

# Mesoporous Nanocomposites of Mn and Ti Oxides for Supercapacitors

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## ABSTRACT

In this investigation, several nanocomposites with varying amounts of Mn and Ti oxides were prepared using surfactant assisted sol-gel method. To prepare these nanocomposites, sol-A with Ti precursor and sol-B containing Mn precursor were separately prepared using the required precursor amounts in ethanol and 5-30 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 500°-1000°C for 5 hrs. These powdered electrode materials were analyzed by x-ray diffraction and BET surface area analysis. For the nanocomposite prepared with Mn:Ti at 65:35 wt.% and calcined at 500°C, both anatase and rutile phases alongwith Mn<sub>2</sub>O<sub>3</sub> were observed. As calcination temperature increased to 1000°C, rutile and Mn<sub>2</sub>O<sub>3</sub> phases were decreased with the formation of MnTiO<sub>3</sub>. BET SSA of 30.6 m<sup>2</sup>/g was observed for the powdered material calcined at 500°C with avg. pore diameter of 7.5 nm. Supercapacitors were fabricated using these nanocomposites and cyclic voltammetry measurements were performed to infer specific capacitance. Higher specific capacitance of 125 F.g<sup>-1</sup> was observed for the supercapacitor fabricated with the Mn:Ti nanocomposite calcined at lower temperature of 500°C.

**Keywords:** Supercapacitor, mesoporous, Mn and Ti oxide nanocomposites, sol-gel.

## 1 INTRODUCTION

Electrical energy storage has numerous applications in portable devices, transport vehicles, and stationary energy systems [1]. Energy or electric charge storage can be accomplished using batteries and capacitors or electrochemical supercapacitors. A supercapacitor has superior power delivery performance, which acts as a bridging function for the power/energy gap between dielectric capacitors and batteries/fuel cells, characterized by high power output and energy storage, respectively [2-5]. In a typical supercapacitor, a separator and an electrolyte are placed in between similar or dissimilar electrode materials. When a potential is applied, fast and reversible faradaic reactions take place 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 [7-9], ii) conducting polymers [10,11], and iii) metal oxides [2]. Different synthesis methods have been reported in the literature to prepare the electrode materials [12-15]. Few examples include RuO<sub>2</sub>, MnO<sub>2</sub>, SnO<sub>2</sub>-RuO<sub>2</sub> etc. The performance characteristics, primarily specific capacitance, of RuO<sub>2</sub> and MnO<sub>2</sub> was 710 F g<sup>-1</sup> and 1100 F g<sup>-1</sup>, respectively. In an attempt to reduce the cost of precious metal use, RuO<sub>2</sub> was combined with inexpensive metal oxides such as SnO<sub>2</sub> to produce a specific capacitance of 342 F g<sup>-1</sup>. 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 our recent investigation [16], we made supercapacitors using the nanofiber mat obtained after electrospinning the hydrothermally biochar and polyacrylonitrile (PAN), which exhibited the specific capacitance of 37.6 F.g<sup>-1</sup>.

In this study, sol-gel synthesis method was used to prepare the electrode materials containing Mn and Ti oxides, which were characterized using the x-ray diffraction and Brunauer-Emmett-Teller (BET) specific surface area analysis. Furthermore, supercapacitors were made using the electrode materials prepared with nanocomposites of Mn and Ti oxides and graphene, and their specific capacitance F.g<sup>-1</sup> was measured.

## 2 EXPERIMENTAL

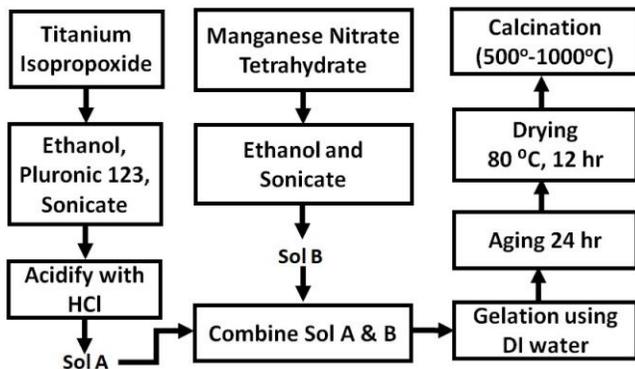
### 2.1. Material and Synthesis Approach

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<sup>2</sup>/g) was purchased from Aldrich and used as one of the electrodes in a supercapacitor.

### 2.2 Preparation of Electrode Material

Sol-A was prepared by sonicating Ti-isopropoxide precursor in ethanol containing pluronic 123 (5 wt.%). Sol-B was prepared by dispersing Mn nitrate, tetrahydrate in ethanol

until a visually clear solution was obtained. Sol-A was acidified 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. As obtained 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 500-1000 °C. The entire sol-gel synthesis approach is schematically shown in Figure 1. Gels were also prepared with different Mn:Ti weight ratios (65:35, 60:40, 50:50, 40:60), which were aged, dried and calcined at 1000°C. In addition, the surfactant was varied from 5 wt.% to 30 wt.% based on total weight of the Mn and Ti precursors taken.



**Figure 1:** Sol-gel synthesis approach to prepare powdered electrode materials containing Mn and Ti oxides.

Calcination of the dried gel samples was carried out as per the set temperature, soak time, and ramp rate reported in Table 1.

**Table 1:** Calcination conditions used to prepare powdered electrode materials.

| T (°C)     | 500 | 700 | 800 | 1000 |
|------------|-----|-----|-----|------|
| t (hr)     | 5   | 5   | 5   | 5    |
| R (°C/min) | 1   | 1.4 | 1.6 | 2    |

(T-temperature, t- soak time, and R-heating ramp rate)

### 2.3. Characterization of Powdered Materials

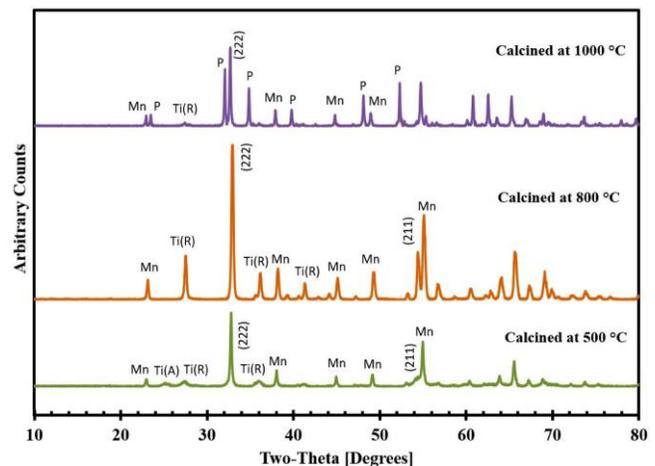
The phase composition and other crystallographic information of the sol-gel derived Mn:Ti based calcined powdered materials were analyzed using the Rigaku Ultima IV x-ray diffractometer with ICDD database. The diffractometer was operated at 40 kV, 44 mA (1.76 kW) and the phase angle ( $2\theta$ ) in the range of 8° to 80° was scanned at the rate of 2° per min. The specific surface area (SSA) and the pore volume (Pv) were determined by using Micromeritics Gemini II – 2375 BET (Brunauer-Emmett-Teller) surface area analyzer.

### 2.4. Supercapacitor Fabrication and Performance Evaluation

The experimental set-up designed to test the charging cycle through cyclic voltammetry was a mock supercapacitor design. Sol-gel derived ferrite powder was homogeneously mixed with fast drying polyurethane and uniformly applied to adhere to 0.5 in<sup>2</sup> and 0.016 inch thick copper plate, which was polished with 250 grit sandpaper. The other copper plate was coated with graphene platelets mixed with polyurethane. With the electrode layers facing each other, a separator (Nylon 6,6) was sandwiched between them with the electrolyte, KOH (90%, Sigma Aldrich). A vacuum sealer roll of plastic was used to seal to prevent it from dust contamination and exposure to air. The system was then encased tightly in tape to ensure proper interaction between electrodes as well as to provide additional containment. It was then charged with a DC power supply of 2 volts and approx. 0.01 amps. Once fully charged, the supercapacitor was then analyzed using G-300 potentiostat/galvanostat/ZRA from Gamry. This system performs cyclic voltammetry tests through a series of charging-discharging cycles. For testing purposes, four cycles were performed and the specific capacitance values are reported for Mn:Ti electrode materials.

## 3 RESULTS AND DISCUSSION

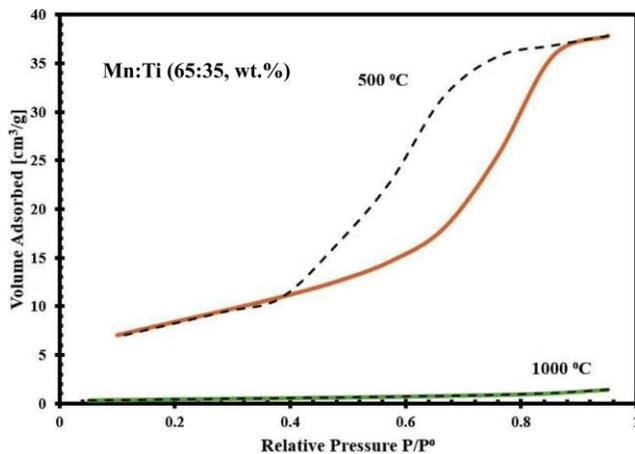
The powdered x-ray diffraction (XRD) patterns of powdered materials prepared with Mn:Ti (65:35, wt.%) precursors and calcined at different temperatures are shown in figure 2. All 2-theta reflections were thoroughly analyzed to understand phase formation. For the powdered material calcined at 500°C, TiO<sub>2</sub> rutile (R) and anatase (A) phases were observed as 14.5wt.% and 7.2 wt.%, respectively alongwith Mn<sub>2</sub>O<sub>3</sub> as 78.3 wt.%. As calcination temperature increased to 800°C, rutile phase was increased to 23.5 wt.% whereas no anatase was not observed. Further increase in



**Figure 2:** X-ray diffraction patterns of calcined powdered materials prepared with Mn:Ti (65:35 wt.%) at different temperatures.

calcination temperature to 1000°C, Mn<sub>2</sub>O<sub>3</sub> was decreased to 48.4 wt.% and a new perovskite (P) phase, MnTiO<sub>3</sub> was observed in the amount of 47.4 wt.%.

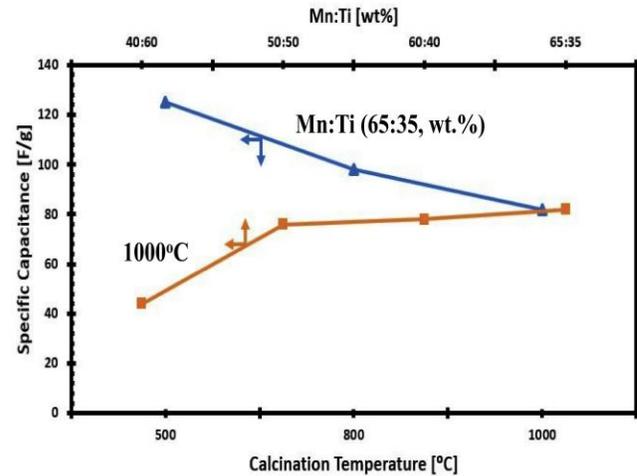
Nitrogen adsorption-desorption isotherms for the powdered material prepared with Mn:Ti (65:35, wt.%) and calcined at two different temperatures of 500°C and 1000°C are shown in Figure 3. Hysteresis loop observed at the relative pressure P/P<sub>0</sub> between 0.4 to 1.0 indicates that the powdered material calcined at 500°C contains mesopores and the average pore diameter was found to be 7.5 nm. However, no hysteresis loop was observed for the material calcined at 1000°C. BET specific surface area (SSA) of 30.6 m<sup>2</sup>/g was observed for the powdered material calcined at 500°C whereas much reduced SSA of 1.4 m<sup>2</sup>/g was observed for the material calcined at 1000 °C. About 96% reduction in pore volume was observed with increase in calcination temperature from 500°C to 1000°C.



**Figure 3:** Nitrogen adsorption and desorption profiles for the Mn:Ti (65:35 wt.%) powdered material calcined at 500°C and 1000°C.

Specific capacitance (F.g<sup>-1</sup>) values calculated from the cyclic voltammetry plots generated using Gamry G-300 potentiostat/galvanostat/ZRA are plotted as a function of temperature and composition of the powdered materials (Figure 4). A maximum capacitance of 125 F.g<sup>-1</sup> was observed for Mn:Ti (65:35 wt.%) calcined at 500°C. For the same composition, as calcination temperature increased to 1000°C, the specific capacitance decreased to 82 F.g<sup>-1</sup>. Additional powders with Mn:Ti (65:35 wt.%) were prepared with 20wt.% and 30 wt.% pluronic 123 surfactant, which were calcined at 1000°C. The specific capacitance values were found to increase from 82 F.g<sup>-1</sup> to 99 F.g<sup>-1</sup> with increase in surfactant loading of 5 wt.% to 30 wt.%. It will be interesting to see if lower calcination temperatures indicate higher gravimetric capacitance. Different powders were prepared by varying the weight ratios of Mn and Ti and their capacitance values are plotted in Figure 4. For the powdered material prepared with Mn:Ti of 65:35 wt.% the specific capacitance of 82 F.g<sup>-1</sup> was found to decrease with increase

in TiO<sub>2</sub> in a nanocomposite. For instance with Mn:Ti 40:60 wt.%, the specific capacitance of only 44 F.g<sup>-1</sup> was noticed suggesting that increase in TiO<sub>2</sub> would decrease capacitance. The specific capacitance as a function of Mn:Ti composition reveals that higher wt.% Mn oxide in a composite yields higher capacitance.



**Figure 4:** Specific capacitance as a function of calcination temperature and composition.

Currently we are working on modifying the morphology of the powdered material to understand its effect on the specific capacitance.

## 4 CONCLUSIONS

Nanocomposites containing different amounts of Mn:Ti oxides were synthesized using the sol-gel technique followed by calcination at 500°-1000°C. It was observed that as calcination temperature increased from 500° to 800°C, rutile phase was increased from 14.5 wt.% to 23.5 wt.% whereas further increase in calcination temperature was found to decrease rutile phase with the formation of perovskite phase of MnTiO<sub>3</sub>. BET specific surface area (SSA) of 30.6 m<sup>2</sup>/g was observed for the powdered material calcined at 500°C whereas much reduced SSA of 1.4 m<sup>2</sup>/g was observed for the material calcined at 1000 °C. Hysteresis loop observed at the relative pressure P/P<sub>0</sub> between 0.4 to 1.0 indicates that the powdered material calcined at 500°C contains mesopores and the average pore diameter was found to be 7.5 nm. A maximum capacitance of 125 F.g<sup>-1</sup> was observed for Mn:Ti (65:35 wt.%) calcined at 500°C, however at higher calcination temperature of 1000°C, the specific capacitance was decreased to 82 F.g<sup>-1</sup>. It was observed that higher wt.% of Mn oxide in a nanocomposite of Mn and Ti oxides yields higher capacitance.

## ACKNOWLEDGEMENTS

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