Effect of surface modification of TiO₂ on the electrochemical performance of lithium–sulfur cell

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MS received 29 August 2017; accepted 1 September 2018; published online 28 November 2018

Abstract. Surface of TiO₂ is known to chemically bind the polysulfides in Li–S cell. In the present study, the effect of surface defects or oxygen vacancies in TiO₂ present as a composite with sulfur cathode on the performance of Li–S cell was investigated by using NaBH₄ reduced (black colour) TiO₂ and pristine (white) TiO₂ in cathode. Results show that former is superior in performance.

Keywords. Polysulfide; reduction; NaBH₄; black TiO₂.

1. Introduction

Lithium–sulfur (Li–S) battery is a fascinating system due to its high theoretical capacity (1675 mAh g^{−1}) as well as energy density (2500 Wh kg^{−1}) [1]. In addition, sulfur is cheap and abundant. The overall cell reaction involving Li₂S as the end discharge product of sulfur is

In practice, unfortunately, it is difficult to achieve a high energy density with long life cycle from Li–S system due to certain intrinsic factors. Among them, formation of several lithium polysulfides as intermediates during reduction of S₈ to Li₂S, and their solubility in the electrolyte were the major drawbacks in the development of commercial Li–S batteries [1]. The dissolved lithium polysulfides in organic liquid electrolytes shuttle between the cathode and anode during charge–discharge cycling. This leads to a decrease in capacity of the cell as well as cycling efficiency. Hence, one of the solutions to prevent the dissolution of polysulfides is to trap them in the cathode by a suitable additive.

Lithium polysulfides can be either physically or chemically trapped by suitable modification of the cathode among which the former was demonstrated to be more effective [2]. Various porous structures of carbon were extensively studied as hosts for sulfur [3–5]. Most of the porous carbons physically capture polysulfides. In a few studies, carbon was modified to chemically bind polysulfides apart from physical trapping [6–8]. This was found to enhance the capacity and cycling stability as compared to pristine carbon. Metal oxides (TiO₂, MnO₂, etc.) were studied to host sulfur in Li–S batteries [9–13]. Evers *et al* [2] have reported that

mesoporous TiO₂ added to the cathode captures polysulfides in pores and plays a major role in capacity retention. Tao *et al* [14] have used various metal oxides as additives to sulfur cathode and shown that adsorption of polysulfides on surface of metal oxides is an essential process in capacity retention.

Among the metal oxides, TiO₂ was extensively studied to prepare composites with sulfur and promising results were reported [9,11,15]. TiO₂ is a wide band gap semiconductor and it absorbs light in the ultraviolet region and hence, appears white [16]. Colour of TiO₂ changes from white to yellow, blue or black on doping or introducing defects into the structure due to changes in band gap and absorption in the visible region of light [17,18]. Black TiO₂ (BT) was synthesized by several ways including reduction of white TiO₂ [19]. The black colour of BT originates from the oxygen vacancies or surface disorder in TiO₂, which lowers the band gap as compared to pure TiO₂ [18]. Due to lower band gap, it absorbs in the visible region of solar spectrum and finds applications in photocatalytic studies [19]. Presence of trivalent titanium was observed in BT, which enhances the electrical conductivity [20]. BT was used in lithium ion cells and superior performance over white TiO₂ was reported [20].

Several reports have appeared on various materials including TiO₂ as hosts to sulfur in cathode. However, in the present study, the effect of surface defects or oxygen vacancy in metal oxides on the performance of Li–S cell was examined. Surface defects were created by heating TiO₂ under a reducing environment. Performance of BT–S composite is compared with pristine TiO₂–S composite in Li–S cells. It is found that BT-based Li–S is superior resulting in higher capacity and better cycling stability than pristine TiO₂-based cell.

2. Experimental

2.1 Materials

Titania (Aeroxide TiO₂ P25, Evonik) and sodium borohydride (LR, S.D. Fine Chemicals Limited) were used to synthesize BT. sulfur (LR, S.D. Fine Chemicals Limited), carbon disulfide (LR, S.D. Fine Chemicals Limited), acetylene black (99.9+%, Alfa Aesar), poly(vinylidene fluoride) (Aldrich) and N-methyl-2-pyrrolidinone ($\geq 99\%$, Sigma-Aldrich) were used to prepare cathodes. 1,2-dimethoxyethane (DME) (99%, Alfa Aesar), 1,3-dioxolane (DOL) (99.5%, Alfa Aesar), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99.95%, Aldrich), lithium nitrate (anhydrous, AR, Thomas Baker), glass microfibre filter separator (Whatman, binder free, grade GF/C) and lithium foil (99.9%, Aldrich) were used for fabrication of cells.

2.2 Synthesis of BT

Synthesis of BT was carried out as reported in literature with some modifications [19]. P25 or T (250 mg) was mixed with NaBH₄ (125 mg) using a mortar and pestle. Then the mixture was transferred into an alumina crucible and heated in a tubular furnace at 350°C for 1 h under nitrogen flow. It was allowed to cool to room temperature. A black colour mass was obtained, which was crushed into fine powder and then washed several times with distilled water and separated by centrifugation. It was finally washed with ethanol and dried in oven at 60°C for 12 h.

2.3 Preparation of composites

In the composites, weight ratio of TiO₂ (T or BT) to sulfur was 1:2. For preparation of composites, 60 mg of sulfur was dissolved in 0.2 ml of carbon disulfide and then 30 mg of T or BT was added to it and sonicated in for 30 min. It was dried in an oven at 60°C to remove the solvent, followed by crushing into fine powder using a mortar and pestle.

2.4 Fabrication of cells

For fabrication of cathode, T-S or BT-S, acetylene black and poly(vinylidene fluoride) in a ratio of 7:2:1 were dispersed in N-methyl-2-pyrrolidinone. The slurry was coated onto a cleaned aluminium foil of diameter 16 mm. Then, the electrodes were dried at 60°C for 12 h. Sulfur loading in each electrode was found to be 0.7–0.8 mg cm⁻². Electrolyte containing 1 wt% of LiNO₃ as additive in 1 M LiTFSI solution in DME and DOL (1:1 v/v) was prepared. CR 2032 type coin cells were assembled in a glove box (MBRAUN, UNILAB) in argon atmosphere using a composite cathode, lithium foil, filter paper separator and electrolyte.

2.5 Characterization of powders and composites

Phase analysis of powders was carried out by X-ray diffraction (XRD) technique using CuK α radiation (Philips X'Pert Pro Diffractometer). Samples were excited with a laser of wavelength 532 nm as the source and Raman spectra were recorded using LabRAM HR system. Transmission electron microscope (TEM) (JEM-2100F, JEOL) was used to observe the morphology of T and BT nanoparticles. Particle-size distribution was measured using ImageJ software. Specific surface area and pore volume of T and BT were determined by using Micromeritics surface area analyzer model ASAP-2020. Diffuse reflectance spectra of samples were collected using PerkinElmer Lambda-35 spectrophotometer. Chemical characteristics of powders were studied using X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA). TG 209 F1 Iris, NETZSCH instrument was used for thermogravimetric analysis (TGA). Samples were heated from room temperature to 300°C at a heating rate of 10°C min⁻¹ under continuous flow of argon.

2.6 Electrochemical characterization of cells

Galvanostatic discharge–charge cycling of Li–S cells were carried out between 3.0 and 1.8 V at 0.2 C rate (1 C = 1675 mA g⁻¹ for sulfur) by using BioLogic SA multichannel potentiostat/galvanostat model-VMP3. Cyclic voltammetry measurements were performed at a scan rate of 0.1 mV s⁻¹ within 3.0 and 1.8 V.

3. Results and discussion

XRD patterns of both commercial pristine TiO₂ (T) from Evonik and BT are shown in figure 1a. The T sample consists of both anatase (PDF-01-084-1285) and rutile (PDF-01-087-0920) phases of TiO₂, as expected. Additional peaks (marked in the pattern) are observed in the pattern of BT, which correspond to the reduced phases of TiO₂. Tan *et al* [19] have also reported additional peaks in the XRD pattern of sample synthesized under similar experimental conditions. They have attributed these peaks to a mixture of Ti₉O₁₇, Ti₈O₁₅ and Ti₃O₅. The oxygen vacancies are created at the surface of TiO₂ crystal due to reduction by the NaBH₄ treatment. The surface of BT is modified and contains disordered structure or oxygen vacancies in addition to the presence of the original anatase and rutile phases as the major constituents. To further gain insight into the structural changes due to NaBH₄ treatment, Raman analysis was carried out and spectra of both samples are presented in figure 1b. In the T sample, peaks at 143, 198 and 638 cm⁻¹ correspond to E_g mode, whereas peaks at 399 and 513 cm⁻¹ correspond to B_{1g} and A_{1g} modes, respectively, for anatase phase of TiO₂ [21]. Weak peaks corresponding to rutile are observed due to lower rutile content in the TiO₂ powder. The intense peak at 143 cm⁻¹ for T sample is shifted to 145 cm⁻¹ for BT sample and also the peak

Figure 1. (a) XRD patterns and (b) Raman spectra of T and BT.

appears broader with diminished intensity. This indicates the presence of oxygen vacancies in the BT sample [20,22].

The size distribution for non-spherical particles of T sample is in the range of 19–29 nm (figure 2a), whereas it is in the range of 17–28 nm for BT sample (figure 2b). The values of average particle size as found from the histograms are 23 and 21 nm for T and BT samples, respectively, which indicates that T do not undergo any significant change after converting to BT. Disintegration, agglomeration or shape change of the particles has not taken place when T is converted to BT. A mild temperature treatment (350°C) and a short duration (1 h) has affected only the surface of the particles leaving the core unaffected (figure 2c).

Nitrogen gas adsorption/desorption studies were carried out on both T and BT samples. The isotherms and BJH curves are shown in figure 3. Hysteresis loop is observed for both the samples indicating that both are porous (figure 3a, b). The specific surface area for T and BT samples are 56 and 66 m² g⁻¹,

Figure 2. TEM images of (a) T, (b) BT and (c) high resolution image of BT showing disordered outer layer marked by an arrow.

respectively. From the BJH curves shown in figure 3c, d, pore-size distributions for T and BT are found to be 5–75 and 5–60 nm, respectively, and average pore diameter are 18 and 24 nm, respectively. Cumulative pore volume for T is 0.23 cm³ g⁻¹ and it increases to 0.43 cm³ g⁻¹ for BT. The results indicate that the gas adsorption properties of TiO₂ are enhanced due to surface modification with NaBH₄ treatment.

After NaBH₄ treatment, colour of sample changed from white (T) to black (BT) as reported previously [19]. The effect of conversion of T into BT on band gap of the material was

Figure 3. Nitrogen adsorption/desorption isotherms and pore size distribution of (a, c) T and (b, d) BT.

studied by diffuse reflectance spectroscopy. For estimation of band gap, Kubelka–Munk function ($F(R)$) and energy of incident photon ($h\nu$) were utilized [20]. From the intercept of the line with abscissa, band gap for T is found to be 3.23 eV (figure 4a). The band gap decreases for BT and is estimated to be 1.29 eV (figure 4b). Similar change in colour from white to black and lowering of band gap in TiO₂ was observed by Myung *et al* [20], which was attributed to the presence of trivalent titanium in the sample.

Reduction of TiO₂ surface to lower valency oxides of Ti is clearly evident from XPS studies. XPS spectra of Ti 2p in T and BT are shown in figure 5a and b, respectively. Two deconvoluted peaks are obtained for T at 458.2 and 463.9 eV corresponding to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺, respectively [19]. For the BT sample, deconvolution of Ti 2p_{3/2} results in two peaks at 458.0 and 458.5 eV, which are assigned to Ti³⁺ and Ti⁴⁺, respectively [19,23]. Peak at 464.0 eV corresponds to Ti 2p_{1/2}. From the area of Ti³⁺ and Ti⁴⁺ peaks, the

content of Ti³⁺ is calculated as 53%. From XPS analysis, it is concluded that Ti⁴⁺ is reduced to Ti³⁺ in BT and oxygen vacancy is created.

Thermal analysis was carried out to determine the sulfur content in the composites. As observed from figure 6, sulfur loses mass completely at 275°C and thereafter, the mass remains unchanged. For T and BT composites with sulfur, major mass loss occurs between 150 and 240°C, which correspond to the mass of sulfur in the composites. Taking mass loss of pristine powders and composites into account, sulfur content in composites of T and BT are estimated to be 67.7 and 67.1%, respectively.

Cyclic voltammograms of T–S and BT–S electrodes recorded by cycling the corresponding coin cells at a scan rate of 0.1 mV s⁻¹ are similar in shape, in current peak positions and also, in magnitude of peak currents (figure 7). In the first sweep starting from 3.0 to 1.8 V, there are two cathodic current peaks for T–S (figure 7a) at 2.23 (peak P_{c1}) and 2.05 V (peak

Figure 4. Tauc plots using Kubelka–Munk function and photon energy for determination of band gap for (a) T and (b) BT.

P_{c2}), respectively. In the reverse sweep, a split anodic current peak (P_{a1}) appears at 2.40 V. It is known that the reduction of S_8 is a multistep process involving different intermediate species [15]. The reduced species of S_8 combine with Li^+ in the electrolyte to produce lithium polysulfides with a general formula Li_2S_n . The polysulfides, such as Li_2S_8 and Li_2S_6 with long chain length are soluble in the electrolyte. During the discharge, the polysulfide chain length is shortened as the sulfur is further reduced. The current peak P_{c1} is due to the reduction of S_8 to Li_2S_4 with Li_2S_8 and Li_2S_6 as intermediates and P_{c2} is due to the formation of Li_2S with Li_2S_4 and Li_2S_2 as intermediates. These two processes are separated by about 0.20 V. The anodic peak P_a is attributed to the oxidation of Li_2S to S_8 . The splitting of P_a in the first cycle reflects the oxidation involving intermediates. However, the split peak (P_a) becomes a single peak on repeated cyclings (figure 7a). In contrast, multiple cycling does not alter the cathodic peaks substantially. The cyclic voltammograms of BT–S electrode

Figure 5. XPS spectra of (a) T and (b) BT. Raw data (black line), sum (red line) and deconvoluted peaks (dashed) are shown.

Figure 6. TGA curves of T, BT and composites (T–S and BT–S).

Figure 7. Cyclic voltammograms for (a) T-S- and (b) BT-S- based cells.

(figure 7b) are nearly identical to those of the T-S electrode (figure 7a). Thus, the surface modification does not result in noticeable changes in cyclic voltammetric features of S electrode in Li-S cells. However, the cycling stability is greatly improved as detailed below.

The discharge-charge voltage profiles of Li-S cells employing T-S and BT-S cathodes (figure 8a) are also similar with voltage plateaus, but with a small increase in capacity of BT-based cell in relation to T-based cell. The voltage plateaus noticed during discharge and charge stages agree well with the cyclic voltammetry data. The discharge capacity values obtained in the 2nd cycle are 541 and 622 mAh g⁻¹, for T- and BT-based Li-S cells, respectively at 0.2 C rate. On subjecting the cells to repeated discharge-charge cycling (figure 8b), the cycling stability of BT-based cell is found to be much superior to that of T-based cell. The discharge capacity values

Figure 8. (a) Discharge-charge curves of T-S- and BT-S-based cells at 0.2 C for 2nd cycle and (b) cycling performances and coulombic efficiencies of T-S- and BT-S-based cells at 0.2 C.

obtained after 100 galvanostatic discharge-charge cycles are 338 and 567 mAh g⁻¹ for T- and BT-based Li-S cells, respectively. Thus, the capacity falls from 2nd cycle to 100th cycle is about 37% (i.e., 0.37% per cycle) for T-based Li-S cell. On the other hand, the capacity fall under identical experimental conditions is only about 9% (i.e., 0.09% per cycle). Thus, there is about four times improvement in capacity stability due to surface modification of TiO₂ used as an additive to the sulfur cathode made for Li-S cells. The TiO₂ added to the S-electrode plays important role in holding lithium polysulfides and minimizing their diffusion to the lithium negative electrode. The main interaction of lithium polysulfides with TiO₂ particles is their adsorption. The surface modification of TiO₂ is shown to substantially improve the performance of S-electrode by yielding stable discharge capacity.

4. Conclusions

In conclusion, black-coloured TiO₂ was prepared by reduction of white TiO₂ using NaBH₄. The origination of

black colour was due to formation of oxygen vacancies or surface defects. Black TiO₂-S-based cell delivered a discharge capacity of 622 as compared to 541 mAh g⁻¹ for pristine TiO₂-S-based cell at 0.2 C. After 100 cycles, discharge capacity of 338 mAh g⁻¹ was obtained in TiO₂-based cell, whereas 567 mAh g⁻¹ was obtained in black TiO₂-based cell. Such better capacity retention in black TiO₂-based cell was ascribed to enhanced polysulfide retention property of black TiO₂.

Acknowledgements

University Grants Commission, India and Evonik, India, are acknowledged for Dr D S Kothari's postdoctoral research fellowship (SPM) and TiO₂ (P25), respectively.

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