

RESEARCH ARTICLE

## Investigation of MgTiO<sub>3</sub> as an anode material for rechargeable Li-ion batteries

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**Abstract:** Magnesium Titanate (MgTiO<sub>3</sub>) is a common and commercially available dielectric material used in electronics applications. The potential of using MgTiO<sub>3</sub> as an anode material in rechargeable Li-ion batteries has been investigated under this study. MgTiO<sub>3</sub> particles were synthesized by both wet-chemical Pechini method and solid state ball milling method. The subsequent material characterizations were carried out using X-ray diffraction and scanning electron microscopic techniques. The electrochemical performance of MgTiO<sub>3</sub> as an anode material in Li-ion rechargeable battery was carried out with Li metal electrode in coin half cells. For wet-chemically synthesized MgTiO<sub>3</sub>, the potentials associated with lithiation were 1.14 V and 0.76 V vs Li/Li<sup>+</sup> with an initial discharge capacity of 103 mAh/g at C/10 rate. Lithiation potential for ball milled MgTiO<sub>3</sub> was found to be at 1.3 V vs Li/Li<sup>+</sup> with an initial discharge of 63 mAh/g cycled at C/10 rate.

**Keywords:** Li-ion battery, magnesium titanate, anode material, Pechini method, ball milling.

### INTRODUCTION

Rechargeable Lithium-ion batteries (LIB) are mainly used in the electrification of transportation and renewable energy integration due to their long lifetime, high energy density and low environmental impact. However, there is an increasing concern on the cost and the availability of lithium for the use of Li-ion batteries in large scale energy storage applications (Tarascon *et al.*, 2001; Jeong *et al.*, 2011) In order to employ LIB in electric vehicles (EV) it is necessary to achieve from two to five times more energy density than what the present lithium battery technology can offer. The increase of the energy density of lithium batteries can be achieved by either using positive

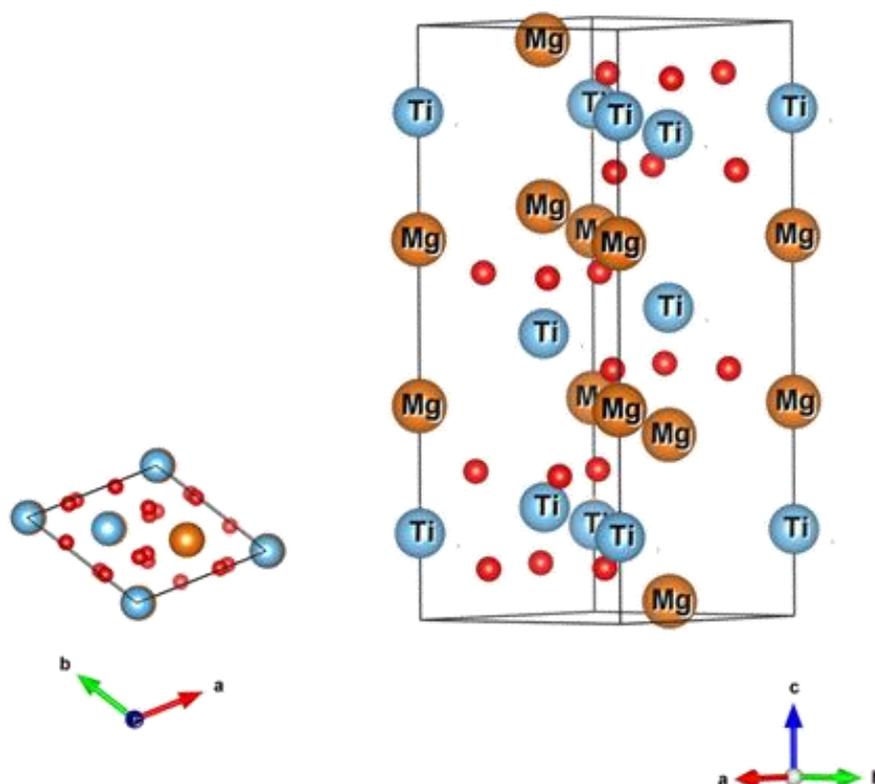
electrode materials operating at high voltages (4V and above) or by developing high capacity anode and cathode materials (Goriparti, *et al.*, 2014). However, most of these new high capacity cathode materials do not work well with traditional graphite based anode materials. Hence, new compatible anode materials are needed to be explored.

Titanium based oxides are attractive anode materials for Li-ion rechargeable batteries owing to their low cost, environmental friendliness, promising cycling performance and safety. In addition to LiTiO<sub>2</sub>, transition metal titanates such as SrTiO<sub>3</sub> and CoTiO<sub>3</sub> have shown their potentiality for Li-ion rechargeable batteries (Johnson and Prieto, 2011; Brown *et al.*, 2015). One such titanate which is promising, but has not been previously studied is MgTiO<sub>3</sub>. It is one of the most common and commercially available dielectric materials which has been used in electronics and composite applications such as microwave antennas, filters and resonators (Chen, *et al.*, 2008).

MgTiO<sub>3</sub> is a mineral known as geikielite which belongs to the ilmenite group with R3 space group. It has a rhombohedral layered structure with a theoretical specific capacity of 220 mAh/g (460 mAh/cc) (Momma and Izumi, 2011).

A schematic diagram of the typical crystal structure of the rhombohedral MgTiO<sub>3</sub> is shown in Figure 1. The layered structure of MgTiO<sub>3</sub> that allows it to accommodate Li<sup>+</sup> ions via intercalation makes MgTiO<sub>3</sub> a potential candidate for the anode of rechargeable Li-ion batteries (Yamanaka *et al.*, 2005).

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**Figure 1:** Crystal structure of rhombohedral  $\text{MgTiO}_3$  (space group  $R\bar{3}/148$ ) (Momma, K. and Izumi, F., 2011)

For the present study,  $\text{MgTiO}_3$  was synthesized by wet-chemical Pechini method and solid state ball milling method. The Pechini method is a wet-chemical technique that is easy to perform and yields oxides with high chemical homogeneity. It is based on the ability of an alpha-hydroxy carboxylic acids to form a polybasic acid chelate (Liu *et al.*, 1996; Pechini, 1967; Samarasinghe *et al.*, 2014; Samarasinghe *et al.*, 2008). When heating with a polyalcohol, the chelate undergoes polyesterification. Further heating removes the excess solvent and forms a viscous resin, a glassy polymer and finally an ash product consisting of a fine oxide powder. Calcining the ash product at a higher temperature such as  $900\text{ }^\circ\text{C}$ , completes the process resulting highly homogeneous fine powder.

On the other hand high-energy ball milling is an effective grinding method, which gives rise to a series of physicochemical changes to the material. This method not only makes the material finer rapidly, but also induces structural changes, phase transformations and even solid state reactions among the solid particles. These physico-

chemical changes are due to the efficient transformation from the mechanical energy of the grinding media to the internal energy of the particles and the intensive mechano-chemical force (Nanru, 2000). In this work, we have investigated the electrochemical performance and carried out material characterization of  $\text{MgTiO}_3$  prepared by both the Pechini wet-chemical synthesis as well as the solid state ball milling method.

## EXPERIMENTAL

### Preparation of Materials

$\text{MgTiO}_3$  was synthesized by solid state ball milling method and wet-chemical Pechini method. The following precursor reagents were used as purchased for ball milling method. A Stoichiometric mixture of 1.34 g  $\text{MgO}$  (325 mesh, 99%, Sigma-Aldrich) and 2.66 g  $\text{TiO}_2$  (99-100.5%, Sigma-Aldrich) were ball milled followed by annealing. Ball milling was done in a Spex mixer-mill (Model 8000-D, SPEX CertiPrep, Metuchen, N.J.) in 64 ml hardened steel vial with 115 g of 3/16 " tungsten carbide balls. The ball milled

powders were then heated in a tube furnace at 900 °C for one hour in air. In the wet-chemical Pechini method, stoichiometric amounts of 9.89 g  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (ACS reagent, 99%, Sigma-Aldrich) and 3.35 g  $\text{TiO}_2$  (99-100.5%, Sigma-Aldrich) were mixed. Then Citric acid: Ethylene Glycol in the ratio of 1:4 was added to the above mixture. The resulted mixture was vigorously stirred for overnight. The temperature of the solution was raised to 60 °C and stirred for another one hour. Then the solution temperature was increased stepwise (50 °C) from 100 °C to 400 °C and the solution was stirred for 30 minutes at each temperature. The resulted ash coloured product was then calcined at 900 °C for one hour in a box furnace under air.

### Material Characterization

The prepared materials in the form of fine powders were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray Diffractometer equipped with a Cu anode and dual detectors. A Phenom G2-Pro Scanning Electron Microscope (SEM, Nanoscience, Arizona) was used to study the particle size and morphology of the samples.

### Electrochemical Cell Assembly and Cycling

Coin type Li-half cells were assembled using commercially available coin cells (2325 type) in order to investigate the electrochemical performance of electrode materials in Li half-cells. The prepared electrodes consisted of active material, carbon black (Super P, Erachem Europe), and PvdF binder (polyvinylidene fluoride, Kynar HSV 900) in an 8:1:1 weight ratio. These components were thoroughly mixed with N-methyl-2-pyrrolidone (Sigma Aldrich, anhydrous 99.5%) with two 0.5 " hardened steel balls in a Retsch PM200 rotary mill (100 rpm, 1 hour) to get a uniform slurry. The slurry was then coated on a copper foil having dimension of 0.006 " coating bar and dried under air at 120 °C for one hour. Circular electrodes of 2 cm<sup>2</sup> in area were punched from the resulting coatings. Coin cell preparation was carried out in an argon filled glove box. Li discs were punched from thin foil (0.015 ") that was rolled from thick Li foil (Sigma Aldrich, ACS

reagent grade). The used electrolyte was made by dissolving 1M  $\text{LiPF}_6$  (98%, Sigma-Aldrich) in ethylene carbonate (EC)/ diethylene carbonate (DEC)/ monofluoroethylene carbonate (FEC) (all from Novolyte Technologies) 30/60/10 by volume at 30 °C. Two 2300 Celgard and one BMF (blown microfiber separator, 3M Company) were used as separators. The assembled cells were tested using a Maccor Series 4000 Automated battery cycling test system (Maccor Inc., Tulsa, Oklahoma) by cycling between 0 to 1.5 V at constant current of 22 mA/g at C/10 rate.

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## RESULTS AND DISCUSSION

### Structural Identification of the prepared samples

The X-ray diffractograms of the prepared samples are shown in Figures 2 and 3 along with the standard Powder Diffraction File (PDF) number (International Centre for Diffraction Data., 2002). As shown in Figure 2, the sample synthesized by ball milling method resulted a major crystalline  $\text{MgTiO}_3$  (PDF# 96-901-0588) phase and a minor crystalline  $\text{MgTi}_2\text{O}_5$  (PDF# 00-035-0796) phase. The major peak of  $\text{MgTi}_2\text{O}_5$  phase is present at 25.83° whereas other peaks are indistinguishable from the background noise of the XRD pattern. Therefore, it is quite likely that only a minor quantity of  $\text{MgTi}_2\text{O}_5$  is present in the sample prepared by the ball milling method. Figure 3 shows the XRD pattern of the sample synthesized by Pechini method. It indicates the existence of two main phases:  $\text{MgTiO}_3$  (PDF# 96-901-0588) and  $\text{MgTi}_2\text{O}_5$  (PDF# 00-035-0796). Contrast to ball milled sample, the  $\text{MgTi}_2\text{O}_5$  (which was the secondary phase in the ball milled sample) is a major phase present in this sample prepared by Pechini wet-chemical method. All the matching peaks with respect to the reference pattern (PDF# 00-035-0796) are present in the diffractogram with relevant intensities. There are no traces of the starting materials, as evident from the X-ray diffractograms of both samples and it implies the effectiveness of both types of the synthesis methods used in this study.

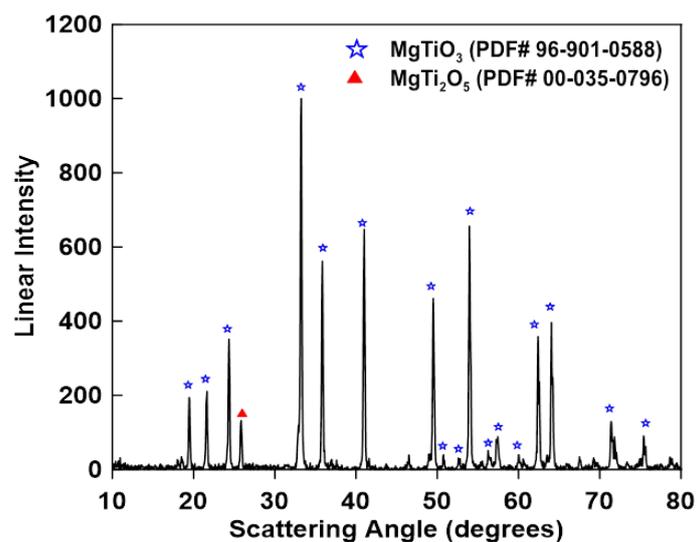


Figure 2: X-ray diffractogram of the MgTiO<sub>3</sub> prepared by ball milling and calcined at 900 °C.

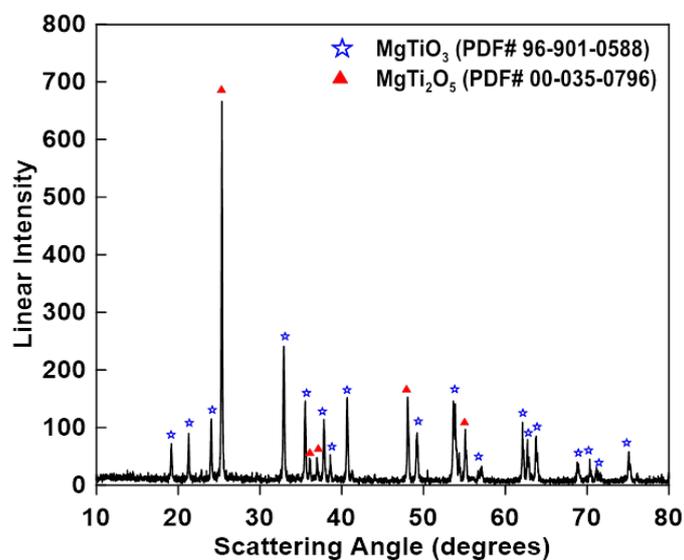


Figure 3: X-ray diffractogram of the MgTiO<sub>3</sub> prepared by Pechini method and calcined at 900 °C.

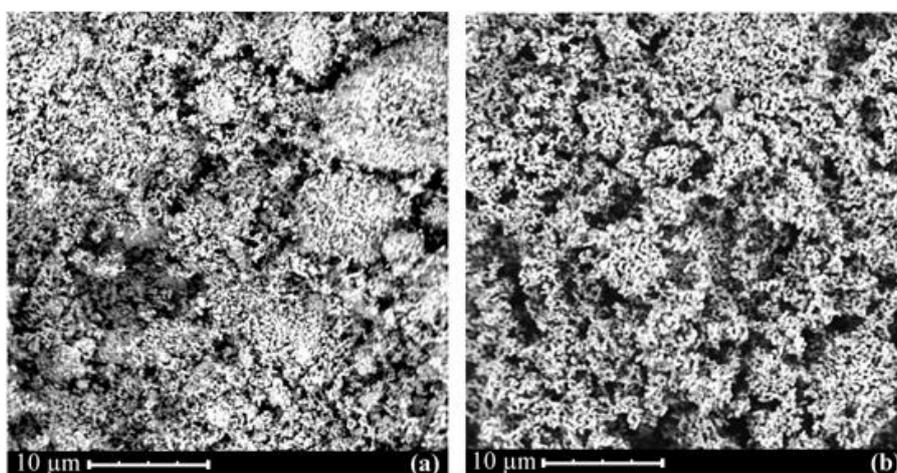
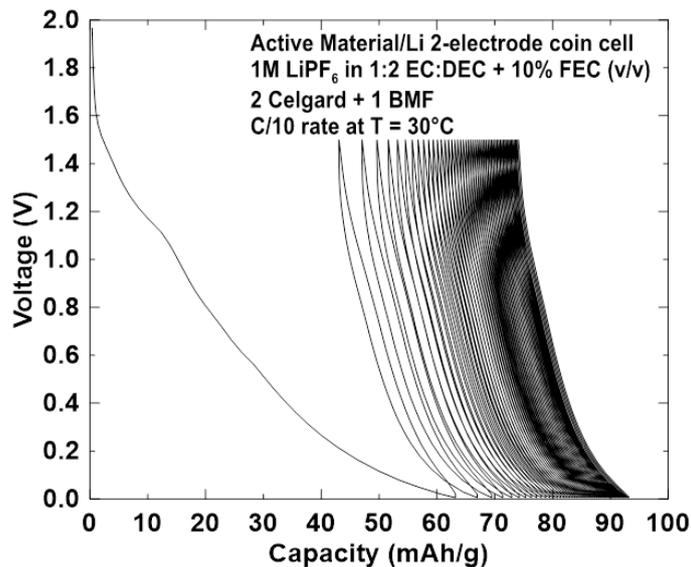


Figure 4: SEM images of MgTiO<sub>3</sub> prepared by (a) ball milling (b) Pechini method.

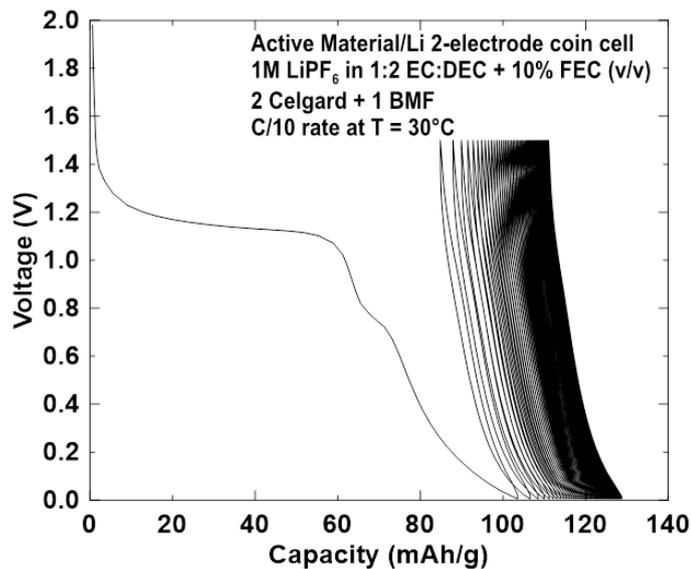
Figures 4 (a) and (b) show the scanning electron microscopic (SEM) images obtained for the samples prepared by ball milling method and Pechini method, respectively. According to these images, no significant difference can be seen in the particle morphology between the samples prepared by these two different methods. However, in both samples, the sub-micron sized primary particles had formed into micron size softly bound agglomerates resulting higher surface area. This suggests that the resulted surface area of the particles is sufficient to increase the reactivity with the electrolyte leading to an unstable SEI, resulting a high irreversible capacity, which is evident by the electrochemical study (Wang *et al.*, 2001).

### Electrochemical Performance Study

Figure 5 shows the voltage vs. capacity behavior of  $\text{MgTiO}_3$  prepared by the ball milling method. The average lithiation potential for ball milled sample was 1.3 V vs  $\text{Li}/\text{Li}^+$  with an initial discharge capacity of 63 mAh/g. Similarly, Figure 6 shows the voltage vs. capacity behavior for sample prepared by Pechini method. Here, the voltage-capacity curve consists of two plateaus, which indicates the presence of a secondary phase ( $\text{MgTi}_2\text{O}_5$ ) as evident from the XRD analysis. The average lithiation potentials for the two phases were found to be at 1.14 V and 0.76 V vs.  $\text{Li}/\text{Li}^+$  with an initial discharge capacity of 103 mAh/g.



**Figure 5:** Voltage – Capacity curves for the half-cells prepared from ball milled samples vs Li at C/10 rate.



**Figure 6:** Voltage – Capacity curves for the half-cells prepared from Pechini method samples vs Li at C/10 rate.

The difference between initial discharge capacity (103 mAh/g) of the sample synthesized by Pechini method compared to the sample synthesized by ball milling method (63 mAh/g) may come from the secondary  $\text{MgTi}_2\text{O}_5$  phase present in this sample synthesized by Pechini method. Therefore, it can be suggested that  $\text{MgTi}_2\text{O}_5$  phase could be an active material. The voltage-capacity curves for both samples show low initial lithiation capacity and a low polarization. These features are typical of materials that undergo intercalation reactions

(Brown *et al.*, 2015). This confirms the electrode material is undergoing an intercalation reaction with  $\text{Li}^+$  ions, therefore there is a potential to use this electrode material for the anode in Li-ion rechargeable batteries. However, since the observed capacities in both cases are below the theoretical capacity, it indicates incomplete intercalation reactions. Figures 7 and 8 show the cycling performance of the samples prepared by ball milling method and Pechini method respectively. A high irreversible capacity

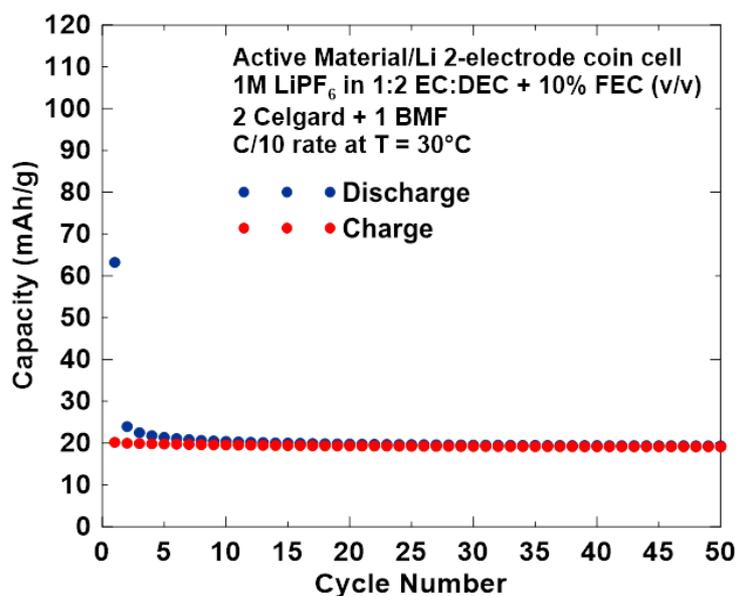


Figure 7: Cycling performance of the half-cells prepared from ball milled samples.

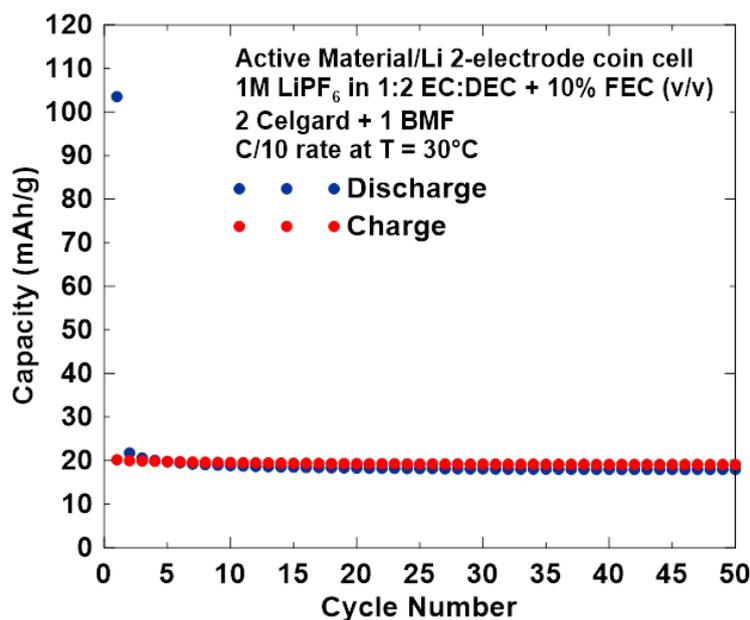


Figure 8: Cycling performance of the half-cells prepared from Pechini method samples.

with a reversible gravimetric capacity of about 20 mAh/g was observed with both samples. However, in both cases, the cycling performance was stable after the 2<sup>nd</sup> cycle. The corresponding reversible capacities were 32% and 19% for the ball milled sample and the sample prepared by Pechini method (Figures 7 and 8), respectively.

Though the sample prepared by Pechini method, which contained a considerable amount of the MgTi<sub>2</sub>O<sub>5</sub>, showed high initial discharge capacity of 103 mAh/g (Figure 8), the secondary phase may have hindered the kinetic processes (Brown *et al.*, 2015). Therefore, the cycling performance of this material has to be improved in order to be used in practical applications. Especially, further improvements are needed to increase the gravimetric capacity as well as initial coulombic efficiency of these materials. With high reversible capacity and low irreversible capacity MgTiO<sub>3</sub> would be an attractive anode material for Li-ion batteries.

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## CONCLUSIONS

In this work, MgTiO<sub>3</sub> was prepared by employing both the ball milling and Pechini wet-chemical method. The electrochemical properties of the synthesized material were investigated in order to determine its suitability as an anode material in lithium-ion batteries. The phase analysis showed that ball milling sample contained MgTiO<sub>3</sub> as major phase with a minor MgTi<sub>2</sub>O<sub>5</sub> secondary phase. The sample prepared by Pechini method contained both of these MgTiO<sub>3</sub> and MgTi<sub>2</sub>O<sub>5</sub> phases. The study further revealed the existence of micron size secondary powder particles formed with softly agglomerated finer particles in both cases.

There is no significant difference in the electrochemical performance of the material prepared by both wet-chemical Pechini method and solid state ball milling method with respect to the reversible capacity (20 mAh/g) obtained. Electrochemical studies revealed that though the Pechini method sample resulted significantly high initial discharge capacity, the presence of the MgTi<sub>2</sub>O<sub>5</sub> secondary phase may cause poor electrochemical performance which complicates the reactions and lowers the stability of the cell. However, the moderate initial discharge capacity and low voltage polarization suggest that the material had undergone intercalation and thus it is suitable to be used as a negative electrode

material in rechargeable Li-ion batteries. Further improvements are necessary to increase the gravimetric capacity and coulombic efficiency of these materials.

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