



## Lithium based battery-type cathode material for hybrid supercapacitor

V. Shobana\*<sup>1,2</sup>, P. Parthiban<sup>2</sup> and K. Balakrishnan<sup>2</sup>

<sup>1</sup>Department of Physics, Sathyabama University, Chennai, Tamil Nadu, India

<sup>2</sup>Centre for Nanoscience and Technology, Pondicherry University, Pondicherry, India

---

### ABSTRACT

Lithium based battery type supercapacitors has replaced the batteries for electric energy storage. A novel improved occurs in energy density and the electrodes carried the good electrochemical performances of specific capacitance, charge-discharge, high power density and high life cycle. In this paper describes, the lithium combined with metal/ transition metal oxides/ carbon based material or conducting polymer as an electrode in the lithium based battery type supercapacitors. In addition, to that this cathode material has synthesized in different methods and mention with their characterization, electrochemical performances and applications from the literatures.

**Key words:** Battery-type, Energy density, Supercapacitor, Lithium based, cathode, Energy storage.

---

### INTRODUCTION

Supercapacitor electrodes have to store large amounts of energy in the small volume which is otherwise called such as double layer capacitors, ultracapacitors, gold capacitors or power cache, supercap, superbattery, power capacitors and electric double layer capacitors (EDLC). The supercapacitor having a lot of applications in electric circuits, UPS systems, power conditioners, welders, inverters, automobile regenerative braking systems, power supplies, cameras, power generators, power quality, etc. Supercap properties are quickly charged and discharged than the batteries, good stability and high power density, however the lagging of energy density. To rectify these problems, supercapacitor electrodes are impregnated differently, based on that it is classified [1] shown in the Fig.1. Supercapacitor is divided into three types (i) electric double layer capacitors (ii) pseudocapacitors (iii) hybrid capacitors, their depends on the non-Faradaic process, Faradaic process and combination of both processes, respectively. The charge particles transfer through the surface between electrode and electrolyte, i.e., redox reaction occur in Faradaic process. The no transfer of charges in the non-Faradaic process [2], the schematic represented as shown in the Fig.2.

The electric double layer capacitor is subtitled by the carbon electrodes of activated carbon, aerogel carbon and carbon nanotubes [3, 4]. Pseudocapacitor is distinguished by conducting polymer electrodes and metal oxide electrodes [5, 6]. The third type of hybrid supercapacitors has subclass of composites hybrids, asymmetric hybrids and battery-type hybrids supercapacitors [7, 8, 9]. Battery-type hybrids are the merging of supercapacitors electrode with the batteries material like lithium, potassium or sodium [10, 11, 12]. Hereby, lithium storage mechanisms of  $\text{Li}_x\text{X/M}$  (X=O, F, N or S where M=Fe, Co, Ni, Cr, Mn, Cu) compounds interface area have extremely large, this conventional mechanism can be formed the bridge between a supercapacitor and a battery electrode. [13]. Lithium based battery –type supercapacitor is powered by the batteries and can overcome the drawback of energy density. This hybrid supercapacitor made in any shape, size, light weight, cost effective, flexible and biodegradable which is used in electronic devices, aircrafts, automobiles, phones, and car batteries etc.

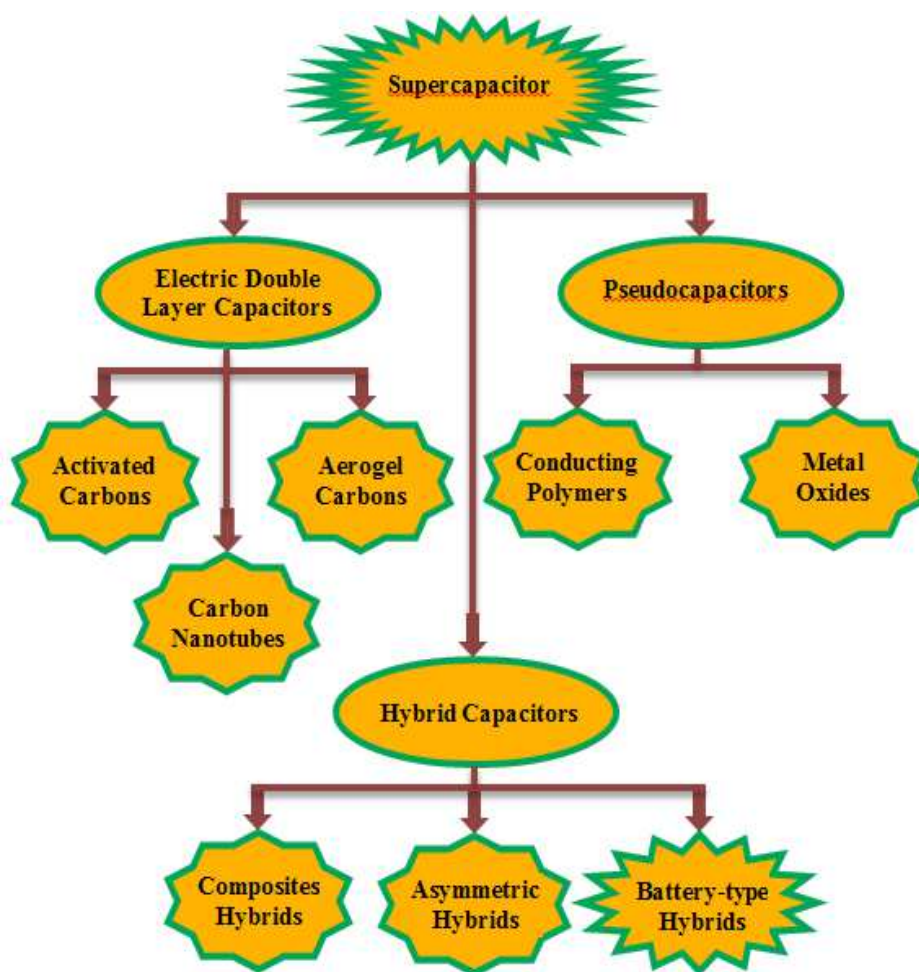


Fig.1 Classification of Supercapacitor

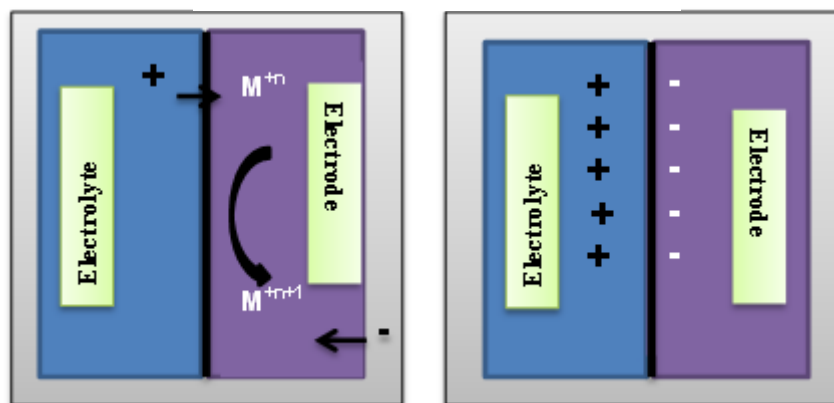


Fig.2 Faradaic and non-Faradaic process

In this article, we reported the overview of lithium based cathode material used in the battery type hybrid supercapacitors from the literatures in which the positive electrode preparation methods, characterization, electrochemical performance and their applications. The battery type supercapacitors proved that the high energy storage, good specific capacitance and long life cycle.

### BATTERY-TYPE HYBRIDS

#### Cathode materials preparation, characterization and electrochemical performance

A stoichiometric cubic spinel  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  nanoparticle was used as the cathode material synthesized by a very simple sol-gel method. Basically, the spinel-type lithium manganese oxides have more advantages are environmental

friendly, potentially low cost and recently the authors have been widely surveyed. LT-Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> was prepared by using LiAc.2H<sub>2</sub>O and MnAc<sub>2</sub>.4H<sub>2</sub>O dissolved with distilled water and start to stirred, citric acid was added in the above solution and then, ammonia solution was dropped until the pH value of 8–9. Finally clear solution occurred, the sol was continuously heated and stirred until water was removed from the sol and resultant a viscous gel was obtained. The gel precursors were preheated at the low temperature of 300 °C for 2 h in air and calcined. After the calcination Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> nanoparticle was prepared. The nanoparticle was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and the measurement of electrochemical properties was studied by the Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> as the cathode material and activated carbon (AC) as the anode material within aqueous electrolyte, which provides good electrochemical performances. This hybrid cell exhibited an estimated specific capacity of 43 F g<sup>-1</sup> based on the total weight of the active electrode materials. Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub>/AC pseudocapacitor also exhibited good cycling performance with the capacity fading rate of 0.0078 F g<sup>-1</sup> per cycling over 1,000 cycles at the current density of 100 mA g<sup>-1</sup> [14].

The composite material of LiMn<sub>2</sub>O<sub>4</sub> (LMO) and activated carbon (AC) as the positive electrode and AC as the negative electrode used to form the hybrid supercapacitor [15]. They prepared the different composition of electrodes shown in table 1 and investigated the capacitance balance. The hybrid supercapacitor of (LMO + AC)/AC have the high electrochemical performances than the electrode of LMO/AC. Especially, at volume ratios of (LMO + AC)/AC = 1: 1.7 and 1: 2 was best electrochemical impedance spectra, rate charge–discharge and cycle performance. And the specific volumetric capacitances of 32.7 Fcm<sup>3</sup> and 36.1 Fcm<sup>3</sup> and retention rate of 88.4% and 90.0 %, respectively at above volume ratio of (LMO+ AC)/AC. Finally, the result to expose the addition of AC to the positive electrode of LMO has improved electrochemical performances of the LMO /AC system.

The review paper of research progress in high voltage spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> material provides an overview of the material synthesis in different methods of solid state, sol-gel, co-precipitation, characterization, effect of doping and effect of coating on the battery performance and the application in asymmetric supercapacitors. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> as the cathode combine with the activated carbon as the anode could provide the high energy density for the supercapacitors and excellent electrochemical performances. In addition LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrode shows the high voltage of 4.7V, good life cycle, rate capability, and thermal stability, which also suitable for the lithium-ion batteries [16]. Song Yi Han et al synthesized the composition of lithium metal oxide (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiMn<sub>2</sub>O<sub>4</sub>) and reduced graphene oxide (RGO) by solvothermal treatment. They reported the first nanocomposites of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>–RGO showing the better anode performance with a larger discharge capacity of ~175 mAhg<sup>-1</sup> and also enhanced the photocatalytic activity by the coupling with RGO. Next LiMn<sub>2</sub>O<sub>4</sub>–RGO nanocomposite was exhibit the greater electrode performance than LiMn<sub>2</sub>O<sub>4</sub>. In these compounds has electrocatalytic activity, electrode activity, and redox catalytic activity etc. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> -RGO, LiMn<sub>2</sub>O<sub>4</sub> –RGO nanocomposites used in the form of electrode for supercapacitor application [17]. Lithium manganese oxide as cathode and the activated carbon as anode with in a mild Li<sub>2</sub>SO<sub>4</sub> aqueous electrolyte were used for the hybrid supercapacitor. In this paper discussed the electrochemical behaviors of LiMn<sub>2</sub>O<sub>4</sub>. This hybrid cell reveals the cyclic voltammetry has the two pairs of redox peaks located at voltage of 1.0 and 1.13 V, charge/discharge studied at a current rate of 3 mA/cm<sup>2</sup> between the sloping voltage of 0.8 to 1.8 V and the outstanding cycling performance of less than 5% capacity loss upto 20,000 cycles at 10 C charge/discharge rate.

The new concept of carbon/ LiMn<sub>2</sub>O<sub>4</sub> /aqueous electrolyte of hybrid electrochemical supercapacitor overcome the drawback of the electrolyte depletion and increased the energy density. It is used in the energy storage device especially for electric vehicle (EV) with a long cycling life, high energy density, high power, low cost, low toxicity and more safety, etc [18]. Nanocrystalline MnFe<sub>2</sub>O<sub>4</sub> negative electrode, LiMn<sub>2</sub>O<sub>4</sub> positive electrode and aqueous LiNO<sub>3</sub> electrolyte were used for the new type of asymmetric supercapacitor. They discussed the electrode preparation, characterization and the electrochemical performance. Specific capacitance of anode and cathode material has a 99 F g<sup>-1</sup> and 130–100 mAhg<sup>-1</sup> under 10–100 C rate, respectively. The increase with anode-to-cathode mass ratio (A/C) increased with increasing the specific power and specific energy of the full-cell. The asymmetric cell exhibits good cycling stability and significantly slower self-discharge rate than symmetric cell of MnFe<sub>2</sub>O<sub>4</sub> or the other asymmetric cells [19].

Xuebu Hu et al investigated the hybrid battery–supercapacitor of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode and a LiMn<sub>2</sub>O<sub>4</sub>/activated carbon (AC) composite cathode. The prepared anode material by the solid state reaction method and cell was aligned a cathode, polypropylene membrane as a separator and a anode with the 1M LiPF<sub>6</sub> electrolyte in the mixture of ethylene carbonate, dimethyl carbonate and ethylene methyl carbonate (1:1:1 by weight). The electrochemical performances of cyclic voltammograms, electrochemical impedance spectra, rate charge–discharge and cycle performance testing were studied. They compared to this hybrid battery–supercapacitor good electrochemical properties to the hybrid capacitor AC/ Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and the high capacity from secondary battery LiMn<sub>2</sub>O<sub>4</sub>/ Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. Moreover, the supercapacitor has good cycle life performance at 4C rate, the capacity loss in constant current mode

is no more than 7.95% after 5000 cycles, and the capacity loss in constant current–constant voltage mode is no more than 4.75% after 2500 cycles [20].

The authors described the compounds are carbon/carbon for conventional supercapacitor, lithium ion for Li-ion battery, asymmetric hybrid supercapacitors use a nanostructured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as anode, activated carbon /  $\text{LiCoO}_2$  /  $\text{LiMn}_2\text{O}_4$  as cathode and an acetonitrile electrolyte containing a lithium salt. Fig.3 shows the overview of all devices was built using common plastic Li-ion technology developed by Telcordia Technologies. And in this paper was compared to the specific energy, specific power, fast-charge capability, low temperature operation, cycle-life and self-discharge of five energy storage devices (Table 1) [21].

The lithium boron oxide (LBO) -modified  $\text{LiMn}_2\text{O}_4$  cathode powder was prepared by a one step process of ultrasonic spray pyrolysis method. The powder has spherical shape, dense structure, and large grain size in that 1 and 5 wt% glass material have a best performance compared to the without LBO and 2, 3, 4 wt%.  $\text{LiMn}_2\text{O}_4$  powder morphological characteristics, discharge capacities, the cycle properties were improved using the addition of the  $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$  glass material. The discharge capacity of  $\text{LiMn}_2\text{O}_4$  powders without any glass material decreases from 116.3 to 92.6  $\text{mAh g}^{-1}$  after 100 cycles, the reduced capacity being 80% of the initial capacity. However, the discharge capacity of the  $\text{LiMn}_2\text{O}_4$  powders with 1 wt% glass material decreases from 131.0 to 113.2  $\text{mAh g}^{-1}$  after 100 cycles; thus, the capacity retention is 86% of the initial capacity. The optimum amount of the LBO glass material is 1 wt% of the  $\text{LiMn}_2\text{O}_4$  powder. The addition of an appropriate amount of LBO glass material improves the first charge/discharge capacities, Coulombic efficiencies, and cycle performances of the powders. The LBO glass material covering the  $\text{LiMn}_2\text{O}_4$  powders improves the electrochemical properties of the powders by decreasing the reactivity of the powders with acidic electrolytes [22].

The cathode nanofiber of  $\text{LiNi}_{0.4}\text{Co}_{0.6}\text{O}_2$  was prepared by electrospinning and characterized by thermal analysis, X-ray diffraction, FTIR and scanning electron microscopy studies. The asymmetric supercapacitor cell was fabricated and electrochemical performance was found by cyclic voltammetry studies, impedance measurements, charge-discharge studies. Which exhibited a highest specific capacitance of  $72.9 \text{ F g}^{-1}$ , charge transfer resistance of  $5.05 \Omega$ , energy density and power density of the capacitor cell was  $180.2 \text{ Wh kg}^{-1}$  and  $248.0 \text{ W kg}^{-1}$ , respectively [23].

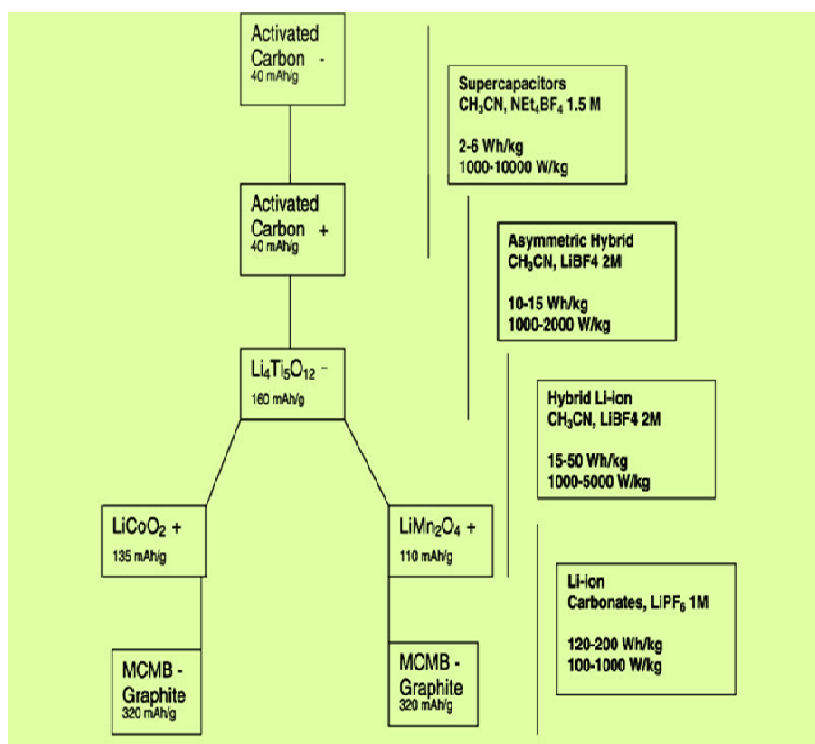


Fig.3 Overview of the components used in the family of electrochemical storage devices developed by Telcordia Technologies since 1994 [21]

Table 1

Properties	C/C	LTO/C	LTO/LCO	LTO/LMO	Li-ion
Weight (g)	8.8	11.7	9.9	9.5	3.6
ESR at 1000 Hz ( $\Omega$ )	0.0225	0.033	0.039	0.032	0.09
ESR ( $\Omega \text{ cm}^2$ )	1.74	5.1	6.03	4.95	N/A
Capacity (mA h)	26	56	208	170	147
Energy	0.39	0.76	3.3	3	10
Power	9	10	7.5	7.6	5.4
Fast charge	10	9.4	9.1	8.2	3.9
Cycle-life	10	7.5	0.57	0.08	2.6
Self-discharge	7.48	7.98	9.49	9.01	10

Lithium ion intercalated manganese oxide as cathode material and activated carbon as anode material with in a neutral  $\text{Li}_2\text{SO}_4$  aqueous electrolyte were used for hybrid supercapacitor. The electrochemical study was carried by cyclic voltammetry, charge/discharge. According to the charge/discharge process, Li ions moved from one electrode to another electrode and the ionic conductivity increased in the function of electrolyte. This hybrid supercapacitor worked in the principle of "rocking chair battery." They optimized the ratio of the positive/negative electrode mass loading 2:1 and an operating voltage of 0.8–1.8 V. The cell cycling performance was studied which exhibited the less than 5% capacityloss over 20,000 cycles at 10 C charge/discharge rate [24]. Kyoungho Kim et al synthesized the Non-aqueous supercapacitors with lithium transition-metal oxides. /AC composite as used as the cathode. The  $\text{LiMn}_2\text{O}_4$  electrochemical properties were analyzed by AC impedance, charge-discharge test and cyclic voltammetry. The results of cyclic voltammetry and AC impedance analyses showed that the pseudocapacitance may stem from the synergistic contributions of capacitive and faradic effects; the former is due to the electric double layer which is prepared in the interface of activated carbon and organic electrolyte, and the latter is due to the intercalation of lithium ( $\text{Li}^+$ ) ions. The specific capacitance and energy density of a supercapacitor improved as the lithium transition-metal oxides content increased, showing 60% increase compared to those of supercapacitor using a pure activated carbon positive electrode [25].

## CONCLUSION

In this review provide the useful information tool for energy storage source of supercapacitors. We discussed about the supercapacitor classifications of (i) electric double layer capacitors (ii) pseudocapacitors (iii) hybrid capacitor, based on the presence of electrode material and especially the lithium based battery type cathode material from the literatures. The positive electrodes of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -RGO,  $\text{LiMn}_2\text{O}_4$ -RGO,  $\text{LiMn}_2\text{O}_4$ /activated carbon (AC) composite,  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.4}\text{Co}_{0.6}\text{O}_2$  are used to make the battery type hybrid supercapacitors. Lithium intercalated metal oxide cathode as a barrier between supercapacitor and Li-batteries. Each material exhibited the improved charge storage, ion dispersion with in the electrodes, which has helped to overcome the energy density and as well as increased the other electrochemical properties of power density, cycle life time, specific capacitance, high charge-discharge, etc.

## Acknowledgment

The authors like to acknowledge the DST-Nano Mission, New Delhi for the financial support and to thank Dr. Jeppiaar, Chancellor of Sathyabama University, Chennai.

## REFERENCES

- [1] Meisam Valizadeh Kiamahalleh; Sharif Hussein Sharif Zein, *Nano brief reports and reviews.*, **2012**, 7(2), 1230002-1-123002-27.
- [2] Aaron Davies; Aiping Yu, *Can. J. Chem. Eng.*, **2011**, 89(6), 1342-1357.
- [3] U Fischer; R Saliger; V Bock; R Petricevic; J Fricke, *J. Porous Mater.*, **1997**, 4(4), 281–285.
- [4] Aaron Davies; Aiping Yu, *Can. J. Chem. Eng.*, **2011**, 89(6), 1342–1357.
- [5] Indrajit Shown; Abhijit Ganguly; Li-Chyong Chen; Kuei-Hsien Chen, *Energy Science & Engineering.*, **2014**, 3(1), 2-26.
- [6] Shen-MingChen; Rasu Ramachandran; Veerappan Mani; Ramiah Saraswathi, *Int. J. Electrochem. Sci.*, **2014**, 9(1), 4072 – 4085.
- [7] D Ghosh; S Giri; M Moniruzzaman; T Basu; M Mandal; CK Das, *Dalton Trans.*, **2014**, 43(28), 11067-76.
- [8] Zaher Algharaibeh; G Peter Pickup, *Electrochem. Commun.*, **2011**, 13(2), 147–149.
- [9] Jianling Li; FeiGao, *J. Power Sources.*, **2009**, 194(2), 1184–1193.
- [10] Qunting Qu; Lei Li; ShuTian; WenlingGuo; Yuping Wu; Rudolf Holze, *J. Power Sources.*, **2010**, 195(9), 2789–2794.
- [11] QT Qu; Y Shi; S Tian; YH Chen; YP Wu; R Holze, *J. Power Sources.*, **2009**, 194(2), 1222–1225.

- [12] Sheng Liu; Cheng-Zhi Fan; Yuan Zhang; Cheng-Hui Li; Xiao-Zeng You, *J. Power Sources.*, **2011**, 196(23), 10502– 10506.
- [13] By Yu-GuoGuo; Jin-Song Hu; Li-Jun Wan, *Adv. Mater.*, **2008**, 20(15), 2878–2887.
- [14] Yan-Jing Hao; Yan-Ying Wang; Qiong-Yu Lai; Yan Zhao; Lian-Mei Chen; Xiao-Yang Ji, *J Solid State Electrochem.*, **2009**, 13(1), 905–912.
- [15] Min-Young Cho; Sun-Min Park; Jae-Won Lee; Kwang-ChulRoh. *J. electrochem. sci. technol.*, **2011**, 2(3), 152-156.
- [16] R Santhanam; B Rambabu, *J. Power Sources.*, **2010**, 195(17), 5442–5451.
- [17] Song Yi Han; In Young Kim; Kyung Yeon Jo; and Seong-Ju Hwang, *J. Phys. Chem. C.*, **2012**, 116(13), 7269–7279.
- [18] Yong-gang Wang; Yong-yao Xia, *Electrochem. Commun.*, **2005**, 7(11), 1138–1142.
- [19] Yen-Po Lin; Nae-Lih Wu, *J. Power Sources.*, **2011**, 196(2) 851–854.
- [20] Xuebu Hu; Zhenghua Deng; Jishuan Suo; Zhonglai Pan, *J. Power Sources.*, **2009**, 187(2), 635–639.
- [21] Aurelien Du Pasquier; Irene Plitz; Serafin Menocal; Glenn Amatucci, *J. Power Sources.*, **2003**, 115(1), 171–178.
- [22] Seung Ho Choi; Jung Hyun Kim; You Na Ko; Young Jun Hong; Yun Chan Kang, *J. Power Sources.*, **2012**, 210(1), 110–115.
- [23] G Bhuvanalogini; N Muruganathan; V Shobana; A Subramania, *J Solid State Electrochem.*, **2014**, 18(9), 2387-2392.
- [24] Yong-gang Wang; Yong-yao Xia, *J. Electrochem. Soc.*, **2006**, 153(2), A450-A454.
- [25] Kyoungho Kim; Min-Soo Kim; TaewhanYeu, *Bull. Korean Chem. Soc.*, **2010**, 31(11) 3183-3189.