for secondary lithium ion battery. Lithium manganese oxide with cubic spinel structure has attracted a great deal of attention due to its advantages like low cost, abundance of manganese in earth crust, environmental harmlessness and high theoretical lithiation capacity (~148 mAh/g) [1].

Development of the cathode materials for lithium–ion battery is vital to meet the demands of portable devices, power tools, e-bikes, future usages of electric vehicles, and so on. Among three promising candidates for cathode materials ($LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$), lithium manganese oxides ($LiMn_2O_4$) are inexpensive cathode materials with a high energy density, environmental acceptability, and are more abundant in nature. In spite of these advantages, $LiMn_2O_4$ has the problem of severe capacity fading during charge and discharge cycles, which makes it unsuitable for commercial application. Intensive research has particularly focused on the mechanism of capacity fading and has suggested numerous solutions. Among these projects,

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doping is considered to be an effective path to improve the electrochemical performance of spinel $LiMn_2O_4$, so several attempts have been made for improving the lithium manganese spinels by doping various metals ions. Although such substitutions often result in enhancing the stability of spinel, the first discharge capacity of them is considerably lower than that of the parent compound. The reduction in the first discharge capacity is mainly due to the fact that the substituent ions do not contribute to the discharge capacity [2].

$LiMn_2O_4$ was first synthesized is 1958 by heating a mixture of lithium carbonate and manganese oxide at 850 ^0C in air. In 1981, Hunter [3] reported that lithium ions could be de-intercalated completely from the spinel $LiMn_2O_4$ structure to form λ-MnO_2 by a chemical procedure. Given this performance, Thackeray et al. used $LiMn_2O_4$ as a cathode material in 1983 [4]. The theoretical specific capacity of $LiMn_2O_4$ is 148 mAh/g and the practical specific capacity approaches to 120 mAh/g. For some applications, however, a capacity of about 120 mAh/ g is acceptable, provided the value remains stable under extended charge-discharge cycling. During de-intercalation, lithium ions leave the spinel $LiMn_2O_4$ structure and this leads to the formation of Mn_2O_4 in which the spinel structure is retained. It is supposed that lithium ions can be intercalated fully from the host structure and that the structure does not deteriorate as do $LiNiO_2$ and $LiCoO_2$ when lithium ions are extracted [5]. The spinel $LiMn_2O_4$ has been considered as a promising candidate for replacement of $LiCoO_2$ in lithium ion batteries (LIBs), on the basis of its low cost, low toxicity and high safety. These merits make $LiMn_2O_4$ an ideal material, in principle, for use in large scale batteries for powering electric vehicles (EV) or hybrid electric vehicles (HEV), but the energy density of LIBs is still too low to support their practical application. Fabrication of high energy density LIBs requires a cathode material with high specific capacity and high density. Thus increasing the tap density of $LiMn_2O_4$ cathode materials will be helpful to increase the energy density of LIBs. It has been shown that the particle morphology is a very important factor affecting the density of materials, and materials composed of spherical particles have higher tap density than that of irregular particles. Indeed, there have been many reports of spherical particles of battery electrode materials showing high tap densities, including $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ [6].

Fig.1 represents a simple, template-free and high yield method for preparing solid and hollow spherical particles of $LiMn_2O_4$. As shown in Fig.1, $MnCO_3$ solid microspheres and MnO_2 hollow microspheres as precursors were synthesized. They were subsequently transformed into $LiMn_2O_4$ solid and hollow microspheres respectively. Furthermore, the electrochemical properties of $LiMn_2O_4$ solid and hollow microspheres have been evaluated and compared [7, 8]. The capacity loss has been ascribed to several possible factors, (i) Slow dissolution of the $LiMn_2O_4$ electrode into the electrolyte according to the disproportion reaction:

$$2Mn^{3+} \rightarrow Mn^{4+}+Mn^{2+}$$

(ii) Transformation of an unstable two-phase structure in the high-voltage region to a more stable single-phase structure via a loss of MnO, (iii) electrochemical reaction of the electrolyte at high voltage. The capacity fading phenomenon is primarily linked to the dissolution of the spinel electrode [9].

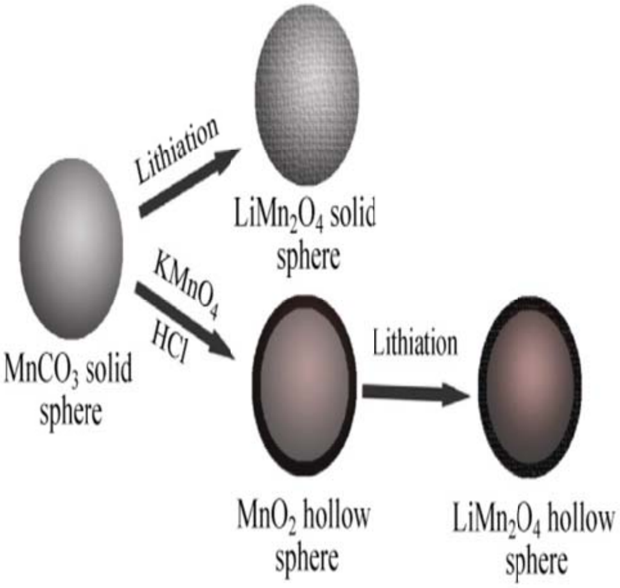

Fig.1 Schematic illustration of the formation of $LiMn_2O_4$ *solid microspheres and* $LiMn_2O_4$ *hollow microspheres*

Most of the electrochemical studies of $LiMn_2O_4$ have been carried out with a composite electrode which consists of powdered electro active materials an organic binder such as polyvinylidene fluoride (PVdF) and a conductive additive. Consequently, care has to be taken in evaluating the intrinsic kinetic and electrochemical properties of the active material itself when using a composite electrode because it involves interference derived from other additives. To avoid these complications, various strategies have been introduced to produce an additive-free electrode such as a thin film of electrode material on a substrate by deposition techniques including chemical vapour deposition [10]. $LiMn_2O_4$ has been usually synthesized using solid-state reactions that involve the mechanical mixing of oxides and carbonates followed by high temperature firing and extended grinding. This method, which requires long-range diffusion of metal ions, may result in non-homogeneity, larger particles, and poor control of stoichiometry. Several solution methods using soluble metal ion sources have been used to synthesize mixed-cation oxide powders. Among the solution methods, techniques based on using organic polymers as a gelling and/or complexing agent have been developed by several investigators. Recently, $LiMn_2O_4$ powders have been successfully synthesized through the formation of polymeric precursors [11].

Electrolytic manganese dioxide (EMD) has been widely used as manganese compound precursor for synthesis of $LiMn_2O_4$ powders. However, the EMD precursors usually have a large amount of impurities such as Na^+ and SO_4^{2-}. Nowadays, the commercial EMD is primarily produced by electro deposition from manganese sulphate. The deposit consists of manganese hydroxide and manganese dioxide with low crystallinity, loose structure and abounding micro cavities, which results in serious absorption and sandwich inclusion of SO_4^{2-} and sodium impurities. Many efforts have been made to eliminate these impurities but little effect is achieved. Therefore, $LiMn_2O_4$ cathode made from EMD contains a large amount of those impurities, which may be the important causes to the failure of the $LiMn_2O_4$ cathode in the lithium ion batteries. But, there is no research on the effects of sodium reported yet [12]. The removal of Li is accompanied by a reversible decrease in lattice parameter from a = 8.24 Å at Li = 1 to a = 8.03 Å at Li = 0.33. In practical applications the Li content in $LiMn_2O_4$ is varied between 1 and nearly 0 (cycling between 3.0 and 4.4 V). Heating of λ-MnO_2 does not show any significant loss of oxygen or lattice transformation up to temperatures 400 °C [13].

2. Structure

Fig. 2 shows the schematic diagram of lattice atom group of $LiMn_2O_4$. The structure of $LiMn_2O_4$ belongs to the face centre cubic lattice and each lattice is made up of 2 lithium atoms, 4 manganese atoms and 8 oxygen atoms [14]. In contrast to the layered oxides (Li_xCoO_2 or $Li_xM_yCo_yO_2$, M = Ni, Mg, Ti) presently used in commercial Li-ion cells $LiMn_2O_4$ adopts a (3D) structure that can simply be three-dimensional described as a cubic close packing (ccp) of oxygen atoms with Mn occupying half of the octahedral and Li an eighth of the tetrahedral sites referring to the 16d and 8a sites ($[Li]_{tet}$ $[Mn_2]_{Oct}$ O_4), respectively (Fig. 3). However, this structure is complicated by possible cations mixing between the two types of sites. It is well documented that, within the spinel family, the degree of cations mixing and extent of cationic or anionic non stoichiometry affecting the spinel magnetic or optical properties is strongly dependent on the thermal story of the sample. Thus, it was important to first determine whether or not the Li intercalation/deintercalation process within $LiMn_2O_4$ was sensitive to the sample history (precursors, heat-treatments) and subsequent cation mixing as the early electrochemical data suggested [15]. In the $LiMn_2O_4$ spinel structure (space-group: Fd3m), a ccp array of oxygen ions occupy the 32e position, Mn ions are located in the 16d site and Li in the 8a site. The Mn ions have an octahedral coordination to the oxygens, and the MnO_6 octahedra share edges in a three-dimensional host for the Li guest ions (Fig. 4). The 8a tetrahedral site is situated furthest away from the 16d site of all the interstitial tetrahedra (8a, 8b and 48f) and octahedra (16c). Each of the 8a-tetrahedron faces is shared with an adjacent, vacant 16c site. This combination of structural features in the stoichiometric spinel compound constitutes a very stable structure [16].

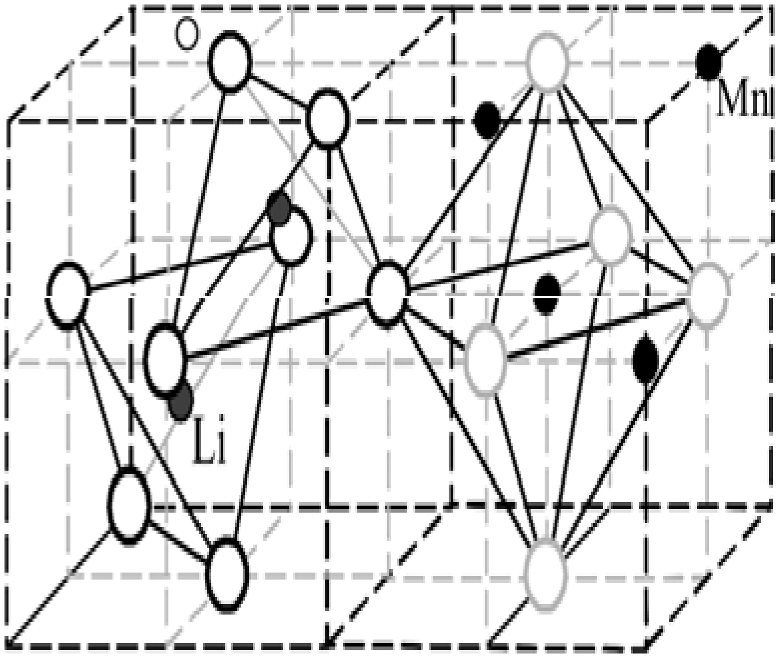

Fig.2 Schematic diagram of lattice atom group

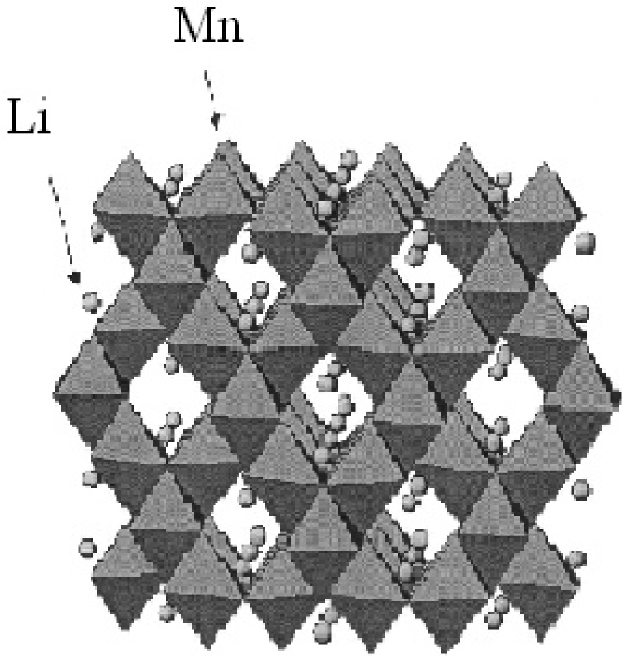

Fig.3 The spinel structure showing the MnO_6 octahedra and the Li 8a tetrahedral positions

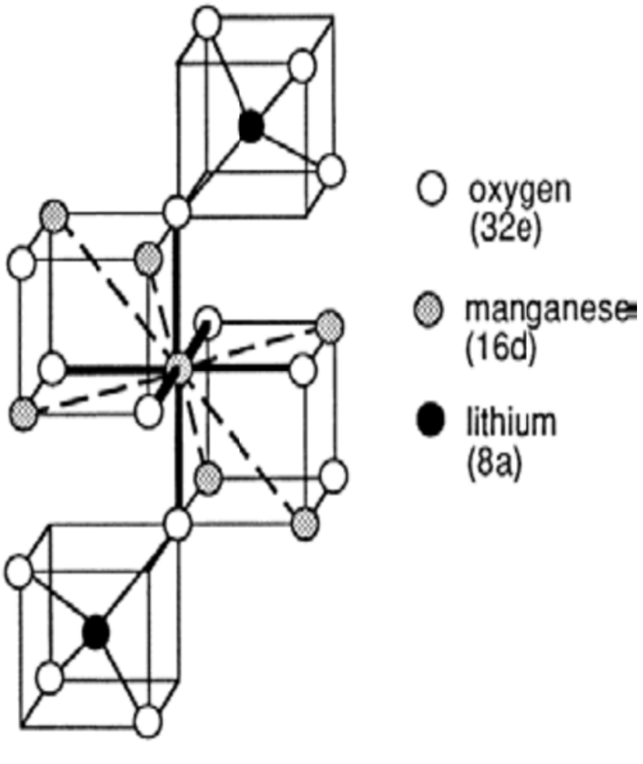

Fig.4 Part of the unit cell of $LiMn_2O_4$ showing the local structure around octahedrally coordinated manganese in an ideal spinel lattice. Mn-O bonds are represented by heavy solid lines; linear chains of manganese ions in neighbouring edge-sharing octahedra are indicated by dashed lines

3. Nanostructured $LiMn_2O_4$

In $LiMn_2O_4$ nanosized systems, synthetic procedures are generally complex, cost affected, and difficult to scale up. A number of soft chemistry techniques such as sol-gel, solution phase, combustion, and templating methods have been explored to prepare $LiMn_2O_4$. Moreover, electrochemical performances of the electrode materials are closely associated with the preparation methods. $LiMn_2O_4$ prepared by the traditional solid-state reaction method exhibits good performance but it requires prolonged high temperature (calcinations) of 800 ºC, which causes coarsening of the powders. Thus, a simple and convenient route to synthesize $LiMn_2O_4$ nanostructures without loss of electrochemical properties is highly desired [17]. A tartaric acid method was developed to synthesize nano- $LiMn_2O_4$ powder directly from lithium acetate and manganese acetate. Without using other chemicals (such as glycol, ammonium hydroxide, ammonium chloride or polyhydric alcohol) and additional processing steps, this synthesis method was considered to be inexpensive and simple [18].

4. Properties

$LiMn_2O_4$ is ideal as a high-capacity Li-ion battery cathode material by virtue of its low toxicity, low cost and the high natural abundance of Mn. Unlike V_2O_5 and LiV_3O_8, lithium can be extracted from $LiMn_2O_4$ in the form it is made, qualifying $LiMn_2O_4$ as a positive electrode material for Li-ion batteries. $LiMn_2O_4$ is a leading positive electrode material alternative to $LiCoO_2$ due to its lower cost, slightly higher electrochemical potential vs. graphite, and its improved thermal stability. High power applications such as electric vehicles require that Li-ion batteries have a high specific power and energy. One route to increase specific power is to significantly increase the interfacial area between electrochemically active material and electrolyte, thereby increasing the charge and discharge rates. This opportunity has led many groups to develop nano-structured and/or nanosized $LiMn_2O_4$ particles and with promising results [19-21].

5. Applications

$LiMn_2O_4$ has found important applications as a cathode material in secondary lithium ion batteries. The spinel $LiMn_2O_4$ is of great interest for the replacement of $LiCoO_2$ as cathode material in the Li ion batteries because of its high voltage, low cost and low toxicity. The rapid capacity fading with cycling is thought to be the main obstacle that prevented it from being commercialized [22-24]. During several decades, many researchers have achieved new materials and fabrication techniques of cathode thin films for micro batteries. Among many materials, $LiMn_2O_4$ thin film is particularly interesting, since it can reversibly intercalate one Li ion per mole, without altering the λ-MnO_2 framework. In general, to investigate electrochemical properties of cathode films, half-cell test were carried out using liquid electrolyte like 1 M $LiPF_6$ or $LiClO_4$ in organic solvent [25].

The $LiMn_2O_4$ carbon nanocomposites had a considerably higher specific galvanostatic specific charge (Li-ion insertion) at a 5C-rate or greater than the electrode with powder of pure $LiMn_2O_4$. The significance of these results is 94 illustrated by calculation of the specific energy of a thin-layer Li-ion battery containing the flame-made $LiMn_2O_4$/carbon nanocomposite as positive electrode and LiC_6 as negative electrode (78 $Whkg^{-1}$ at 50C-rate). If the nanocomposites were used in a Li-ion battery, such a device could replace electrochemical super capacitors in high power applications for durations longer than super capacitors could sustain [26-28].

6. Conclusions

$LiMn_2O_4$ is ideal as a high-capacity Li-ion battery cathode material by virtue of its low toxicity, low cost, and the high natural abundance of Mn. Unlike V_2O_5 and LiV_3O_8, lithium can be extracted from $LiMn_2O_4$ in the form it is made, qualifying $LiMn_2O_4$ as a positive electrode material for Li-ion batteries. The spinel $LiMn_2O_4$ has been considered as a promising candidate for replacement of $LiCoO_2$ in lithium ion batteries, on the basis of its low cost, low toxicity and high safety. The electrochemical studies of $LiMn_2O_4$ have been carried out with a composite electrode which consists of powdered electro active materials an organic binder such as polyvinylidene fluoride and a conductive additive. High power applications such as electric vehicles require that Li-ion batteries have a high specific power and energy. One route to increase specific power is to significantly increase the interfacial area between electrochemically active material and electrolyte, thereby increasing the charge and discharge rates. This opportunity has led many groups to develop nano-structured and nanosized $LiMn_2O_4$ particles with promising results. In this paper the detailed technological aspects of properties, structures of $LiMn_2O_4$ as candidate cathode material for solid state lithium ion batteries with wide applications are reported.

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References

[1] S. Balaji, T. Manichandran and D. Mutharasu, Bull. Mater. Sci. **35**, 471 (2012).
[2] Yudai Huang, Rongrong Jiang, Shu-Juan Bao, Yali Cao and Dianzeng Jia, Nanoscale Res. Lett. **4**, 353 (2009).
[3] J.C. Hunter, J. Solid State Chem. **39**, 142 (1981).
[4] M.M. Thackeray, W.I.F. David, P.G. Bruce and J.B. Good enough, Mater. Res. Bull. **18**, 461(1983).
[5] H.W. Chan, J.G. Duh and S.R. Sheen, J. Power Sources **115,** 110 (2003).
[6] Xiaoling Xiao, Jun Lu and Yadong Li, Nano Res. **3**, 733 (2010).
[7] J. B. Fei, Y. Cui, X. H. Yan, W. Qi, Y. Yang, K. W. Wang, Q. He and J. B. Li, Adv. Mater. **20,** 452 (2008).
[8] J. Cao, Y. C. Zhu, K. Y. Bao, L. Shi, S. Z. Liu and Y. T. Qian, J. Phys. Chem. **113,** 17755 (2009).
[9] Mi-Ra Lim, Wan-Il Cho and Kwang-Bum Kim, J. Power Sources **92,** 168 (2001).
[10] C. Chen, E.M. Kelder and J. Schoonman, J. Electrochem. Soc. **144,** 289 (1997).
[11] Hyu-Bum Park, Jeongsoo Kim and Chi-Woo Lee, J. Power Sources **92,** 124 (2001).
[12] Guo Hua-jun, LI Xiang-qun, HE Fang-yong, LI Xin-hai, Wang Zhi-xing and Peng Wen-jie, Trans. Nonferrous Met. Soc. **20,** 1043 (2010).
[13] Heike Gabrisch, Yasunori Ozawa and Rachid Yazami, Electrochim. Acta **52,** 1499 (2006).
[14] Yu Ze-min and Zho Lian-cheng, Trans. Nonferrous Met. Soc. **17,** 659 (2007).
[15] G. Amatuccia and J.M. Tarasconb, J. Electro. Chem. Soci. **149,** K31 (2002).
[16] S.H. Kang, J.B. Good enough and L.K. Rabenberg, J. Chem. Mater. **13,** 1758 (2001).
[17] Hyun-Wook Lee, P. Muralidharan and Do Kyung Kim, J. Korea. Cer. Soc. **48**, 379 (2011).
[18] Y.M. Hon, S.P. Lin, K.Z. Fung and M.H. Hon, J. Eur. Cer. Soc. **22,** 653 (2002).
[19] S.H. Park, S.T. Myung, S.W. Oh, C.S. Yoon and Y.K. Sun, J. Electrochim. Acta **51,** 4089 (2006).
[20] J.Y. Luo, L. Cheng and Y.Y. Xia, J. Electrochem. Comm. **9,** 1404 (2007).
[21] Z. Bakenov, M. Wakihara and I. Taniguchi, J. Solid State Electrochem. **12,** 57 (2008).
[22] S.T. Yang, J.H. Jia, L. Ding and M.C. Zhang, J. Electrochim. Acta **48,** 569 (2003).

[23] Hee-Soo Moon, Seung Won Lee, You-Kee Lee and Jong-Wan Park, J. Power Sources **119,** 713 (2003).
[24] Lihong Yu, Xinping Qiu, Jingyu Xi, Wentao Zhu and Liquan Chen, J. Electrochim. Acta **51,** 6406 (2006).
[25] M. Jayalakshmi, M. Mohan Rao and F. Scholz, Langmuir **19**, 8403 (2003).
[26] A. S. Wills, N. P. Raju and J. E. Greedan, J. Chem. Mater. **11**, 1510 (1999).
[27] Sung Yeon Kim and Sehun Rhee, Int. J. Electrochem. Sci. **6,** 5462 (2011).
[28] C. Nithya, R. Lakshmi and S. Gopukumara, J. Electrochem. Soc.**159,** A1335 (2012).