Combustion synthesis of nanocrystalline $MgFe_2O_4$ as anode material for lithium ion batteries applications

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ABSTRACT

Spinel ferrites such as $MgFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, etc., are considered as promising anode materials for lithium ion battery (LIB), since these exhibit high capacity, environmental friendly, availability of very cheap precursors, etc. $MgFe_2O_4$ stands out from other ferrites, due to its high abundance, low toxicity, high theoretical capacity (1072 mAh g^{-1}), etc. Hence, the present work focused on the preparation of nanocrystalline $MgFe_2O_4$ by using urea assisted citrate combustion process and characterized using XRD, FE-SEM, BET. Also, lithium battery was fabricated using the developed nanocrystalline $MgFe_2O_4$, as anode material, and investigated its electrochemical performance through cyclic voltametry (CV) and charge-discharge characteristics, to find out its suitability, as a anode material, for lithium battery applications.

Keywords: Nanocrystalline $MgFe_2O_4$; combustion synthesis; XRD; FE-SEM; BET; cyclic voltametry; charge – discharge

1 INTRODUCTION

Lithium ion battery considered as a promising power sources for portable electronics and hybrid electric vehicles owing its high energy density and long cycle life [1]. Graphite is widely used as a anode material for commercial LIB's, due to its low cost and highly abudant but theoritical capacity limited to 372 mAh g^{-1} [2]. Hence, there is a need to develop anode material with high theoritical capacity, low cost and environmental friendly. Recently, ferrites, such as $CoFe_2O_4$ $ZnFe_2O_4$, $MgFe_2O_4$ and etc., received a great attention as a anode materials for LIBs, owing their high theoritical capacity of 1000 mAh g^{-1}, which is very much higher compared to commercial used graphite [2-5]. Among them, $MgFe_2O_4$ exhibit high theoritical capacity of 1072 mAh g^{-1} [3]. Very recently, sivakumar et al firstly prepared $MgFe_2O_4$ as a anode material by high energy ball milling method [6]. But delived less discharge capacity of 300 mAh g^{-1} after 10 cycles. Yanhong Yin et al, prepared $MgFe_2O_4$ nanoparticle by sol gel method and deliverd discharge capacity of 635 mAh g^{-1} afetr 50 cycles [7]. Hence, preparation methods play an important role in elctrochemical perfomance of battery. Many methods such as hydrothermal, sol gel, co-precipatation, combustion, etc., are used to prepare the $MgFe_2O_4$ nanopartcles [1, 7, 8]. Among them, combustion method is found to be simple and low cost synthesis process. By using combustion method, one can produce the nanocrystalline material at low temperature with high phase pure material .

Hence, in present investigatation, nanocrystalline $MgFe_2O_4$ material was prepared by combustion method and the prepared nanocrystalline $MgFe_2O_4$ powder was characterized by XRD, FE-SEM and BET analysis. Finally, lithium battery was fabricated using the newly developed nanocrystalline $MgFe_2O_4$ material and tested its electrochemical perfomance through charge-discharge measurements and cyclic voltametry (CV) studies.

2. EXPERIMENTAL

2.1 Combustion synthesis of $MgFe_2O_4$

Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$, Qualigence, India), Ferric nitrate ($Fe(NO_3)_3.9H_2O$, Qualigence India), Citric acid (Qualigence, India) and urea (Qualigence, India) and ammoniu solution (Qualigence, India) were used as a starting chemicals. All chemical are dissolved in appropriate amount of distilled water. Magnesium nitrate hexahydrate and ferric nitrate were used as a metal ion sources and maintained at 1:2 ratio respectively. Citric and urea were used as chelating agents and were mainted at 1:0.5 ratio. Finally, 3 ml of ammonia solution was added to the mixed solution and then continiuosly stirred at 80 ˚C till formation of gel. Polymeric intermediate was obtained by heating the gel at 150 ˚C for 6 hours and finally calcined at 700 ˚C for 2 hours to obtained nanocrystalline $MgFe_2O_4$.

3.CHARACTERIZATION

3.1.XRD

Fig.1 shows the XRD pattern of $MgFe_2O_4$ obtained at 700 ˚C. The observed crystalline peaks of $MgFe_2O_4$ matching well with the standard JCPDS (Card No.73-2410)

data, confirms the formation of pure cubic spinel phase of $MgFe_2O_4$ sample [9]. The cystalline size of the $MgFe_2O_4$ sample calculated using Scherres formula is found to be 29.98 nm. Hence, XRD results confirmed the formation of pure cubic spinel phase of nanocrystalline $MgFe_2O_4$ sample.

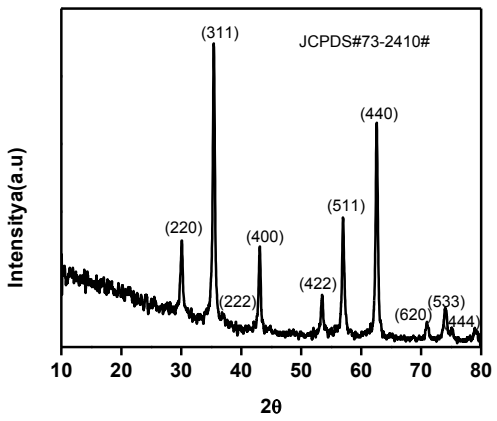

Fig.1.XRD pattern of $MgFe_2O_4$ obtained at 700 ˚C.

3.2.SEM

Fig.2 shows the FE-SEM image of the $MgFe_2O_4$ sample**.** From fig.2, large voids/pore type structure is observed. The observed pore structure may be due to the release the carbon dioxide and nitrozen gases respectevly from the decompositon of carboxilic acids (citric acid and urea) and metal nitrates during the calcining process.

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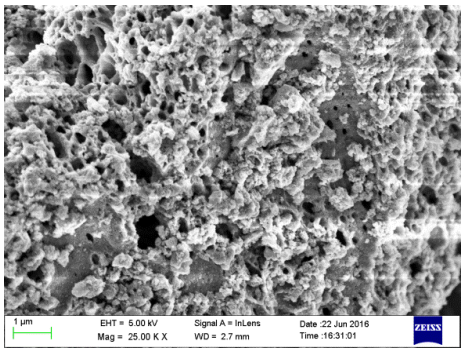

2. FE-SEM image of the $MgFe_2O_4$ sample**.**

3.3. BET analysis

Fig.3 shows the N_2 adsorption-desorption isotherm of $MgFe_2O_4$ sample obtained at 77 K. From measured N_2 adsorption-desorption data, the specific surface area of the sample calculated using Brunauer-Emmett-Teller (BET) method and pore volume calculated by using Barrett Joyner-Halenda (BJH) desorption method respectevely. The BET specific surface area and pore volume of $MgFe_2O_4$ sample found to be 29.4 m^2 g^{-1} and 35.5330 nm respectevely.

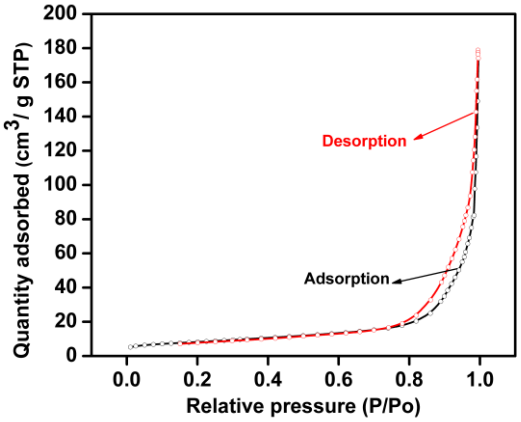

Fig.3.N_2-adsorption-desorption isotherm of $MgFe_2O_4$ sample obtained at 77 K.

4.ELECTROCHEMICAL MEASUREMENTS

The $MgFe_2O_4$ composite slurry was prepared by mixing of 70% of $MgFe_2O_4$, 20% of carbon black and 10% of PVDF binder in NMP solvent. Prepared composite slurry was coated on copper foil and dried in a woven for 12 h at 120 ˚C. The CR2032 coin type lithium cell was fabricated in argon filled glove box using the composite $MgFe_2O_4$ as an anode, Li foil as a reference/counter electrode and 1M of LiPF6, dissolved in a 1:1 ratio of ethylene carbonate and diethyl carbonate, as electrolyte. The charge-discharge measurements were carried out using “Bitrode” battery cycling tester (USA), between 0.005-V. The cyclic voltametry measurement was made by using Bio-Logic instrument between 0.0-3 V at scan rate of 0.1 mV/s.

4.1 Cyclic volatametry

Fig.4 shows the cyclic volametry (CV) curves of the $MgFe_2O4$ electrode for intial 4 cycles, between 0.0-3 V at a scan rate of 0.1 mV/s. From fig.4, CV curves showed two cathodic peaks. The observed first irreversible cathodic peak at 0.18 V corresponds to formation of solid electrolyte interface (SEI) layer at electrode/electrolyte interface [10]. The observed second cathodic peak at 0.69 V is attributed to the reduction of Fe^{+3} to Fe^{o} and Mg^{+2} to Mg and it is slightly shifted to lower potential for subsequent cycles [11, 12]. The observed anodic peak at 1.55 V corresponds to the oxidationof Fe^{0} to Fe^{+3} and Mg to Mg^{+2} [11, 12]. The peak intensity and integrated area of CV curves related to the capacity of the material. The observed decresing peak

intensity and integrated area for first to subsequent cycles indicating the loss of capacity of the materials upon cycling. Further, it is varified from the charge-discharge cycles measurements.

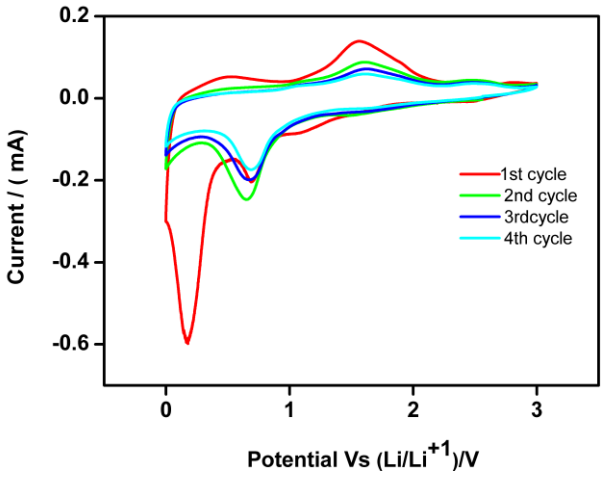

Fig.4. Cyclic voltametry curves of $MgFe_2O_4$ elctrode for initial 4 cycles between 0-3 V at scan rate of 0.1 mV/s

4.2 Charge-discharge measurements

Fig.5 shows the charge-discharge curves obtained between 0.005-3V at current density of 300 mA g^{-1} for LIB made of nanocrystalline $MgFe_2O_4$ as a anode material. The deliverd first discharge and charge capacities are respectively found to be 1366.6 $mAhg^{-1}$ and 794.4 $mAhg^{-1}$. The observed irreversible capacity loss for the first cycle attributed to the formation solid electrolyte layer at electrode electrolyte interface at first cylce [13]. For the subsequent 2^{nd}, 10^{th} and 20^{th} cycles, discharge capacity is respectively found to be 816.6, 516.6 and 411.1 mAh g^{-1}. The observed capacity loss for the subsequent cycles may be due to the pulverization and aggregation of $MgFe_2O_4$ nanoparticles upon cycling [13].After 50 cycle, delivered discharge capacity is found to be 326 mAh g^{-1}. Fig.6 shows the discharge capacity & Coulombic efficiency vs number of cycles of nanocrystalline $MgFe_2O_4$ electrode material. The observed efficiency is about 58.1% and it is improved to 92.4% after first cycle. The improved Coulombic effeciency may be due to the porous structure of the materials.

5.Conclusion

Spinel structured nanocrystalline mesoporous $MgFe_2O_4$ sample was prepared by urea assisted modified citrate combustion process. Formation of phase pure of the $MgFe_2O_4$ sample is confirmed from the XRD resultsPorous net work and high specific surface area of the sample confirmed from the FE-SEM and BET results respectevely

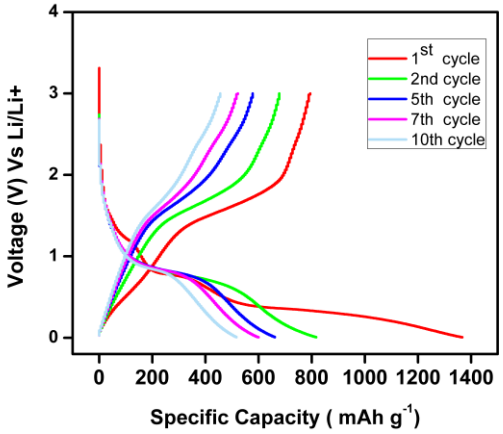

Fig.5.Charge-discharge curves of LIB made of $MgFe_2O_4$ as aanode material between 0.005-3 V at current density of 300 mA g^{-1}

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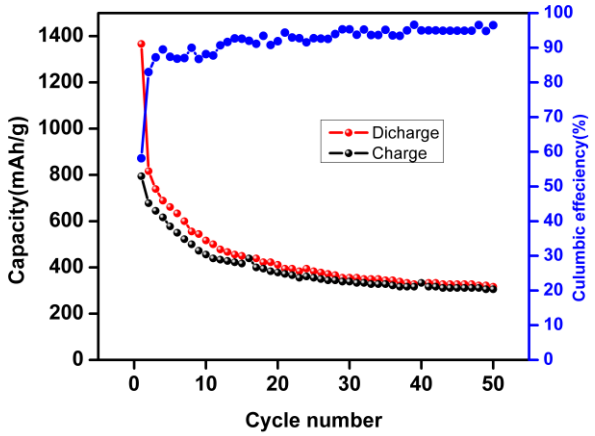

Fig.6. Cyclic perfomance and Coulombic efficiency of $MgFe_2O_4$ electrode between 0.005-3 V at current density of 300 mAh g^{-1}.

The deleved high discharge capacity of 316.6 mAh g^{-1} suggests that the developed nanocrystalline $MgFe_2O_4$ could be a better anode material for lithium battery applications.

ACKNOWLEDGMENT

Dr. N. Satyanarayana is gratefully acknowledges DST - Nano mission, AICTE, UGC, CSIR and DRDO, Govt. of India, for financial support through major research project grants. Authors thank CIF, Pondicherry University, for

providing Raman, BET Surface area and TG/DTA measurements. Authors also thankful to Dr. P. Elumalai, Centre for Green Energy Technology, Pondicherry University for providing Cyclic voltammetry measurements.

REFERENCES

[1] C. Gong, YJ. Bai, YX. Qi, N.Lun, J. Feng, preparation of carbon-coated MgFe 2 O 4 with excellent cycling and rate performance, electrochimica acta, 90,119-127, 2013

[2] H. Qiao, L. Luo, K. Chen, Y. Fei, R. Cui, Q. Wei, electrospun synthesis and lithium storage properties of magnesium ferrite nanofibers, electrochimica acta, 160 43-49, 2015

[3] N. Huo, Y. Yin, W. Liu, J. Zhang, Y. Ding, Q. Wang, Z. Shi, S. Yang, facile synthesis of MgFe 2 O 4/C composites as anode materials for lithium-ion batteries with excellent cycling and rate performance, new journal of chemistry, 40 7068-7074, 2016

[4] Z. Li, T. Zhao, X. Zhan, D. Gao, Q. Xiao, G. Lei, high capacity three-dimensional ordered macroporous CoFe 2 O 4 as anode material for lithium ion batteries, electrochimica acta, 55, 4594-4598, 2010

[5]X. Guo, X. Lu, X. Fang, Y. Mao, Z. Wang, L. Chen, lithium storage in hollow spherial znfe2o4 for lithium-ion batteries, meeting abstracts, the electrochemical society, , pp. 297-297, 2010

[6] N. Sivakumar, S. gnanakan, K. Karthikeyan, S. Amaresh, W. Yoon, G. Park, Y. Lee, nanostructured MgFe 2 O 4 as anode materials for lithium-ion batteries, journal of alloys and compounds, 509 , 7038-7041, 2011

[7] Y. Yin, B. Zhang, X. Zhang, J. Xu, S. Yang, Nano MgFe 2 O 4 synthesized by sol–gel auto-combustion method as anode materials for lithium ion batteries, journal of sol-gel science and technology, 66 , 540-543, 2013

[8] S. Verma, P. Joy, Y. Khollam, H. Potdar, S. Deshpande, synthesis of nanosized MgFe 2 O 4 powders by microwave hydrothermal method, materials letters, 58 1092-1095, 2004

[9] W.B. Cross, L. Affleck, M.V. Kuznetsov, I.P. Parkin, Q.A. Pankhurst, self-propagating high-temperature synthesis of ferrites MgFe 2 O 4 (M= Mg, Ba, Co, ni, Cu, Zn); reactions in an external magnetic field, journal of materials chemistry, 9, 2545-2552, (1999)

[10] Y. Xiao, X. Li, J. Zai, K. Wang, Y. Gong, G. Li, Q. Han, X. Qian, CoFe 2 O 4-graphene nanocomposites synthesized through an ultrasonic method with enhanced performances as anode materials for li-ion batteries, nano-micro letters, 6,307-315, 2014

[11]Y. Pan, Y. Zhang, X. Wei, C. Yuan, J. Yin, D. Cao, G. Wang, MgFe 2 O 4 nanoparticles as anode materials for lithium-ion batteries, electrochimica acta, 109 89-94, 2013

[12] A.K. Rai, T.V. Thi, J. Gim, J. Kim, combustion synthesis of MgFe 2 O 4/graphene nanocomposite as a high-performance negative electrode for lithium ion batteries, materials characterization, 95, 259-265, 2014

[13] A.K. Rai, L.T. Hnh, CJ. Park, J. Kim, electrochemical study of nio nanoparticles electrode for application in rechargeable lithium-ion batteries, ceramics international, 39, 6611-6618, 2013