

NANO-SIZED Mn_2O_3 PREPARED BY A NOVEL SOLVOLYSIS ROUTE AS AN ELECTROCHEMICAL CAPACITOR ELECTRODE MATERIAL

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ABSTRACT

Nano-sized manganese oxide (Mn_2O_3) was synthesized using a solvothermal route with the presence of citric acid as the chelating agent and acetone as the handle. The sample obtained was heated at 400°C, 600°C and 800°C respectively. The nanostructure of Mn_2O_3 at different heating temperature was investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM) and Field-Emission Scanning-Electron Microscopy (FE-SEM). The obtained spherical shape Mn_2O_3 (400°C) particles were found to be within 7-30nm range in diameter. Single electrode redox properties were studied using the cyclic voltammetry (CV) method utilising the treated Mn_2O_3 (400°C) as the working electrode in a three electrode configuration against standard calomel electrode with a polished platinum as the counter electrode. Thus, the redox and pseudocapacitance (197.14 F/g) of the product were assessed up to 0.45V in a 2M KOH electrolyte.

Keywords: Electrochemical Capacitor, Manganic Oxide, Nano-structure, Solvothermal Route

1.0 INTRODUCTION

Of late, nano-structural materials have been in the limelight and been pursued actively by scientists and researcher around the globe for scientific interest and potential applications [1-3]. Increasing number of products are utilising nano-structural materials and finding their way into the global market. Focus now had been shifted towards the synthesis of nano-rods, nano-wires, or nano-fibers as these nano-structures are found to be useful in the application of nano-devices [4-7]. There have been reports of various methods of synthesis of such nano-materials such as sol gel [8-10], precursor thermal decomposition [11,12], laser ablation [13,14], electrospinning technique [15] and arc discharge [16,17].

Nano-sized manganic oxide (Mn_2O_3) which has extremely large surface area and remarkably reduced size would contribute to the better performance of applications employing the material as their active substance. This includes the increasingly attractive field of lithium batteries where much attention has been focused on the lithiation of Mn_2O_3 for intercalation compounds of Li-Mn-O as electrode material [18,19]. Mn_2O_3 is used as a catalyst for nitrogenoxide decomposition, isopropanol alcohol decomposition and so on [20-24]. As a catalyst, it is cheap, environmental friendly and most suitable to be used for removing carbon dioxide and nitrogen oxide from smoke emitted by heavy industries. Mn_2O_3 plays an important role in the production of soft magnetic materials, i.e. manganese zinc ferrite for applications such as magnetic cores in transformers for power supplies [25].

A few techniques of synthesizing nano-sized particles of Mn_2O_3 have been reported [15, 26-28]. In this research, the

preparation of nano-crystalline Mn_2O_3 was done through the use of citric acid and acetone from the commercially available $Mn(NO_3)_2 \cdot 4H_2O$. The study of Mn_2O_3 as electrode material in electrochemical capacitors (EC) has not been widely reported in the literatures. Thus, this study is intended to examine the possibility of application of Mn_2O_3 nano-particles as capacitive electrode material in the EC.

2.0 EXPERIMENTAL DETAILS

2.1 MATERIAL SYNTHESIS

In this study, we report a solvothermal route to synthesizing nano-sized Mn_2O_3 at low temperatures. The nano-structured Mn_2O_3 is a direct product of the combustion of $Mn(NO_3)_2 \cdot 4H_2O$ with acid citric and acetone. The aqueous solution of $Mn(NO_3)_2$ of 0.1M was first prepared. Then the aqueous solution was thoroughly mixed with acid citric and acetone and vigorously stirred with temperature maintained at 200°C for 1 hour. Citric acid acting as a chelating agent induced the molecular level mixing through the disassociation of the ionic species of the starting material. Acetone, a solvent, acts as a handle to promote non-hydrolytic condensation of $Mn(NO_3)_2$ dissolute. The acetone which was used in great access for the complete reduction of $Mn(NO_3)_2$ through the solvothermal process, a portion of it is oxidised. After the combustion was completed, the resulting solid was ground to fine powder before post-annealing in air. Post-annealing was carried out at temperatures 400°C, 600°C and 800°C for 1 hour respectively in order to soften the metal through the removal of crystal defects and the internal stresses caused by

these defects. Defects were caused by the incomplete chemical reaction and combustion during the synthesis process. Heating at different temperatures allowed the nano-crystalline structures of the Mn_2O_3 to be studied. XRD analysis shows that crystalline Mn_2O_3 is the resulting product.

2.2. ELECTRODE PREPARATIONS

The working electrode for the three-electrode sets of electrodes was fabricated utilising 80 wt. % nano-sized Mn_2O_3 , 10 wt. % acetylene black to improve conductivity of the electrode and 10 wt. % polyvinylidene fluoride (PVdF) (Elf Atochen, France) as binder with a few drops of *N*-methyl-2-pyrrolidone (NMP). The mixture was stirred and mixed thoroughly using agate pestle and mortar to form thick slurry. The square electrode was fabricated by coating the slurry on the stainless steel mesh (EXMET, U.S.A.) on an area of 4 cm². The square electrode was dried overnight in the vacuum oven at the temperature of 100°C.

2.3. THREE-ELECTRODE ELECTROCHEMICAL CELL CONSTRUCTION

To enable the study of the redox properties of the single electrode, the three-electrode electrochemical cell was constructed with platinum as the counter electrode, Mn_2O_3 square composite electrode as the working electrode and a reference electrode; a saturated calomel electrode (mercury/mercurous chloride) Standard Reference Electrode (SCE). A 2M KOH aqueous solution was prepared and used as the electrolyte for the three-electrode electrochemical cell. Prior to the use of the square composite electrode of Mn_2O_3 in the three-electrode system, it was vacuum-wetted (degassed) in the electrolyte solution (2M KOH) for 1hr. Degassing is done to enable the electrolyte to reach the distributed pores of the electrode.

2.4. CYCLIC VOLTAMMETRY MEASUREMENT

The cyclic voltammetry (CV) were done using the Autolab (PGSTAT302) system. The potential window was set to be between 0V to 0.45V and cyclic voltammograms at scan rates 10, 20, 50, 70 and 100mVs⁻¹ were collected to be analysed.

3.0 RESULTS AND DISCUSSION

3.1. MATERIAL CHARACTERISATION

The XRD was recorded on a Siemens Diffraktometer D5000. Figure 1 shows the X-ray diffraction (XRD) patterns of the resulting compound synthesized subjected to heat treatment at different temperatures, *i.e.* 400°C, 600°C and 800°C. The all the diffraction peaks of the resulting product in the XRD results obtained can be indexed to the cubic structure Mn_2O_3 with lattice parameters $a = 9.40800 \text{ \AA}$, $b = 9.40800 \text{ \AA}$ and $c = 9.40800 \text{ \AA}$. As can be seen the peak profile is broad and most of the peaks are indexable to Mn_2O_3 . The broadness of the peaks indicates that the formed compound are mainly nanophased. As can be observed in Figure 1, as the temperature of the calcinations of Mn_2O_3 increases from 400°C to 600°C then to 800°C, the peaks are intensified. The peaks which are present at angles 23°, 33°, 38°, 45°, 49°, 55° and 66° are consistent with literatures on Mn_2O_3 [20, 27].

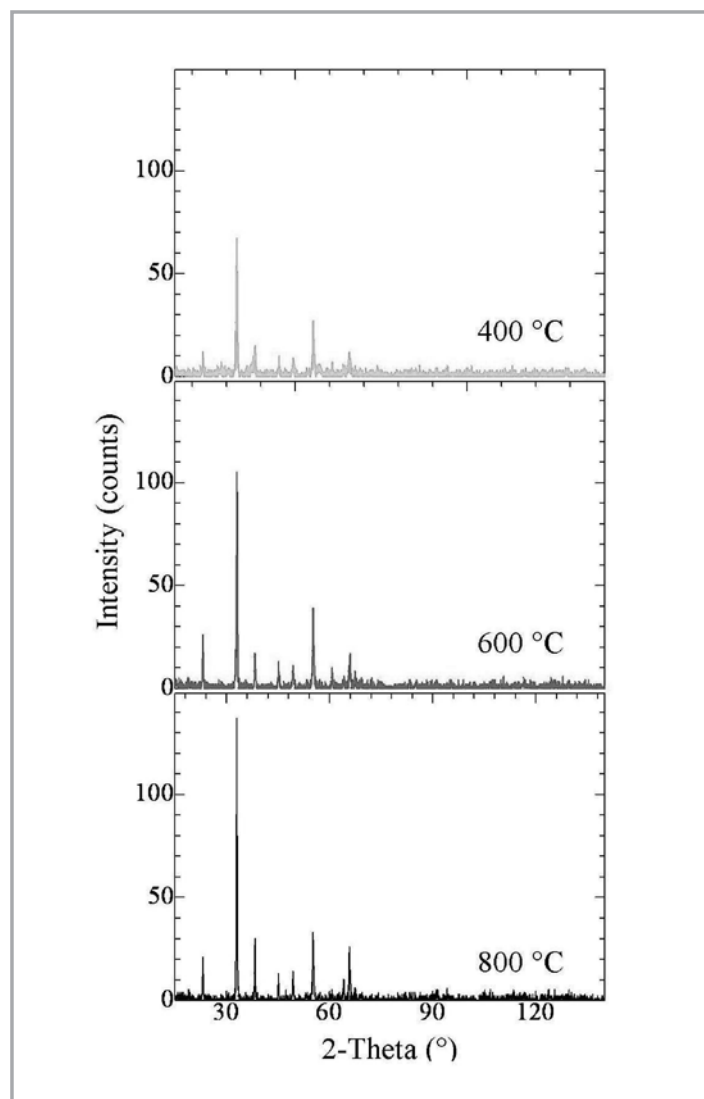


Figure 1: XRD patterns of the synthesized Mn_2O_3 at calcinated at 400°C, 600°C and 800°C

The nano-structured Mn_2O_3 was examined by means of Philips CM12 (S) transmission electron microscope (TEM). The TEM images reveal that the synthesized manganese oxide powder is of rounded particles. It is estimated that the nano-particles of manganese oxide are about 7-30nm in diameter, thus in nanometer range as observed from the TEM images. Nanostructure is beneficial to ionic charge transport.

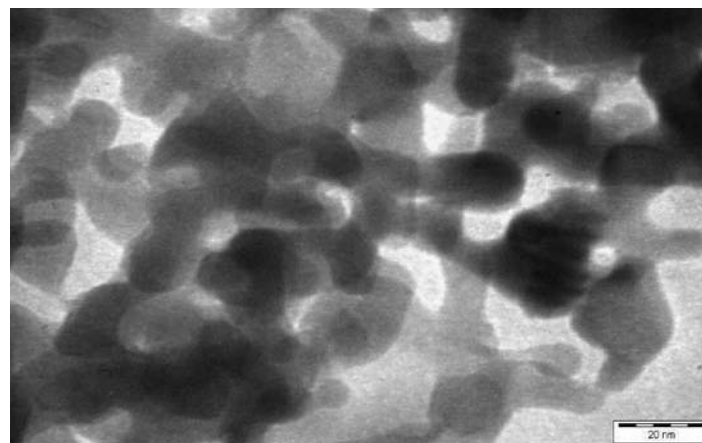


Figure 2: TEM image of the as-synthesized Mn_2O_3 heated at 400°C

The characterisation of the surface of the material (FE-SEM scan) was done using ZEISS - LEO Supra 50VP Scanning Electron Microscopes with 3rd Generation GEMINI field emission column. The FE-SEM images disclose the surface morphology of the manganese oxide synthesized. When heated at $400^\circ C$, Mn_2O_3 nano-crystallites agglomerated into spherical grains. Each grain results from the agglomeration of smaller particles that are regular size and of rounded edges which is consistent with the TEM results.

The well-defined regions of the nano-grains exhibit definite pores which would contribute greatly to the redox reaction for the pseudocapacitance when used as an electrode material for electrochemical capacitors. The grains are of nano-sized and their sizes are uniform throughout within the nanometer range as observed. As the annealing temperature of Mn_2O_3 increases, the grains grow into larger lumps as the agglomerated particles combine at those temperatures. As can be seen in the FE-SEM images below, the crystallite size increases as the heat treatment temperature increases. With an increase in the crystallite size, it is expected that the surface area of the material would decrease. Nonetheless, the particle sizes are still very much uniform throughout. EDX was also performed to determine the elemental composition in the nano-sized Mn_2O_3 synthesized.

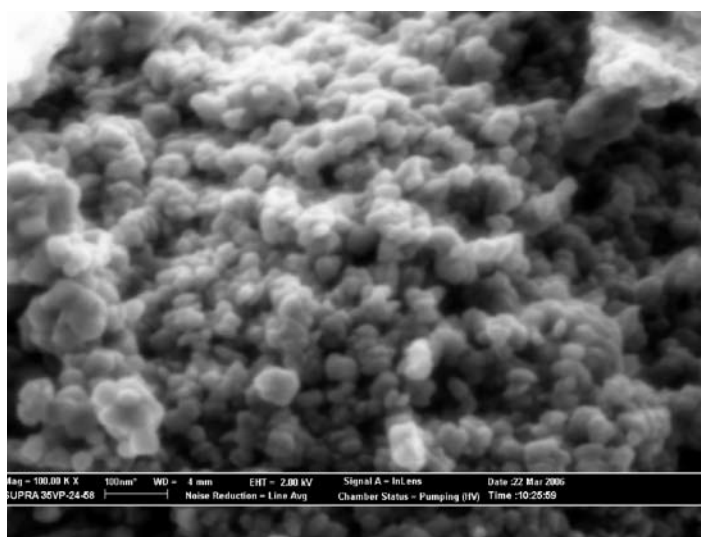


Figure 3: FE-SEM image of the as-synthesized Mn_2O_3 heated at $400^\circ C$

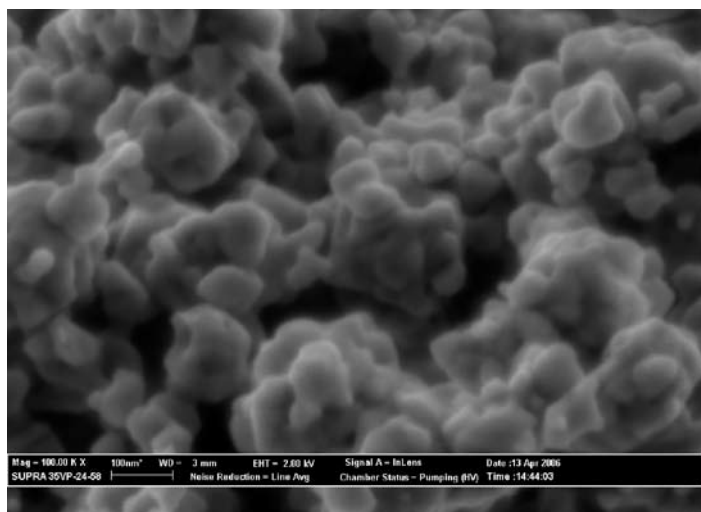


Figure 4: FE-SEM image of the as-synthesized Mn_2O_3 heated at $600^\circ C$

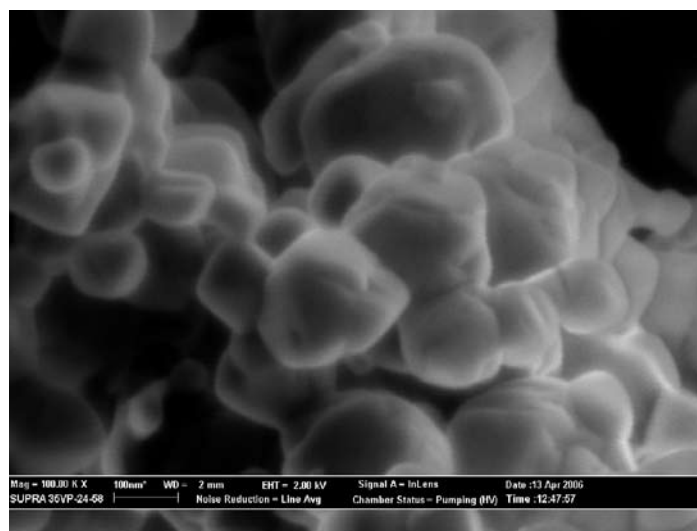


Figure 5: FE-SEM image of the as-synthesized Mn_2O_3 heated at $800^\circ C$

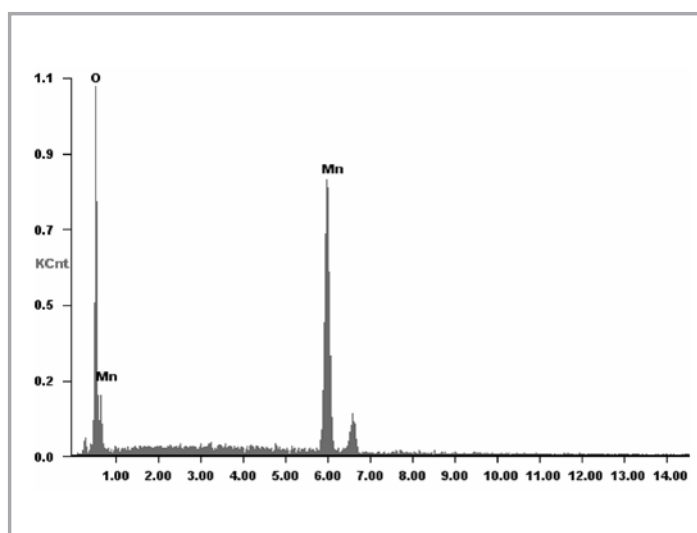
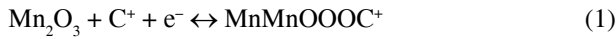


Figure 6: EDX results for the as-synthesized nano-sized Mn_2O_3 post-annealed at $400^\circ C$

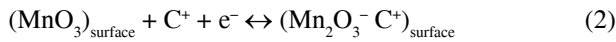
3.2 CYCLIC VOLTAMMETRY (CV)

To get more information on the electrochemical properties of the as-synthesized nano-sized Mn_2O_3 , CV characterisations were done at different scan rates. Cyclic voltammograms for the three-electrode electrochemical cell at scan rates $10mVs^{-1}$, $20mVs^{-1}$, $50mVs^{-1}$, $70mVs^{-1}$ and $100mVs^{-1}$ in a potential range of 0V up to 0.45V are shown in the Figure 7 below. Arrow indicates increasing scan rates. The oxidation of the Mn_2O_3 composite electrode occurs when the scanning potential reaches about 0.38V while the reverse scan produces a reduction peak, 1' at 0.27V. The oxidation of Mn_2O_3 composite electrode is responsible for peak 1. In the increasing scan rate, it is obvious changes are seen in the voltammograms.

Both the oxidation current and the two peaks seen on the oxidation and reduction increase in size and become more obvious with increasing scan rate. CV enables better understanding of the actual participation of the Mn_2O_3 electrode in the redox process. There are two mechanisms proposed for the charge storage in Mn_2O_3 electrode. Faradaic reaction (pseudocapacitance) was expected to occur due to the insertion/extraction (intercalation) of H^+ or alkali metal cation (C^+) *i.e.* K^+ in the electrode in the electrode upon oxidation [31, 32].



Adsorption of cations in the electrolyte on the Mn_2O_3 electrode can happen according to the equation below:



The specific capacitance was calculated from the cyclic voltammograms in the respective scan rates by integrating the area under the current-potential curve and then dividing by the sweep rate, the mass of the electrode and the potential window according to the equation;

$$C = \frac{1}{mV(V_a - V_c)} \int_{V_c}^{V_a} I(V)dV \quad (3)$$

The specific capacitance for the corresponding scan rates are as shown in Table 1. As can be seen in the table, a large specific capacitance of 197.14 Fg^{-1} is recorded at 10mVs^{-1} scan rate. Increasing scan rate has an impact on the specific capacitance recorded where the specific capacitance calculated reduces from 197.14 to 20.94Fg^{-1} when the scan rate is increased from 10 to 100 mVs^{-1} .

This may be due to the redox process which is primarily governed by insertion or extraction of K^+ and H^+ from the electrolyte into the nano-structured Mn_2O_3 electrode pores [32]. At higher scan rate, the cations would not be able to reach the interior pores of the nano-structured Mn_2O_3 electrode, instead only the outer surface of the electrode. Thus, as the scan rate increases, surface contact of the cations with the inner pores reduces, hence the drop in the specific capacitance calculated for the respective scan rates. Lower specific capacitance at higher scan rate is due to the limited participation of the Mn_2O_3 nano-structured electrode in the interior pores.

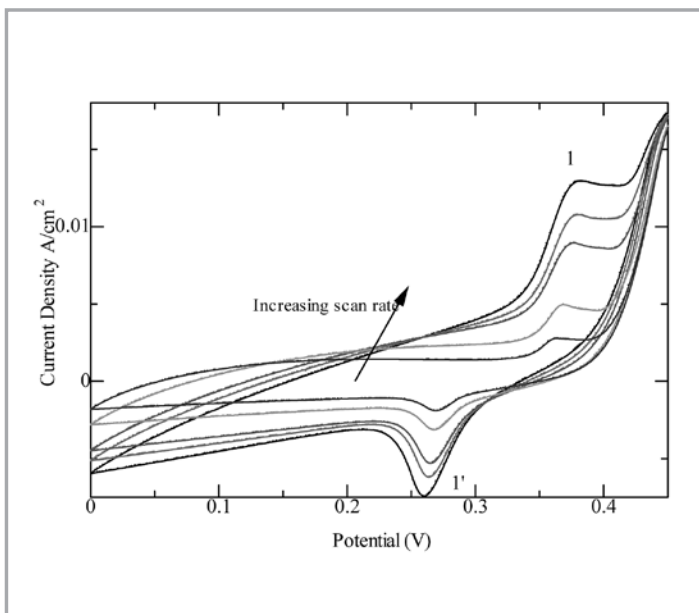


Figure 7: Cyclic Voltammograms recorded using the treated Mn_2O_3 (400°C) as the working electrode in the three electrode configuration at various scan rates ($10, 20, 50, 70$ and 100mVs^{-1}). Arrow indicates increasing scan rates

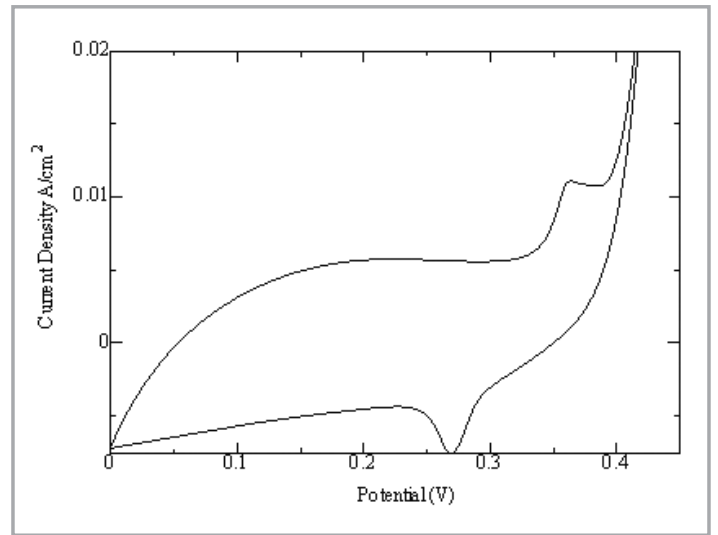


Figure 8: Cyclic Voltammograms for the three electrode system for the scan rate of 10mVs^{-1}

Table 1: Specific capacitance of the hybrid cell at different scan rate; $10, 20, 50, 70,$ and 100mVs^{-1}

Scan rate mVs^{-1}	Specific Capacitance (Fg^{-1})
10	197.14
20	100.00
50	41.25
70	29.83
100	20.94

4.0 CONCLUSION

In summary, nano-crystalline Mn_2O_3 has been directly synthesized through the solvothermal reaction of $\text{Mn}(\text{NO}_3)_2$ with the presence of citric acid as the chelating agent and acetone as the handle. TEM image illustrates that the as-synthesized Mn_2O_3 nano-particles are rounded in shape with the size of $7\text{-}30\text{nm}$ in diameter. FE-SEM images confirmed the results from the TEM images and showed that the resulting as-synthesized particles are agglomerated in nature. As the temperature of the post-annealing of the nano-sized Mn_2O_3 increases, the Mn_2O_3 particles grew in size too. The XRD results confirmed the particles synthesized are indeed Mn_2O_3 with peaks which are consistent with existing literatures. Increased temperatures of post-annealing also reveal an increase in intensity in the XRD results. The as-synthesized Mn_2O_3 nano-sized particles with extremely reduced grain size are suitable for the use as the electrode material for electrochemical capacitors as the specific capacitance is a direct function of the area of the material employed. The obtained specific capacitance at 10mVs^{-1} scan rate revealed a large capacitance *i.e.* 197.14 Fg^{-1} contributed by the pseudocapacitance due to the redox reaction in the electrode.

Further work on the cycling performance and stability of such electrodes in aqueous electrolytes and improvements to the specific power are important to enable the use of such material in real applications in the field of electrochemical supercapacitors.

REFERENCE

- [1] P. Gould, "Nanomaterials face control measures", *Nanotoday*, Vol. 1, No. 2, pp.34-39, May, 2006.
- [2] A.G. Mamalis, "Recent advances in nanotechnology", *J. Materials Processing Technology*, 2006
- [3] Y. Omata, Y. Yamagami, K. Tadano and T. Miyake, "Nanotube nanoscience: A molecular-dynamics study", *S. Saito Physica E: Low-dimensional Systems and Nanostructures*, Vol. 29, pp. 454-468, 2005.
- [4] V. Subramanian, H. Zhu and B. Wei, "Nanostructured MnO_2 : Hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material", *J. Power Sources*, 2006.
- [5] L. Vayssieres, "Advanced semiconductor nanostructure", *Comptes Rendus Chimie*, Vol. 9, No. 5-6, pp. 691-701, 2006.
- [6] J.G. Lu, P.Chang and Z. Fan, "Quasi-one-dimensional metal oxide materials-Synthesis, properties and applications", *Materials Science and Engineering: R: Reports*, 2006.
- [7] S. Kim and K. Lee, "Carbon nanofiber composites for the electrodes of electrochemical capacitors", *Chemical Physics Letters*, Vol. 400, No. 1-3, pp. 253-257, 2004.
- [8] Y. Miao, Q. Zhang, H. Yang and H. Wang, "Low-temperature synthesis of nano-crystalline magnesium titanate materials by the sol-gel method", *Materials Science and Engineering: B*, Vol. 128, No.1-3, pp. 103-106, 2006.
- [9] M. Venkateswarlu, C.H. Chen, J.S. Do, C.W. Lin, T.C. Chou and B.J. Hwang, "Electrochemical properties of nano-sized $Li_4Ti_5O_{12}$ powders synthesized by a sol-gel process and characterized by X-ray absorption spectroscopy", *J. Power Sources*, Vol. 146, No. 1-2, pp. 204-208, 2005.
- [10] C.H. Su, C.R. Lin, C.H. Hung, C.Y. Chang and L. Stobinski, "Novel process to synthesize the well-size-controlled carbon nanotubes using Fe/TiO₂ as catalyst by sol-gel method", *Surface and Coatings Technology*, Vol. 200, No. 10, pp. 3211-3214, 2006.
- [11] G. Shabbir, A.H. Qureshi and K. Saeed, "Nano-crystalline $LaFeO_3$ powder synthesized by the citrate-gel method", *Materials Letters*, 2006.
- [12] I. Mitov, D. Paneva and B. Kunev, "Comparative study of the thermal decomposition of iron oxyhydroxides", *Thermochimica Acta*, Vol. 386, No. 2, pp. 179-188, 2002.
- [13] K. Takada, R. Ma, M. Osada, N. Ohta, L. Zhang and T. Sasaki, "Formation of nano-sized particles of a solid electrolyte by laser ablation" *J. Power Sources*, Vol. 146, No. 1-2, pp. 703-706, 2005
- [14] N. Suzuki, H. Sasaki, Y. Morinaga and Y. Yamada, "Nano-porous manganese oxide formed by self-assembled agglomeration of nanocrystallites", *Applied Surface Science*, Vol. 252, No. 5, pp. 1498-1501, 2005.
- [15] C. Shao, H. Guan, Yichun Liu, X. Li and X. Yang, "Preparation of Mn_2O_3 and Mn_3O_4 nanofibers via an electrospinning technique", *J. Solid State Chemistry*, Vol. 177, No. 7, pp. 2628-2631, 2004.
- [16] N. Parkansky, O. Goldstein, B. Alterkop, R.L. Boxman, Z. Barkay, Yu. Rosenberg and G. Frenkel, "Features of micro and nano-particles produced by pulsed arc submerged in ethanol", *Powder Technology*, Vol. 161, No. 3, pp. 215-219, 2006.
- [17] C. P. Chen, T. H. Chang and T. F. Wang, "Synthesis of magnetic nano-composite particles", *Ceramics International*, Vol. 28, No. 8, pp. 925-930, 2002.
- [18] T. Nakamura and A. Kajiyama, "Synthesis of Li-Mn spinel oxide using Mn_2O_3 particles", *Solid State Ionics*, Vol. 45, pp. 124, 1999.
- [19] Y. Shin and A. Manthiram, "Influence of microstructure on the electrochemical performance of $LiMn^{2-y-z}Li_yNi_zO_4$ spinel cathodes in rechargeable lithium batteries", *J. Power Sources*, Vol. 126, pp. 169-174, 2004.
- [20] T. Yamashita and A. Vannice, "NO Decomposition over Mn_2O_3 and Mn_3O_4 ", *J. Catalysis*, Vol. 163, pp. 158-168, 1996.
- [21] T. Yamashita and A. Vannice, "Temperature programmed desorption of NO adsorbed on Mn_2O_3 and Mn_3O_4 ", *Applied Catalysis B: Environ.*, Vol. 13, pp. 141-155, 1997.
- [22] L. Chen, T. Horiuchi and T. Mori "Catalytic reduction of NO over a mechanical mixture of $NiGa_2O_4$ spinel with manganese oxide: influence of catalyst preparation method", *Applied Catalysis A: General*, Vol. 209, pp. 97-105, 2001.
- [23] M. Misono, Y. Hirao and C. Yokoyama "Reduction of nitrogen oxides with hydrocarbons catalyzed by bifunctional catalysts", *Catalysis Today*, Vol. 38, pp. 157-162, 1997.
- [24] E. F. McCaffrey, D. G. Klissurski and R. A. Ross, "The effect of oxygen content in a series of manganese oxide catalysts on their catalytic activity and selectivity in the decomposition of isopropyl alcohol", *J. Catalysis*, Vol. 26, pp. 380-387, 1972.
- [25] Z. W. Chen, S. Y. Zhang, S. Tan, J. Wang and S. Z. Jin, "Different aspects of the microstructure of nanometer-sized Mn_2O_3 ", *Materials Research Bulletin*, Vol. 34, No. 10-11, pp. 1583-1587, 1999.
- [26] C. Zhiwen, Z. Shuyuan, T. Shun, L. Fanqing, W. Jian, J. Sizhao and Z. Yuheng, "Preparation and electron spin resonance effect of nanometer-sized Mn_2O_3 ", *J. Crystal Growth*, Vol. 180, No. 2, pp. 280-283, 1997.

- [27] Q. Zhao and W. Shih, "Effects of processing parameters on the surface area of Mn_2O_3 at elevated temperatures", *Microporous and Mesoporous Materials*, Vol. 53, No. 1-3, pp. 81-86, 2002.
- [28] W. L. He, Y. C. Zhang, X. X. Zhang, H. Wang and H. Yan, "Low temperature preparation of nanocrystalline Mn_2O_3 via ethanol-thermal reduction of MnO_2 ", *J. Crystal Growth*, Vol. 252, pp. 285-288, 2003.
- [29] Z. Y. Yuan, T. Z. Ren, G. Du and B. L. Su, "A facile preparation of single-crystalline α - Mn_2O_3 nanorods by ammonia-hydrothermal treatment of MnO_2 ", *Chemical Physics Letters*, Vol. 389, No. 1-3, pp. 83-86, 2004.
- [30] Z. Gui, R. Fan, X. Chen and Y. C. Wu, "A simple direct preparation of nanocrystalline α - Mn_2O_3 at ambient temperature", *Inorganic Chemistry Communications*, Vol. 4, No. 6, pp. 294-296, 2001.
- [31] M. S. Michael and S. R. S. Prabaharan, "High voltage electrochemical double layer capacitors using conductive carbons as additives", *J. Power Sources*, Vol. 136, No. 2, pp. 250-256, 2004.
- [32] V. Subramanian, H. Zhu and B. Wei, "Nanostructured MnO_2 : Hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material", *J. Power Sources*, 2006.
- [33] M. Wu, G. A. Snook, G. Z. Chen and D. J. Fray, "Redox deposition of manganese oxide on graphite for supercapacitors", *Electrochemistry Communications*, Vol. 6, pp. 499-504, 2004.

PROFILES



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PROFESSOR DR GEORGE Z. CHEN

At present, Professor Dr George Z. Chen has under his belt, 16 patent applications (6 granted including being one of the pioneers of the Fray-Farthing-Chen (FFC) Cambridge Process), over 110 refereed research publications, over 40 articles in conference proceedings, and 98 original articles in refereed journals which have received more than 2300 citations according to ISI Web of Science. Professor Chen's research focuses on novel technologies that use (1) electricity to bring about new chemical process for making materials, (2) new chemical processes and materials for generation and storage of electricity, and (3) solar energy to drive chemical processes that can clean up the environment.