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TiO₂ Microparticles/Reduced Graphene Oxide Composite as Anode Material for Lithium Ion Battery

S.A.D.R. Madhusanka^{1,2,*}, R.D.L. Sandaruwan^{1,2}, M. M. Athar³, M. Zaib⁴, Hashitha M.M. Munasinghe Arachchige⁵, B.S. Dassanayake^{1,2,}, M. Yoshio⁶ and N. Gunawardhana^{1,5,*}

¹ Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka.

² Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka.

³ Institute of the Chemistry, University of Punjab, New Campus, Lahore, Pakistan.

⁴ Department of Chemistry, Government College Women University, Kutchehry road, Sialkot, Pakistan

⁵Research and International Affairs, Sri Lanka Technological Campus, Padukka, Sri Lanka

⁶ Advanced Research Center, Saga University, 1341 Yoga-machi, Saga 840-0047, Japan.

*E-mail: <u>nandag@sltc.ac.lk</u>, <u>nandagunawardhana@pdn.ac.lk</u>

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Over the past decade, anatase phase titanium dioxide (TiO₂) has attracted a great deal of attention as one of the most promising electrode materials for lithium ion batteries due to its safety, eco-friendliness, price and excellent properties such as high operating potential (~1.75 V vs. Li/Li⁺), chemical and mechanical stability. This work presents an extensive study of the TiO₂ micro particles-based electrode and the composites electrode of micro-TiO₂ with nano-multilayered graphene. Graphene was synthesized from Sri Lankan natural graphite and was characterized using XRD, FTIR, Raman and SEM. The electrochemical performance of the electrodes prepared with anatase TiO₂ micro particles and TiO₂/graphene composites has been tested using constant current charge/discharge studies. TiO₂ electrode shows a discharge capacity of 141.5 mAh g⁻¹ in the 1st cycle and that of 111.2 mAh g⁻¹ after 50 cycles with an initial irreversible capacity loss of 12.3% and a coulombic efficiency of 99.1%. TiO₂-graphene composite electrode shows discharge capacities of 159.2 mAh g⁻¹, 143.0 mAh g⁻¹ in 1st, 50th and 100th cycles, respectively with significantly small initial irreversible capacity loss of 6.5% and a coulombic efficiency of 99.5%. Moreover, this composite presents high material stability at high current rates and good cycle performance.

Keywords: Anatase TiO₂, Lithium ion batteries, Sri Lankan natural graphite, graphene oxide, graphene

1. INTRODUCTION

At present, the expanding market for electric vehicles demands for novel approaches in designing high-efficient lithium-ion batteries with high energy/power densities and long cycle life. Though,

materials such as tin (Sn) and silicon (Si) have been extensively studied as anode materials, owing to their high energy density, they suffer from large volume expansion during charge-discharge process, significant irreversible capacity loss and poor cyclability [1-6]. Among various anode materials, TiO₂ with different electrochemically active polymorphs (anatase, rutile, brookite and TiO₂ (B)) has been widely studied in the past few years due to its superior properties such as high operating potential (~ 1.75 V vs. Li/Li⁺), chemical and mechanical stability even at high current rates (C-rates), low volume expansion (<5%) during Li insertion-de-insertion processes, low cost and eco-friendliness, [7-10]. Further, TiO₂, when used as the anode material, can deliver high specific power and it is compatible with standard electrolyte solvents owing to its high operating potentials (>1 V), therefore, the formation of solid electrolyte interface (SEI) does not occur and the irreversible capacity loss is very low. Nevertheless, the practical application of TiO₂ in Li-ion batteries is severely hindered by its major drawbacks such as, poor electronic conductivity $(10^{-13} \text{ S cm}^{-1})$ and low lithium ion diffusion (10^{-10} --) $10^{-17} \text{ cm}^2 \text{ s}^{-1}$ [10-12]. Different approaches have been tested to overcome the inherent problems of TiO₂. One such approach is to use nanoparticles [13] and nanostructures [14] to enhance the capacity by increasing the active surface area of the electrodes, and also to improve the conductivity by reducing the electronic and ionic transport distances. However, high reactivity and difficulty in handling these nanomaterial-based electrodes do not allow their implementation in the market as for now [15]. Another effective strategy is aimed at improving the electronic conductivity by using high conductive agents such as carbon nanomaterials [16]. In this context, Wang et al. have reported that the reduced graphene oxide (rGO) sheets with non-porous spherical TiO₂ nanoparticles composite gives good capacity retention of 125 mAh g⁻¹ over 5 cycles at 10C rate [17]. A similar composite which exhibits comparable reversible capacities of 97.7 mAh g⁻¹ after 5 cycles at a rate of 10C has also been reported by Cao *et al.* [18]. Also, Zha et al. have reported electrochemical tests of TiO₂-rGO composites reaching a reversible capacity of 100 mAh g⁻¹ at 10 C for 100 cycles, in comparison to 58 mAh g⁻¹ at 10 C for 100 cycles for pure TiO₂ [19]. However, it is quite necessary to find alternative materials or methods to tailor the physical and electrochemical properties of conventional battery materials in order to develop efficient batteries which can meet the current demand.

Therefore, here, we present a novel approach of using TiO_2 microparticles mixed with conducting material to successfully address the low packing density associated with nanomaterials as well as the low conductivity associated with the conventional materials. High electronic conductivity of graphene is expected to compensate the low conductivity of the microparticulate network of TiO_2 electrode. In this work, we prepared two types of working electrodes (WE) based on (a) TiO_2 micro particles and (b) TiO_2 microparticles/multilayer graphene composite. Electrochemical tests of these electrodes were performed in half cell system using lithium (Li) metal as the counter electrode (CE) in the potential window of 1-3 V vs. Li/Li⁺.

2. EXPERIMENTAL

2.1 Synthesis of graphene

Modified Hummer's method was used to synthesize graphene oxide (GO) from Sri Lankan natural graphite [20-23]. GO suspension was reduced to multilayer graphene using L-ascorbic acid

(Finar Chemicals Limited India, 99%) as reported in the literature. The final product obtained is called the L-ascorbic acid reduced graphene oxide (ArGO) [24-26].

2.2 Preparation of composite material and the anode

Graphene (ArGO) and carbon black were added to TiO₂ (anatase) powder (particles size 20 μ m) and ground in a mortar. 5 drops of Triton X-100 (Sigma, USA, 99.5%) surfactant and sodium carboxymethyl cellulose (CMC), dissolved in water, were added while grinding. Then, 10 ml of ethanol (Hayman, England, 99.9%) was added to the mixture and the resulting solution was stirred for 10 minutes and ultra-sonicated for 5 minutes. Finally, it was sprayed on to an aluminum foil paper (5 × 5 cm²) (to obtain coverage of ~ 6 mg cm⁻²) at 100 °C using hand spray method. Several composite anode materials were prepared using the same procedure with following weight ratios; TiO₂: carbon black: CMC- 90: 5: 5 and TiO₂: graphene (ArGO): carbon black: CMC- 85:5:5:5.

2.3 Cell assembly and electrochemical characterization

The synthesized TiO₂-graphene composite was used as the anode material. The working electrodes were prepared by mixing 85 wt% TiO₂, 5 wt% ArGO, 5 wt% carbon black and 5 wt% CMC and the reference electrode was prepared by mixing 90 wt% TiO₂, 5 wt% carbon black and 5 wt% CMC. The electrodes were pressed under a pressure of 300 kg cm⁻² and dried at 160 °C for 4 hours in an oven. The mass loading of electrodes was 4-6 mg cm⁻². The lithium electrode was prepared by pressing the lithium metal on to a stainless-steel plate (~500 µm thick). The electrochemical studies were performed at room temperature in encapsulated CR2032 coin-type cell where the positive and negative electrodes were separated by two glass fiber separators (~ 100 Å) and ca. 0.5 ml of electrolyte was added [27,28]. The electrolyte was 1.0 M LiPF₆-EC: DMC (1:2 by volume) (Ube Chemicals Co., Ltd., Japan) and used as received. The charge/discharge tests were carried out at the current density of 100 mA g⁻¹ using Nagano BST2004W battery testing machine.

2.4 Structural characterizations

The surface morphology of the fabricated electrodes was examined by scanning electron microscopy (Zeiss EVO LS15, 20.0 kV). The structure was characterized by powder X-ray diffraction (XRD, SIEMENS D5000 X-Ray Diffractometer) using Cu K α radiation. Fourier transform infrared (FTIR) spectra were recorded by a FTIR spectrophotometer (Nicolet iS50) using the attenuated total reflection (ATR) method. The Raman spectra of the prepared anode materials were collected using aJASCONRS-7100 spectroscope at 532.1 nm.

3. RESULTS AND DISCUSSION

3.1 Characterization of graphite, GO and ArGO

SEM images of (a) Sri Lankan natural graphite (SLNG), (b) graphene oxide (GO), (c) reduced graphene oxide (ArGO) and (d) TiO₂-ArGO composite are shown in Figure 1. Figure 1(a) very clearly shows that the natural graphite surface displays aligned graphite flakes with distinct edge planes. Exfoliated graphitic layers can be observed in the SEM image of GO (Figure 1b) which results from the oxidation of graphite basal planes. The graphene oxide has layered structure with visible edges and folded areas. Well-exfoliated but crumpled and aggregated ArGO sheets shown on Figure 1(c) are resulting from chemical oxidation and reduction processes. This image reveals that thick flakes of GO were decomposed into many thin ArGO lamellae with different thicknesses. It also confirms that individual graphite nanosheets are not single graphenes, but consist of several layers of graphene sheets. The morphological features of the synthesized GO and ArGO's are similar to those in previous studies [29, 30]. Figure 1(d) shows that TiO₂ particles are well dispersed between the few-layer graphene sheets and these TiO₂ particles are connected through conducting graphen layers.



Figure 1. Scanning electron microscopic (SEM) images of (a) Sri Lankan natural graphite (SLNG), (b) graphene oxide (GO), (c) L-ascorbic acid using reduced graphene oxide (ArGO) and (d) TiO₂/ multilayer graphene composite

Figure 2(a) shows the XRD pattern of graphite. The main peak at $2\theta = 26.54^{\circ}$, which corresponds to the (200) plane, has a very high intensity owing to the high degree of crystallinity of Sri Lankan Natural graphite. As can be seen from the XRD pattern of GO (Figure 2b), the peak corresponding to

(002) plane disappears as a result of the oxidation process and a new peak appears at a lower angle $(2\theta=9.76^{\circ})$ indicating the increase in the interlayer spacing of (200) planes [31]. The interlayer spacing values of GO and graphite, calculated using Bragg's equation [32], are 0.91 nm, and 0.34 nm, respectively. The interlayer spacing of GO has increased approximately three times compared to graphite, potentially be due to oxygen containing functional groups which are attached to the basal planes of graphite [33, 34]. Reduction of GO gives accumulated and randomly packed ArGO sheets and the corresponding XRD pattern (Figure 2c) shows a broad and low intensity XRD peak centered at $2\theta = 25.76^{\circ}$ with an interlayer space of 0.35 nm. The intensity of this peak is very low compared to that of natural graphite indicating the delamination of graphite to form few- layer graphene.



Figure 2. X-ray diffraction (XRD) patterns of (a) SLNG, (b) GO and (c) ArGO

ATR-FTIR spectra of SLNG, GO and ArGO are shown in Figure 3 (a-c). No clear absorption peak can be observed for SLNG due to the absence of any reactive functional groups in the graphite

particles. In the FTIR spectrum of GO (Figure 3b) bands at 1038 cm⁻¹ and 1165 cm⁻¹ can be assigned to C-O functional groups. Also, the absorption bands appearing at 1375 cm⁻¹ and 1617 cm⁻¹ correspond to C-H stretching, and C=C, respectively [35, 36]. The broad band at 3115 cm⁻¹ and the small narrow band at 3615 cm⁻¹ are due to O-H groups of water molecules. Therefore, these results suggest that SLNG has been well oxidized to produce high-quality GO. Further, no observable absorption peaks appear in the FRIR spectrum of the ArGO suggesting that the GO has been successfully reduced to ArGO [37].



Figure 3. Fourier transform infrared (FTIR) spectra for (a) SLNG, (b) GO and (c) ArGO

In the Raman spectra of SLNG (Figure 4a), three prominent peaks can be observed at 1344.2 cm⁻¹ (D band), 1578.7 cm⁻¹ (G band) and 2716.3 cm⁻¹ (2D band) [38]. The D band is associated with defects/disorder and has small intensity as the number of defects is low in graphite. The intensity of D band (I_D) has increased in ArGO (I_D= 92.1) compared to that of graphite (I_D= 330), which indicates that a higher number of defects are present in ArGO [39]. G band is related to the bond stretching of all pairs of sp² atoms and its intensity and peak width decrease when the number of sp² hybridized carbon atoms decreases or defect amount increases and also, when the number of graphene layers becomes low [40,

41]. When graphite transforms into graphene, the 2D band in graphite spectrum disappeared due to the increasing number of defects.



Figure 4. Raman spectra for (a) SLNG and (b) ArGO

3.2 Electrochemical properties

The electrochemical performance of $TiO_2/ArGO$ composite was evaluated using the coin-type cells versus metallic lithium, and for comparison purposes electrochemical performance of TiO_2 was also investigated under the same conditions. Figures 5 and 6 depict the first and second charge/discharge cycles for reference TiO_2 anode and $TiO_2/ArGO$ composite anode at 1C current rate in the potential range of 1.0-3.0 V vs. Li/Li⁺. The chemical intercalation and deintercalation process of Li⁺ ions into

 TiO_2 is given by equation (1). Under the stable conditions, the maximum value of the insertion coefficient, x, has been found to be about 0.5. In general, the lithium ion insertion/extraction activities at anatase TiO_2 nanoparticles are considered reversible only when x< 0.5.

 $TiO_2(s) + x Li^+(s) + x e^- \iff Li_x TiO_2(s)$ (1)

In here x may vary from 0 to 1 depending on the TiO_2 polymorphs, morphologies and sizes. For instance, bulk rutile can accommodate insignificant quantity of Li-ions (<0.1 mol Li/TiO₂) at room temperature [42].

The initial specific charge/discharge capacities of the TiO₂/ArGO composite, (169.5/159.2 mAh g^{-1}) are higher than those of the reference TiO₂ (159.0/141.5 mAh g^{-1}). TiO₂ shows an irreversible capacity loss of 12.4%, whereas TiO₂/ArGO composite shows that of only 6.5 %. These high specific charge capacities of TiO₂/ArGO composite are due to well dispersed TiO₂ particles, which increase the electrochemical reactivity. Also, only a small amount of lithium is stored in graphene sheets in the potential range of 1.0 - 3.0 V. The plateau regions in both the graphs indicate that there is no voltage drop between first two cycles i.e. low polarization of anode materials. The main storage mechanism in anatase TiO₂ is the intercalation reaction, where lithium ions are randomly distributed over half of the available interstitial octahedral sites, leading to a theoretical capacity of 168 mAh g⁻¹. However, it has been reported that when the particle size decreases the proportion region (quick voltage drop+voltage plateau) decreases where as region-C increases [7].



Figure 5. Galvanostatic charge/discharge curves of TiO₂ electrode vs. Li/Li⁺

Figure 6. Galvanostatic charge/discharge curves of TiO₂/ ArGO composite electrode vs. Li/Li⁺

After 50 cycles, the TiO₂/ArGO composite shows excellent discharge capacity of 143.0 mAh g⁻¹ and a capacity retention of 90.1% in comparison to TiO₂ with those of 111.2 mAh g⁻¹ and 79.5% (Figure 7, 8). The TiO₂/ArGO composite was tested for 100 cycles to obtain a discharge capacity of 143.0 mAh g⁻¹ and a capacity retention of 92.1%. The coulombic efficiencies of TiO₂ and TiO₂/ArGO composite were 99.1% and 99.5%, respectively. These results prove that TiO₂/ArGO composite has higher capacity and better cycle performance compared to TiO₂ microparticles. Stability of the prepared composite was tested using different C-rates as shown in Figure 9. The capacity decreases when C-rate increases up to 2C, 5C and 10C. Interestingly, as the current rate is decreased to back to 1C, during the 20th and 30th cycles, capacity increases to give comparable values to that of first five cycles, which implies that TiO₂/ArGO composite show charge/discharge capacities of ~ 95 and 85 mAh g⁻¹, respectively, which suggest that this material is capable of storing considerable amount of charges even at higher current rates. These results thus indicate the importance of conductive graphene sheets to enhance the performance of micro-TiO₂ particles.

Many research groups have synthesized various TiO_2 micro and nano particles with/without graphene/graphene oxide composites. As shown in Table-1, capacities of nano-composites with/without graphene/graphene oxide showed higher capacity than that of micro TiO_2 composites. The prepared $TiO_2/ArGO$ micro composites showed higher capacity than of that of previously prepared micro TiO_2 composites [43]. However, TiO_2 nano structures, such as nano wires, nanorods and nano hollow particles based graphene/TiO₂ composites showed higher capacity than the prepared micro $TiO_2/ArGO$ composites [44-52].

Figure 7. Cycling performance of reference TiO₂ electrode at 1C current rate

Figure 8. Cycling performance of TiO₂/ArGO composite electrode at 1C current rate

Figure 9. Cycling performance of TiO₂/ArGO composite at different current rates from 1C to 10C

Table 1. Summary of LIBs performance reported in TiO ₂ /reduce graphene oxide based anode m	aterial	ıls
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Composition	method	Current rate/density	Capacity mAh.g ⁻¹	Number of cycles	Ref
TiO ₂ /reduced graphene oxide	Hydrothermal synthesis	10C	112.3	100	[43]
Anatase TiO ₂ /graphene nanosheets (GNS)	Hydrothermal synthesis	500	120.3	50	[44]
TiO ₂ /RGO nanocomposite	GO and Anatase TiO2 was treated under the UV irradiation		310		[45]
Mesoporous TiO ₂	Hydrolytic process		158		[46]
TiO ₂ nanoparticles on nitrogen-doped graphene (TiO2/N-rGO)	hydrothermal method		187		[47]
TiO2 nanotube/graphene composites	one-step hydrothermal method	100	255	50	[48]
TiO2 -graphene nanocomposite	facile gas/liquid interface reaction	100	499	initial	[49]
TiO ₂ –GNS composite	in situ chemical synthesis method	50	148	50	[50]
Anatase TiO ₂ nanowires containing minor TiO2(B) phase	hydrothermal chemical reaction	140	280	40	[51]
monodispersed TiO ₂ hollow spheres with nanoporous	carboxyl-functionalized polystyrene spheres as templates	33.5	230	50	[52]
TiO ₂ micro particles	_	1C	111.2	50	This work
TiO ₂ /ArGO		1C	143.0	50	This work

4. CONCLUSION

Graphene oxide was synthesized according to modified Hummer's method using Sri Lankan natural (SLNG) graphite as the raw material. The synthesized graphene oxide was then reduced to graphene (ArGO) using L-Ascorbic acid. Final products were characterized by XRD, FTIR, SEM and Raman spectroscopy and the results indicate that few-layer graphene could be successfully prepared using SLNG. The chemical methods used in this work resulted in crumple and wrinkle graphene sheets, which helps to prevent the agglomeration of TiO₂ microparticles in the prepared composite. Electrochemical characterizations of TiO₂ microparticles showed discharge capacities of 141.5 mAh g⁻¹ and 111.2 mAh g⁻¹ in the 1st cycle and 50th cycle, respectively with an initial irreversible capacity loss of 12.3% and a coulombic efficiency of 99.1%. The TiO₂/ArGO composite electrodes showed discharge capacities of 159.2 mAh g⁻¹, 143.0 mAh g⁻¹ and 143.0 mAh g⁻¹ respectively in 1st, 50th and 100th cycles with a significantly smaller initial irreversible capacity loss (6.5%) and a coulombic efficiency of 99.5%. Moreover, this composite shows high material stability at high current rates and good cycle performance. Therefore, our composite material, consisting of TiO₂ microparticle and few-layer graphene is a promising substitute for the current commercial graphite anode in high-power, high-rate application of lithium ion batteries.

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