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Synthesis and Characterisation of Titanium Oxide Nanopowders for Lithium-Ion Batteries

Raghu C Reddy^{1,a}, R N Rao² and T L Prakash¹

¹ Centre for Materials for Electronics Technology, IDA Phase-3, Cherlapally, HCL Post, Hyderabad-500 051, Andhra Pradesh, India

² Department of Mechanical Engineering, National Institute of Technology (NITW), Warangal – 506 004, Andhra Pradesh, India

ABSTRACT

Lithium ion batteries form an integral part of many modern gadget packages as reliable power sources. Oxide powders of titanium have been reported to offer high charge storage capabilities coupled with enhanced electrode stability when used as anodes in lithium ion batteries. This paper describes a simple room temperature wet chemical method for the synthesis of nano sized titanium oxide powders for use in Li-ion Batteries. Analytical tools like, X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscope (TEM) were used for the determination of phase purity, crystallite size and particle morphologies. The capacity measurements carried out on the powders in anode form indicated that these powders exhibit high charge storage capacity compared to graphite and have good cycling performance.

Key Words: titanium oxide, li-ion battery, electrode, specific capacity, nanoparticles

INTRODUCTION

Alternate anode materials for lithium ion batteries (LIB) based on Sn and Ti have been explored by various researchers for their high theoretical capacity and good structural stability during charge discharge cycles. Nano structures as electrode materials has caught the attention of researchers since the distances Li⁺ ions have to diffuse is limited to the diameter of the nanoparticles compared to micron or sub millimeter-sized particles used in conventional materials and hence offer better capacity utilisation and discharge/charge rates. Apart from this high surface to volume ratio of nano powders contribute to uniform expansion, distribution and accommodation of physical expansion associated with intercalation during charge storage. Recent advances in nanostructured tin (Sn), silicon (Si), aluminium (Al), germanium (Ge) and intermetallic alloys [1, 2-4], Cu₆Sn₅, InSb, Cu₂Sb, Ti₂Sn as replacements for carbon-based anodes have already resulted in batteries with higher specific capacity and enhanced cycle life.

Studies on metal oxides have shown that there are very few systems which can act as anodes by the Li-intercalation/de-intercalation reaction. In most of the cases, these oxides, on reaction with Li at voltages V < 1.0 V, are either reduced to metal particles or give rise to oxygen-deficient lower-valent binary metal-oxides. Recent investigations on Ti oxide have shown that these metal oxides can act as viable anodes for LIB. The Li[Li_{1/3}Ti_{5/3}]O₄ has been investigated extensively and is shown to be a 'zero-strain' anode, meaning that the reversible Li⁺ intercalation does not produce any unit cell volume change. In addition, the Li-intercalation is a two-phase reaction and hence a plateau voltage of 1.5 V vs Li persists till all the virgin oxide is intercalated [5-11]. Except for the relatively high intercalation voltage as compared to graphite, it is a prospective anode for LIB. Carbon encapsulated

nano TiO₂ have been reported [12] to exhibit a capacity of ~200 mAh/g which is more than the theoretical capacity of TiO₂.

This paper enumerates a wet chemical method for the preparation of Titanium Oxide nanopowders for use in Li-ion batteries. The results of materials characterisation by X-Ray Diffraction (XRD), Field Emission Electron Microscopy (FESEM), and Transmission Electron Microscopy (TEM) are presented. The charge storage capacity of these materials has been determined. The suitability of the nano TiO₂ powders for commercial use as anodes in Li-ion battery is discussed.

MATERIALS AND METHODS

TiO₂ nanoparticles were prepared using 30% H₂O₂ solution added to the 10 ml of 1 mol/l ethanol solution of titanium tetra iso propoxide (TTIP). The ratio of H₂O₂: TTIP was kept as 12:1. Ethanol was added to the brown coloured solution obtained, and the total volume of the solution was adjusted to 100 ml. The solution was then heated at 60°C for 1hr in a closed vessel. The solution was calcinated at 600°C for 2hr to obtain white titanium oxide powder.

X-Ray Diffraction studies were conducted by using Schimadzu make, model-7000 maxima XRD machine. Field Emission Scanning Electron Microscope (FESEM) of make: Hitachi and Model: S-4800 and Transmission Electron Microscope (TEM) of Philips make, Model-CM 200 were used for studying the morphology of the nano powders and also to determine the particle size and their distribution.

Electrochemical cells were fabricated using by using the nanopowders produced as anode material. The nanopowders were blended with 10% each of PVDF binder and calcined petroleum coke (CPC) respectively in 1-methyl 2-pyrrolidone medium and coated on cu-foil. After drying and pre-treatment, the cells assembled with 1M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) in 1:1 ratio by volume as electrolyte. Polypropylene microporous membrane was used as the separator and Li metal foil as cathode and reference electrode. The assembly was carried out in an inert atmosphere glove box. The electrochemical characterisation was carried out using a test station supplied by Arbin Instruments, USA, Model: BT2000.

RESULTS AND DISCUSSION

XRD picture shown in figure 1 confirmed the phase purity of titanium oxide. The broad peaks of the XRD confirmed the nano nature of the powders produced. Crystallite size was calculated by Full Width at Half Maximum method. The crystallite size calculated was found to vary from 12 to 24 nm.

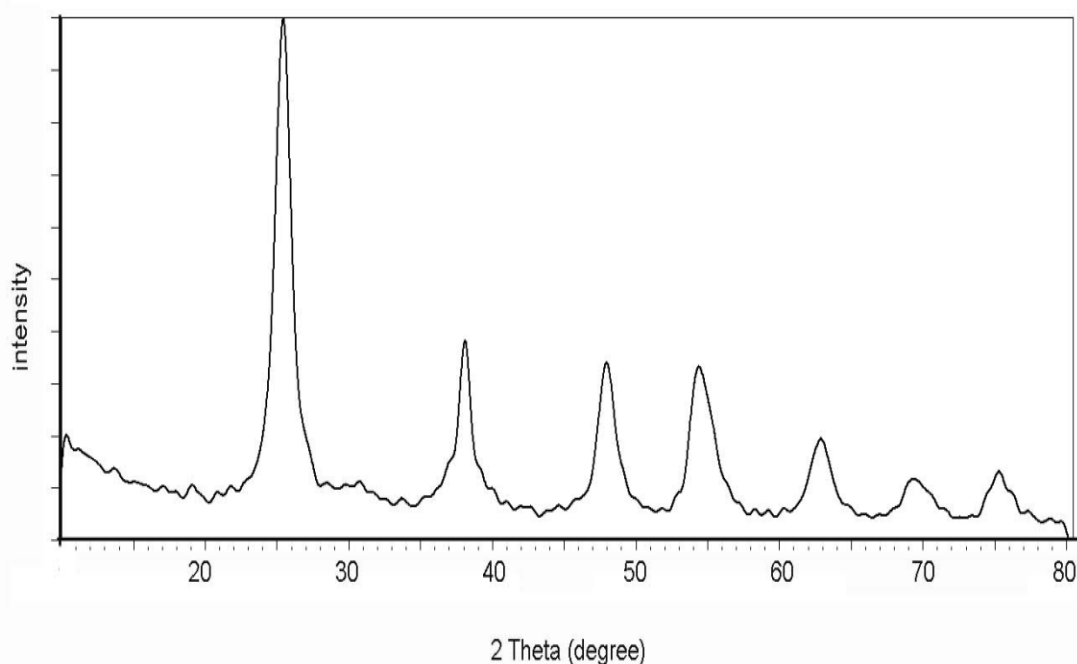


Fig. 1 XRD pattern of titanium oxide prepared by chemical synthesis and calcined at 600°C

Titanium oxide powders prepared were studied using the FESEM and a typical picture is presented pictures in the figure-2. Particle size was determined by image analysis. It was found that the particle size of TiO₂ powder produced ranged from 50 nm to 150 nm. The powders were in agglomerated state and were found to be hexagonal in shape with some cubic to sphericle particles being also present. Figure-3 depicts a typical TEM image generated on nano TiO₂ powders. TEM results showed particle sizes to be nearly of the same range as observed in the FESEM studies. The sample preparation for TEM consisted of dispersing the agglomerated powders in Iso Propyl Alcohol (IPA) and sonification for 20 minutes each. The difference in the crystallite and particle sizes determined by various methods is attributed to growth kinetics involved in the chemical synthesis process. The crystallites formed during nucleation have grown into each other resulting in grains and grains in turn have formed into particles.

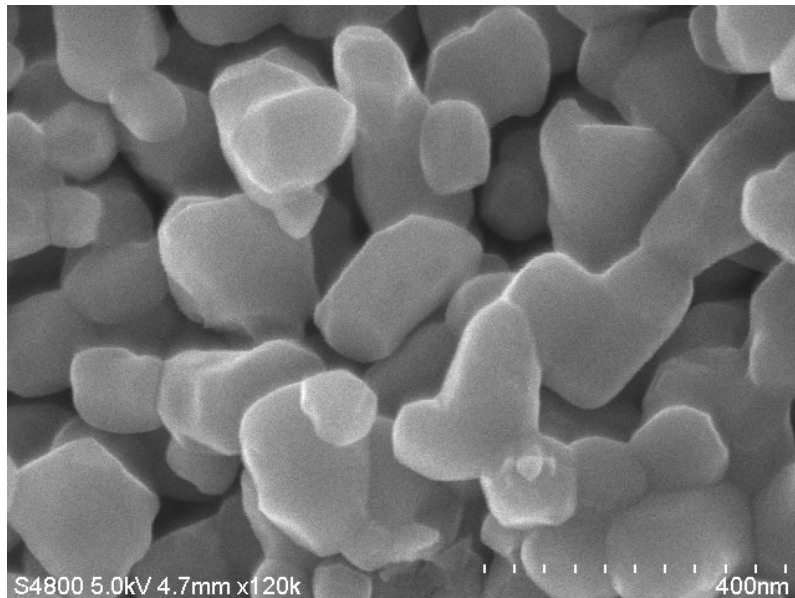


Fig. 3 FESEM image of Titanium Oxide

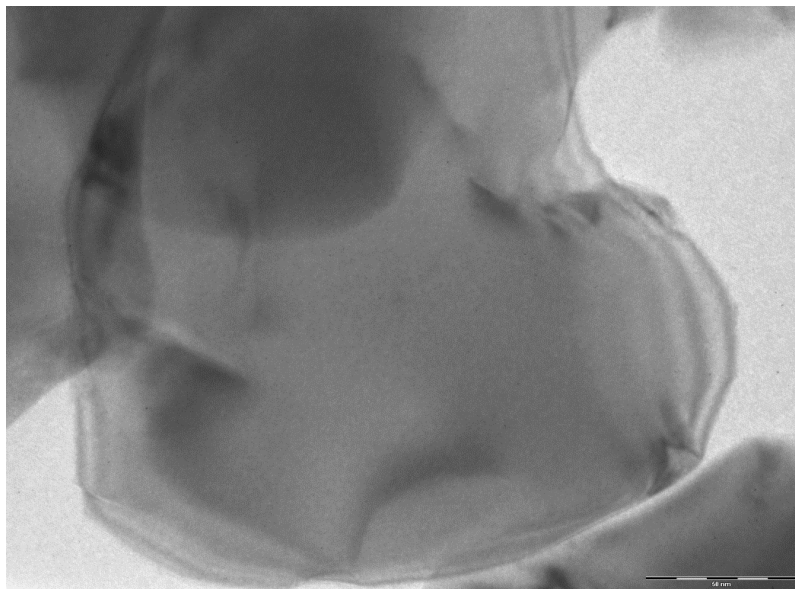


Fig. 4 TEM image of Titanium Oxide

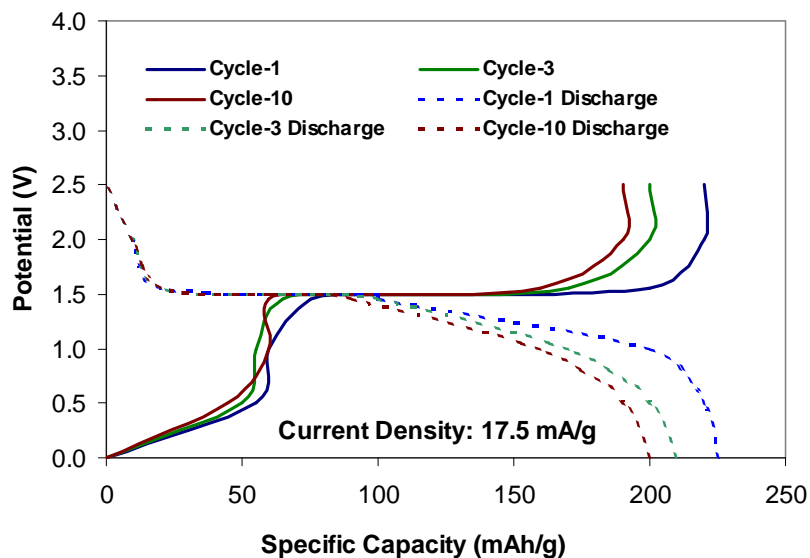


Fig. 5 Specific Capacity of nano titanium Oxide Powders

The results of the electrochemical tests conducted are depicted in figure- 5. The tests were conducted at a current density of 17.5 mAh/g calculated and adjusted based on the weight of anode active material and the applied current. It was found that, TiO₂ exhibited a specific capacity of 220 mAh/g, which is comparable with the published literature. It has good charge discharge characteristics as it is evident from the well defined constant potential plateau seen in figure-5. However, the decay of the electrode with increase in the number of cycles is evident from the widely spaced charge discharge curves signifying progressive loss of charge storage capacity.

CONCLUSIONS

TiO₂ nanoparticles were synthesised with an average particle size of 50 to 150 nm by wet chemical methods. NanoTiO₂ exhibits a specific capacity of 220 mAh/g, which is comparable with the published literature. Electrode decay which was observed from the electrochemical studies needs to be addressed before these materials could be considered for commercial use.

REFERENCES

- [1] Kyu T Lee, Justin C Lytle, Nicholas S Ergang, Seung M Oh and Andreas S Stein, *Adv Funct Mater.*, **2005**, 15(4), 547-56
- [2] Fie Wang, Mingshu Zhao and Xiaoping Song, *Journal of Power Sources*, 175, **2008**, 558-63.
- [3] Heman A Lopez US Patent: 2011/0111294 A1, **2011**
- [4] Ali Reza Kamali and Derek J Fray, *Adv Mater Sci.*, 27, **2011**, 14-24.
- [5] L.Kavan, M. Gratzel, *Electrochem. Solid State Lett.*, 5, **2002**, A39.
- [6] G.X.Wang, D.H.Bradhurst, S.X.Dou, H. K. Liu, *J. Power Sources*, 83, **1999**, 156.
- [7] B. Scrosati, S. Panero, P. Reale, D. Satolli, Y. Aihara, *J. Power Sources*, 105, **2002**, 161.
- [8] Mao-Sung W, Min-Jyle W, Jiin-Jiang J, Wein-Duo Y, *J. Power Sources*, 185, **2008**, 1420
- [9] Min Gyu Choi, Young-Gi Lee, Seung-Wan Song, Kwang Man Kim, *Electrochim. Acta*, 55, **2010**, 5975
- [10] Yi Jin, Tan Chunlin, Li Weishan, Lei Jianfei, Hao Liansheng, *Rare Metals*, 29, **2010**, 505
- [11] M. Pfanzelt, P. Kubiak, M. Fleischhammer, M. Wohlfahrt-Mehrens, *J. Power Sources*, 196, **2010**, 6815
- [12] Vilas G Pol, Sun-Ho-Kang, Jose M. Calderon-Moreno, Christopher S. Johnson, Michael M Thackeray, *J. Power Sources* 195, **2010**, 5039