

# The Advanced Na Storage Properties of TiO<sub>2</sub>/PPy Composite for Sodium-Ion Batteries

Baogui Tian<sup>1</sup>, Xuanyou Long<sup>1</sup>, Kangkang Wang<sup>2,a,\*</sup>, Hailei Zhao<sup>1,b,\*</sup>, Fei Gao<sup>2</sup>, and Yang Kai<sup>2</sup>

<sup>1</sup>School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

<sup>2</sup>State Key Laboratory of Operation and Control of Renewable Energy and Storage Systems, China Electric Power Research Institute, Beijing, 100192, China

\*Corresponding author email: <sup>a</sup>wangkangkang123@163.com; <sup>b</sup>hlzhao@ustb.edu.cn

**Keywords:** TiO<sub>2</sub>; PPy; Composite material; Sodium-ion battery; Anode

**Abstract:** Anatase TiO<sub>2</sub> with high theoretical capacity is emerging as an appealing anode for sodium-ion storage. Nevertheless, the inherent poor conductivity limits its practical use. In our work, anatase TiO<sub>2</sub>/PPy composite material in 10wt.% PPy content was synthesized via a high energy ball-milling method. The electrochemical tests demonstrated its notable Na storage capability. The charge capacity of the first cycle reached 207.5 mAh g<sup>-1</sup> at 0.1 C, and maintained at 191 mAh g<sup>-1</sup> after 40 cycles. Even after a long-term cycling of 150 weeks at rate 1 C, the electrode exhibited a high specific capacity of 103.5 mAh g<sup>-1</sup>.

## 1. Introduction

In recent years, sodium-ion batteries (SIBs) have emerged as an attractive alternative for large-scale electrical energy storage, due to the earth-abundant natural resources of sodium and the lower safety risk. Massive effort and funding were invested to explore appropriate cathode materials for SIBs, therefore the electrochemical performances have been improved[1-5]. However, the development of anode materials is relative lagging behind. Significant works have indicated that hard carbon materials show great potential as anodes for SIBs [6-7]. However, the low sodium-storage potential (ca. 0.1 V vs. Na/Na<sup>+</sup>) easily leads to sodium dendrite formation, which usually causes a catastrophic safety accident.

Although many alloying materials possess high theoretical capacities, the rigorous volume change during cycling causes to the disintegration of electrode with quick capacity degradation and inferior rate capability [8-10]. Generally, compared to hard carbon or alloying materials, insertion materials offer substantial advantages with respect to safety issues and long-term cycling stability. Amongst, anatase TiO<sub>2</sub> stands out as one of the most promising one. However, low capacity and poor electrical conductivity of TiO<sub>2</sub> are its main drawbacks. Therefore, the conductive polymer PPy is introduced in anatase TiO<sub>2</sub> to overcome the challenge of the poor conductivity via a simple ball-milling method.

## 2. Experimental methods

### 2.1 Synthesis of TiO<sub>2</sub>/PPy composite

All of the chemicals used in this work were of analytical grade. Commercial TiO<sub>2</sub> with a size of 25 nm (Aladdin Company) was mixed with polypyrrole (PPy) by ball-milling method at a rate of 300 rpm for 6 h with a mass ratio of 9:1.

### 2.2 Characterization of the structure

The crystal structures of the synthesized samples were measured using X-ray powder diffraction (XRD, Rigaku, Cu K $\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ), with a change in the  $2\theta$  angle of  $8^\circ \text{ min}^{-1}$  in the

range of 5°–80°.

### 2.3 Electrochemical characterization

To characterize the electrochemical performance, the electrodes were prepared by using a mixture of 70 wt.% of active materials, 20 wt.% of Super P as a conductive additive, and 10 wt.% of PVDF as a binder, and some NMP solvents as diluents. The final wet slurry coated on copper foil, then dried in an oven at 80 °C for more than 12 h. Charge–discharge tests were performed using CR2032-type coin cells. Fresh metal Na sheets were used as the counter electrodes, and glass microfiber filters (GF/D Whatman) were used as separators. A 1 M solution of NaClO<sub>4</sub> in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) was used as an electrolyte. The cells were assembled in an argon atmosphere in a glove box.

## 3. Results and discussion

### 3.1 Characterization of the structure

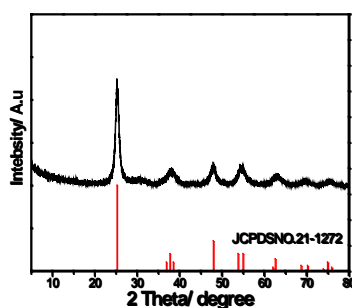


Fig. 1 (a) XRD pattern of the 10 wt.% PPy-coated TiO<sub>2</sub> sample Intensity/a

XRD analyses of the composite is illustrated in Fig. 1(a). All obvious peaks observed at  $2\theta = 25.3^\circ, 37.8^\circ, 48^\circ, 53.8^\circ, 55^\circ, 62.7^\circ, 68.7^\circ,$  and  $70^\circ$  are well match with typical tetragonal anatase TiO<sub>2</sub> (JCPDS NO. 21–1272). No diffraction peaks of impurity are observed in the composite, indicating the amorphous nature of PPy.

### 3.2 Electrochemical properties of the TiO<sub>2</sub>/PPy composite

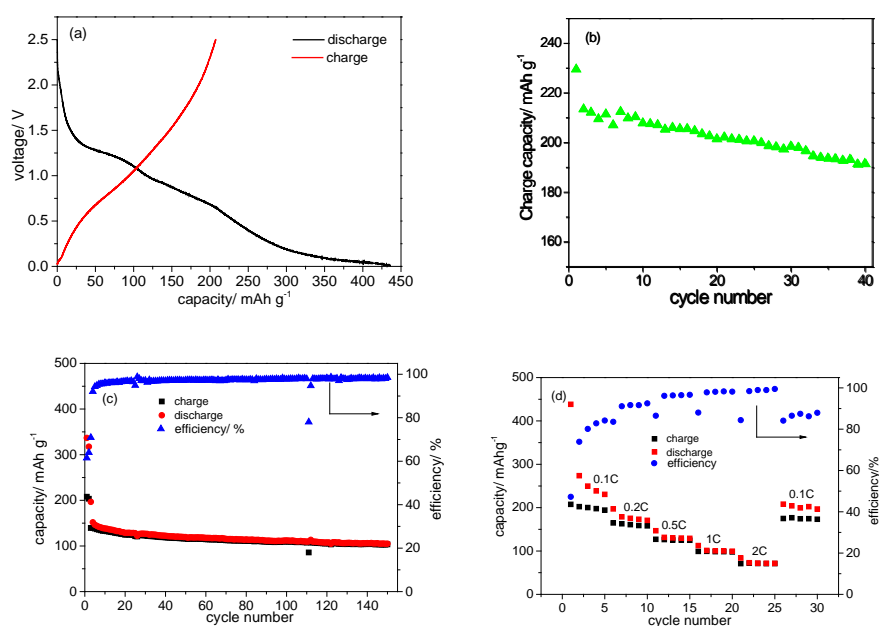


Fig. 2 Electrochemical performances: (a) voltage profiles at 0.1 C; (b) charge capacity at 0.1 C; (c)

long-term cycling stability at 1 C; (d) rates capability.

Charge–discharge curves were measured for the as-prepared electrodes using a current density of  $33.5 \text{ mA g}^{-1}$  (0.1 C) between 2.5 and 0.02 V, the profiles for the first cycle are shown in Fig. 1(a). Long initial discharge curves are observed for the electrode, which attributes to electrolyte decomposition reactions that occurred at approximately 0.8 V in the first discharge process, and a initial charge capacities of  $207 \text{ mAh g}^{-1}$  is obtained. Fig. 2(b) shows the charge capacities at 0.1 C of the  $\text{TiO}_2/\text{PPy}$  composite sample, when cycles to the 40th, the charge capacity remains to  $191.5 \text{ mAh g}^{-1}$ . The long-term cycling stability of the carbon-coated sample at a current density of  $335 \text{ mA g}^{-1}$  (1 C) is presented in Fig. 2(c). The capacity of the electrode slightly drops during the cyclic process and remains to  $103.5 \text{ mAh g}^{-1}$  over 150 cycles. And Fig. 2(d) shows the rates capabilities at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C, a specific capacity of  $80 \text{ mAh g}^{-1}$  obtained even at 2 C.

#### 4. Conclusion

In summary, the anatase  $\text{TiO}_2/\text{PPy}$  composite sample have been successfully prepared, and demonstrated good electrochemical performance when used as anode material for sodium-ion batteries. The sample shows desirable specific capacities at both low and high rates.

#### Acknowledgments

This research was financially supported by the Science and Technology Projects of State Grid Corporation (“Research on key technology of low-strain layered oxides for long-life Na-ion batteries”, No. DG71-16-027).

#### References

- [1] C. Zhao, Q. Wang, Y. Lu, et al., *J. Phys. D-Appl. Phys.* 50, 183001(2017).
- [2] J. Hong, H. Gwon, S.K. Jung, K. Ku, K. Kang, *J. Electrochem. Soc.* 162, A2447–A2467(2015).
- [3] J.W. Choi, D. Aurbach, *Nat. Rev. Mater.* 1, 16013,(2016).
- [4] Y. Lu, C. Zhao, X. Qi, et al., *Adv. Energy Mater.* 1800108 (2018).
- [5] K. Du, J. Zhu, G. Hu, et al., *Energy Environ. Sci.* 9, 2575–2577 (2016).
- [6] J. Zhao, L. Zhao, K. Chihara, S. Okada, J.-i. Yamaki, S. Matsumoto, S. Kuze, K. Nakane, *J. Power Sources* 244, 752–757 (2013).
- [7] W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen, X. Ji, *J. Mater. Chem. A* 1, 10662–10666 (2013).
- [8] D.H. Nam, K.S. Hong, S.J. Lim, H.S. Kwon, *J. Power Sources* 247, 423–427 (2014).  
Y. Park, D. S. Shin, S. H. Woo, N. S. Choi, K. H. Shin, S. M. Oh, K. T. Lee, S. Y. Hong, *Adv. Mater.* 24, 3562–3567 (2012).
- [9] L. Zhao, J. Zhao, Y.S. Hu, H. Li, Z. Zhou, M. Armand, L. Chen, *Adv. Energy Mater.* 2, 962–965 (2012).
- [10] K. T. Kim, G. Ali, K. Y. Chung, C. S. Yoon, H. Yashiro, Y. K. Sun, J. Lu, K. Amine, S. T. Myung, *Nano. lett.* 14, 416–422 (2014).
- [11] Y. Xu, E. M. Lotfabad, H. Wang, B. Farbod, Z. Xu, A. Kohandehghan, D. Mitlin, *Chem. Commun.* 49, 8973–8975 (2013).