Cobalt Doped (Mn,Ti)- Oxides for Supercapacitors

J. D. Houck, V. S. Amar, and R. V. Shende*

Department of Chemical and Biological Engineering,
South Dakota School of Mines & Technology,
Rapid City, SD 57701, USA, *Rajesh.Shende@sdsmt.edu

ABSTRACT

In this investigation, a (Mn,Ti)-oxide (Mn:Ti 65:35 wt%) was prepared using surfactant templating assisted sol-gel method. To prepare this nanocomposite, sol-A with Ti precursor and sol-B containing Mn precursor were separately prepared using the required precursor amounts in ethanol and 5 wt.% pluronic 123 surfactant. Gelation was accomplished by the addition of DI water and catalyzed by HCl. The gels were aged for 24 hrs, dried at 80°C for 12 hrs and calcined at 1000°C for 5 hrs. Additional gels were synthesized using isopropanol and acetic acid. These powdered electrode materials were analyzed by x-ray diffraction, which indicated the presence of a perovskite phase. Supercapacitors were fabricated and cyclic voltammetry measurements were performed to infer specific capacitance. Supercapacitor was also fabricated with cobalt doped (Mn,Ti)-oxide and its performance was evaluated.

Keywords: Supercapacitor, cobalt, (Mn,Ti)-oxide, sol-gel

1 INTRODUCTION

The storage of electrical energy can be used in portable devices, transport vehicles, and stationary energy systems [1]. An upcoming method of electric charge storage is being accomplished using electrochemical supercapacitors or supercapacitors. A supercapacitor has superior power delivery performance when compared with batteries or capacitor. These supercapacitors are considered to have high power output and energy storage [1-3]. In a supercapacitor, a separator and an electrolyte are placed in between an electrode material [4-5]. When a potential is applied, reversible faradaic reactions occur on the electrode materials that allow transport of charges across the double layer [6].

Electrical properties of a supercapacitor such as capacitance and charge storage are highly dependant on the electrode materials. Such electrode materials can be categorized into three groups, such as: i) carbon materials with high specific surface areas [7], ii) metal oxides [2,8,9] and iii) conducting polymers [10,11]. Different synthesis methods have been reported in the literature to prepare the electrode materials [12-15]. Carbon based materials are generally used in electrochemical double layer capacitors, however, they have low capacitance. To improve specific capacitance, transition metal oxides are being investigated. The specific capacitance, of RuO_2 and MnO_2 was 710 $F.g^{-1}$ and 1100 $F.g^{-1}$, respectively. In an attempt to reduce the cost of precious metal use, RuO_2 was combined with inexpensive metal oxides such as SnO_2 that yielded a specific capacitance of 342 $F.g^{-1}$. In addition, cobalt doped Mn_3O_4 have been investigated for supercapacitors.

The combination of additive metal oxides is known to facilitate electron and proton conduction in the oxides, enhance dispersion of the primary material, and minimize the primary materials particle size [2]. In a recent investigation [16], supercapacitors were constructed using the nanofiber mat obtained after electrospinning the hydrothermally derived biochar and polyacrylonitrile (PAN), which exhibited the specific capacitance of 37.6 $F.g^{-1}$.

In our recent study, supercapacitors were fabricated using nanocomposites of Mn and Ti oxides, which were prepared using different ratios of Mn to Ti precusors and surfactant, and varying calcination conditions. Increase in calcination temperature was found to decrease specific surface area (SSA) and specific capacitance accordingly. Increasing surfactant values from 5 wt% to 30 wt% were found to increase specific capacitance by 20% [17]. For the mesoporous nanocomposite of (Mn,Ti)-oxide calcined at lower temperature of 500°C, high specific capacitance of 125 $F.g^{-1}$ was observed.

In this study, surfactant templating assisted sol-gel synthesis method was used to prepare (Mn,Ti)-oxide and cobalt doped (Mn,Ti)-oxide powdered materials. These were characterized using the x-ray diffraction. Furthermore, supercapacitors were fabricated using the elecrode materials prepared with the nanocomposites of Mn and Ti oxides and graphene, and their specific capacitance ($F.g^{-1}$) was measured.

2 EXPERIMENTAL

2.1. Materials

All reagents were analytical grade and used as received. Ti-isopropoxide (98%, Acros Organics), Mn-nitrate tetrahydrate (98%, Alfa Aesar), and pluronic 123 (MW-5800, BASF) were used for the sol-gel synthesis. Ethanol (200% proof) was obtained from AAPER and concentrated HCl (35.5%) was purchased from Fisher- Scientific. Graphene nanoplatelets (SSA 120-150 m^2/g) were purchased from Aldrich and used as one of the electrodes in a supercapacitor. Isopropanol (99.5%), acetic acid (99%), KOH (90%) and cobalt (II) nitrate hexahydrate (98%) were all obtained from Sigma Aldrich.

2.2 Peparation of Electrode Material

Sol-A was prepared by sonicating Ti-isopropoxide precursor in ethanol containing pluronic 123 (5 wt.%) surfactant. Sol-B was prepared by dispersing Mn-nitrate tetrahydrate in ethanol until a visually clear solution was obtained. Sol-A was acidifed with hydrochloric acid and Sol-B was slowly added into Sol-A while stirring for 10 min. Gelation was observed upon addition of water to this homogenous solution mixture. An observed gel was aged for 24 hours at room temperature and dried at 80°C for 12 hours. The dried powder was further calcined for 5 hours at 1000°C. Variations on the sol-gel process were performed by substituting ethanol with isopropanol as well as acetic acid. Cobalt doping was carried out using $Co(NO_3)_2 \cdot 6H_2O$. The entire sol-gel synthesis approach is schematically shown in Figure 1 and 2.

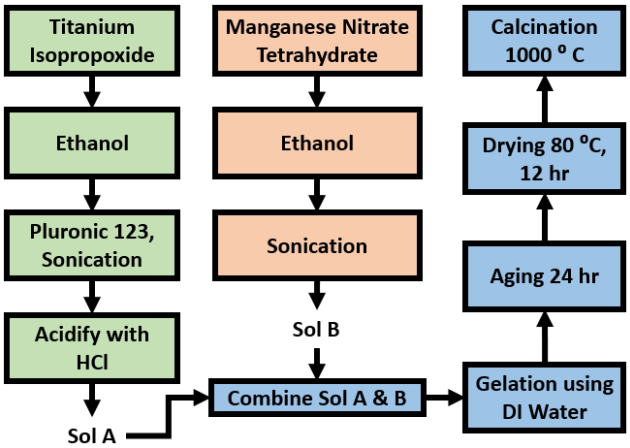

Figure 1: Sol-gel synthesis appproach to prepare powdered electrode material of (Mn,Ti)-oxide.

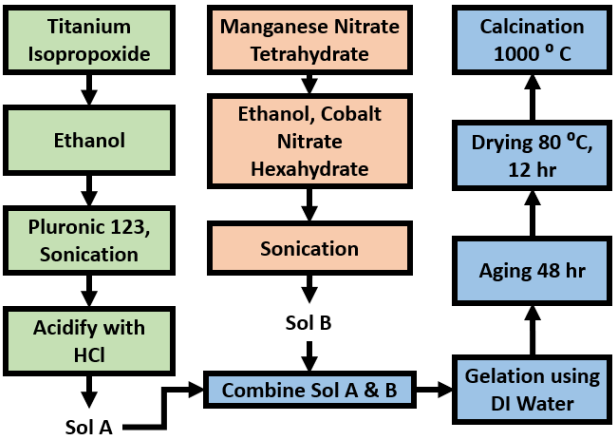

Figure: 2 Sol-gel synthesis appproach to prepare cobalt doped (Mn,Ti)-oxide powdered electrode material.

Calcination of the dried gel samples was carried out as per the set temperature, soak time, and ramp rate reported shown in Figure 3. A temperature ramp rate of 2°C/min was used until a set temperature of 1000°C was attained. The material was soaked at this tempetaure for 5 hours and cooled down to the room temperature at a ramp rate of 8°C/min.

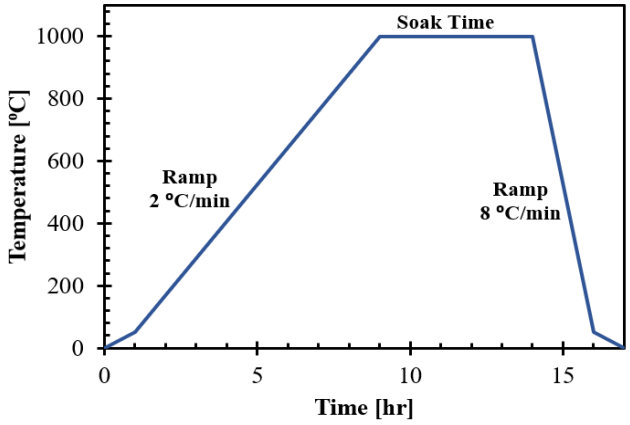

Figure 3: Temperature-time profile used to calcine the gels to obtain powdered materials.

2.3. Characterization of Powdered Materials

Crystallographic information and phase composition of (Mn,Ti)-oxides powdered materials were analyzed using the Rigaku Ultima IV x-ray diffractometer with ICDD database. The diffractometer was operated at 40 kV, 44 mA (1.76 kW) and the phase angle (2θ) in the range of 8° to 80° was scanned at the rate of 2° per min.

2.4. Supercapacitor Fabrication and Performance Evaluation

Sol-gel derived powdered electrode material was homogenously mixed with polyurethane and uniformly applied to 0.5 in^2 and 0.016 inch thick copper plate, which was polished with 250 grit sandpaper. Graphene platelets mixed with polyurethene was applied to the other electrode plate. With each electrode layer facing each other, a seperator (Nylon 6,6) was sandwiched between them with the KOH. A vaccum sealer roll of plastic was used as seal to prevent dust contamination and exposure to air. This apparatus was then sealed tightly with tape to expand the interaction between electrodes as well as to provide containment protection. DC power supply of 2 volts and approx. 0.01 amps was used for charging purpose. Once fully charged, the supercapacitor was analyzed using G-300 potentiostat/galvanostat/ZRA from Gamry. Cyclic voltemmetry tests were performed through a series of charging-discharging cycles. For testing purposes, four cycles were performed and the specific capacitance values are reported for (Mn,Ti)-oxide electrode materials. Additional information can be found elsewhere [17].

3 RESULTS AND DISCUSSION

The x-ray diffraction (XRD) patterns of powdered materials prepared with Mn:Ti (65:35, wt%) precursors and different solvents, and calcined at 1000 ºC are shown in Figure 4. All 2-theta reflections were thoroughly analyzed to understand the phase formation. For the sol-gel derived powdered material synthesized with ethanol, Mn_2O_3 was found at 48.4 wt.% and a perosvkite (P) phase, $MnTiO_3$ was observed in the amount of 47.4 wt%. When isopropanol was used for the sol-gel synthesis, TiO_2 brookite (B) and Mn_2O_3 phases were observed as 36.6%% and 63.7%, respectively. The use of acetic acid led to the formation of TiO_2 rutile (R) and Mn_2O_3 phases at 52.3% and 47.7%, respectively. Thus, the use of different solvents during the sol-gel synthesis was found to influence the crystalline phase formation.

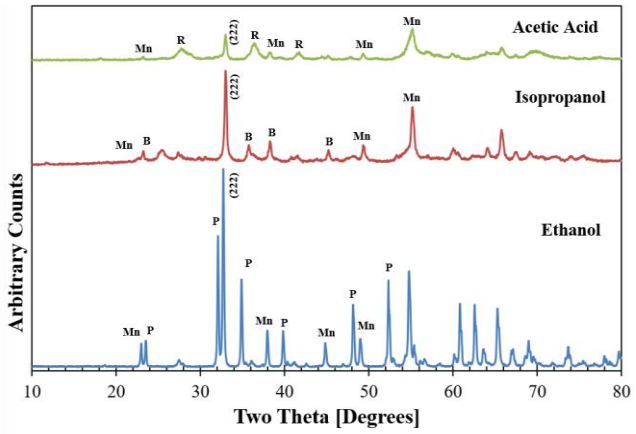

Figure 4: X-ray diffraction patterns of calcined powdered materials prepared with Mn:Ti (65:35 wt.%) using different solvents.

Specific capacitance ($F.g^{-1}$) values calculated from the cyclic voltammetry plots generated using Gamry G-300 potentiostat/galvanostat/ZRA are plotted as a function of cobalt doping (Figure 5). A maximum capacitance of 82.5 $F.g^{-1}$ was observed for Mn:Ti (65:35 wt%) calcined at 1000ºC.

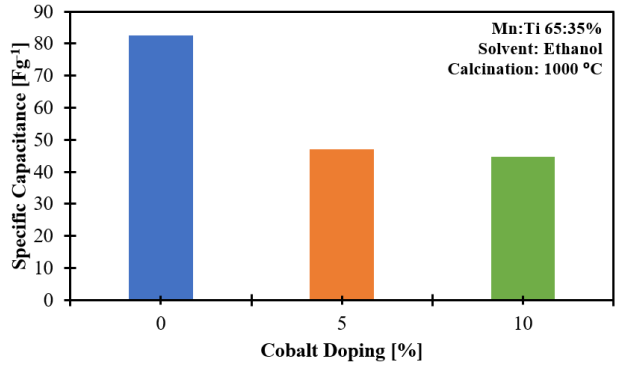

Figure 5: Specific capacitance as a function of cobalt doping in (Mn,Ti)-oxide.

Additional powders of Mn:Ti (65:35 wt.%) were prepared with 5 wt.% and 10 wt.% cobalt doping, which were calcined at 1000 ºC as well. The specific capcitance values were found to decrease from 46.9 $F.g^{-1}$ to 44.6 $F.g^{-1}$. These results suggest that the presence of cobalt hinders the electrostatic double-layer during charging and discharging. A noticable change in hue of the gel can be seen when cobalt was used for doping (Figure 6). Currently our group is working to test variations on the calcination process and impregnation of graphene nanoplatelets on specific capacitance.

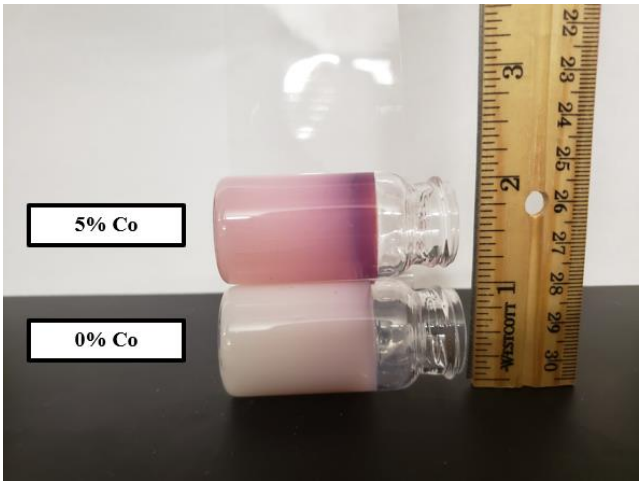

Figure 6: Comparison of gel coloration with and without cobalt doping.

Kong et al. [18] reported specific capacitance of 405 $F.g^{-1}$ at 5 $mA.cm^{-2}$, and the capacitance retention of 95.1% after 1000 cycles for the sol-gel derived Co-Mn composite oxide. Specific capacitance of 186 $F.g^{-1}$ was reported for Co-Mn oxide prepared by anodic deposition. For this material, cobalt addition was found to hinder dissolution of Mn in an electrolyte and enhance reversibility [19]. However, specific capacitance of cobalt doped oxide composite is still lower. In our study, cobalt doping in (Mn,Ti)-oxide was found to lower the specific capacitance.

4 CONCLUSIONS

The effect of various solvents such as ethanol, isopropanol, and acetic acid was studied on the Mn:Ti gel formation. Use of ethanol produced Mn_2O_3 at 48.4 wt.% and a perosvkite phase, $MnTiO_3$. Using isopropanol, TiO_2, Brookite and Mn_2O_3 were observed at 36.6% and 63.7%, respectively. Finally the usage of acetic acid for the gel synthesis yielded TiO_2 rutile and Mn_2O_3 phases at 52.3% and 47.7%. As the solvent was altered from ethanol to isopropanol or acetic acid crystallinity was found to decrease in the powdered materials.

Nanocomposites containing 5 wt.% and 10 wt.% cobalt doping were synthesized using the sol-gel technique followed by calcination at 1000 ºC. It was observed that as

cobalt doping was increased the specific capacitance was found to decrease from of 82.5 $F.g^{-1}$ to 44.6 $F.g^{-1}$.

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REFERENCES

[1] Haisheng Chen, and Thang Ngoc Cong, "Progress in Electrical Energy Storage System: A Critical Review." Progress in Natural Science, 19(3), 291-312, 2009.

[2] Wang, Guoping, Lei Zhang, and Jiujun Zhang, "A Review of Electrode Materials for Electrochemical Supercapacitors." Chemical Society Reviews, 41(2), 797-828, 2011.

[3] Largot, Celine, Cristelle Porter, John Chmiola. Pierre-Louis Taberna, Yury Gogotsi, and Patrice Simon, "Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor." Journal of the American Chemical Society, 130(9), 2730-2731, 2007.

[4] Yu, Z., Tetard, L., Zhai, L., & Thomas, J. (2015). Supercapacitor electrode materials: Nanostructures from 0 to 3 dimensions. Energy & Environmental Science, 8(3), 702-730.

[5] Conway, B.E., "Transition from "Supercapacitor" to "Battery" Behavior in Electrochemical Energy Storage." Journal of The Electrochemical Society, 138(6), 1539-1548, 1991.

[6] Beaudin, Marc, Hamidreza Zareipour, Anthony Schellenberglabe, and William Rosehart, "Energy Storage for Mitigating the Variability of Renewable Electricity Sources: An Updated Review." Energy for Sustainable Development, 14(4), 302-314, 2010.

[7] Ke, Qingquig, and John Wang, "Graphene-based Materials for Supercapacitor Electrodes – A Review." Journal of Materiomics, 2(1), 37-54, 2016.

[8] Tian, Qinghua, and Wang, Xiang, "Nanostructured (Co, $Mn)_3O_4$ for High Capacitive Supercapacitor Applications," Nanoscale Res Lett, 12:214, 3-23, 2017.

[9] Dong, Ruiting, and Ye, Quinglan, "Enhanced Supercapacitor Performance of Mn3O4 Nanocrystals by Doping Transition-Metal Ions." Applied Material Interfaces, 2013.

[10] Snook, Graeme A, Pon Kao, and Adam S. Best, "Conducting-Polymer-based Supercapacitor Devices and Electrodes." Journal of Power Sources, 196(1), 1-12, 2010.

[11] Malinauskas, A., Malinauskiene, J., and Ramanavicius, A, "Conducting Polymer-Based Nanostructurized Materials: Electrochemical Aspects." Nanotechnology, 16(10) R51-R62, 2005.

[12] Wei, Weifeng, Xinwei Cui, Weixing Chen, and Douglas G. Ivey, "Manganese Oxide-based Materials as Electrochemical Supercapacitor Electrodes." Chemical Society Reviews, 40(3), 1697-1721, 2010.

[13] Ahn, Young Rack, Chong Rae Park, Seong Mu Jo, and Dong Young Kim, "Enhanced Charge-discharge Characteristics of RuO_2 Supercapacitors on Heat-treated TiO_2 Nanorods." Applied Physics Letters, 90(12), 122106, 2007.

[14] Jiang, Junhua, and Anthony Kucernak, "Electrochemical Supercapacitor Material Based on Manganese Oxide: Preparation and Characterization." Electrochimica Acta, 47(15), 2381-2386, 2002.

[15] Shende, R. V., Krueger, D. S., Rossetti, G. A., & Lombardo, S. J. (2004). Strontium Zirconate and Strontium Titanate Ceramics for High-Voltage Applications: Synthesis, Processing, and Dielectric Properties. Journal of the American Ceramic Society, 84(7), 1648-1650.

[16] Nan Wei, Yong Zhao, Yichun Ding, Anuradha R. Shende, Hao Fong, and Rajesh V. Shende, "Mechanically Flexible Electrospun Carbon Nanofiber Mats Derived from Biochar and Polyacrylonitrile." Materials Letters, 205, 206-201, 2017.

[17] Houck, J, and Shende, R, "Mesoporous Nanocomposites of Mn and Ti Oxides for Supercapacitors." TechConnect Briefs 2018, TechConnect Org. ISBN 978-0-9988782-3-2, pp 75-78.

[18] Kong LB, Lu C, Liu MC, Luo YC, Kang L, Li XH, Walsh FC. The specific capacitance of so-gel synthesised spinel $MnCo_2O_4$ in an alkaline electrolyte. Electrochim Acta. 115:22–27, 2014.

[19] Chang JK, Lee MT, Huang CH, Huang CH, Tsai WT. Physicochemical properties and electrochemical behavior of binary manganese–cobalt oxide electrodes for supercapacitor applications. Mater Chem Phys. 108:124–131, 2008.