## Supercapacitive performance of nanostructural Nitrogen Substituted TiO<sub>2</sub>

G.Q. Zhang,<sup>a,b</sup> Y.Jiang,<sup>a</sup> Z.C. Xu<sup>b</sup> <sup>a</sup>School of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing, 408100, People's Republic of China <sup>b</sup>School of Material Science and Engineering, Nanyang Technological University, Singapore

Supercapacitors are considered to be very attractive energy storage devices, as they have high power density and cycling stability.<sup>1, 2</sup> However, supercapacitors are still not capable of delivering high energy densities comparable to those of lithium ion batteries, and this drawback restricts the use of supercapacitors mainly to high-power applications such as emergency power supplies, hybrid bus, and portable power tools. So, how to significantly increase the energy density of the cell is the biggest challenge facing electrochemical capacitors. The energy density (E) of supercapacitors depends on the cell potential (V) and capacitance (C), based on  $E = 1/2(CV^2)$ .<sup>3</sup> These two parameters are determined mainly by electrodes, and therefore, for a long period of time, a large amount of work has been done at various electrode materials including carbonaceous materials, conducting polymers, transition metal oxides, and their composites.<sup>4</sup>

In this study, nanostructural nitrogen substituted  $TiO_2$  was prepared by annealing the  $TiO_2$  nanotubes in nitrogen atmosphere at 450 °C. The supercpacitive of this performance material was elementary characterized via electrochemical cycle voltammetry (CV). Test electrodes consisted in active material and binder were constructed successfully with traditional coating method on a Nickel mesh. The electrochemical measurements were conducted in a beaker-type electrochemical cell. It was equipped with a prepared nitrogen substituted TiO<sub>2</sub> electrode as working electrode, a platinum foil counter electrode, and a Hg/HgO electrode as reference electrode. CV was carried out between -0.6 and 0.6V (vs. Hg/HgO) in 1M KOH solution. The measurements were performed using CHI760C electrochemical workstation (CH Instruments, Cordova,

TN) at room temperature. Fig.1. (a) shows the XRD pattern of the as-prepared material. The as-prepared nitrogen substituted  $TiO_2$  has typical diffraction peaks of TiN. No other peaks existing show that the prepared material did not contain any impurities.



Fig.1.Typical XRD pattern of the as-prepared nitrogen substituted TiO<sub>2</sub>.

CV is a useful method to evaluate the intrinsic electrochemical properties of active materials. Therefore, CV of nitrogen substituted TiO<sub>2</sub> electrode in the potential

region between -0.6 and 0.6V (vs. Hg/HgO) was employed to evaluate the electrochemical characteristics. Typical I-E curves at different scan rates of the electrode based on nitrogen substituted TiO<sub>2</sub> in 1M KOH solution are shown in Fig. 2. As a comparison to the shape of typical double capacitor (DC), the CV curve of the nitrogen substituted  $TiO_2$  electrode did not present a symmetric and horizontal curve. Two pair of cathodic (E<sub>p,c</sub>) and anodic (E<sub>p,a</sub>) peaks at 0.4, -0.10V and 0.12, 0.45V are clearly observed in Fig. 2, showing a redox reaction takes place during the scan. We speculate that the cathodic and anodic peaks resulted from potassium ion insertion/extraction reaction or from electrochemical adsorption/desorption of potassium ion on the electrode surface. The anodic and cathodic peak potentials as well as the peak current ratio (I<sub>p,a</sub>/I<sub>p,c</sub>) remain constant as the scan rate is increased from 10 to 100mVs\_1, which indicates a reversible redox electrochemical reaction. This electrochemical characteristic of nitrogen substituted TiO<sub>2</sub> is a typical psedocapacitive behavior and can be utilized for supercapacitor application. The performances of asymmetric supercapacitor, constructed with active carbon (AC) and nitrogen substituted TiO2, are underway in our works.



Fig.2. Cycle voltammograms of the nitrogen substituted  $TiO_2$  electrodes at different scan rates.

References:

[1] Hall, P. J.; Mirzaeian, M.; Fletcher, S. I.; Sillars, F. B.; Rennie, A. J. R.; Shitta-Bey, G. O.; Wilson, G.; Cruden, A.; Carter., R. Energy Storage in Electrochemical Capacitors: Designing Functional Materials to Improve Performance. Energy Environ. Sci. 2010, 3, 1238–1251.
[2] Miller, J. R.; Burke, A. F. Electrochemical Capacitors: Challenges and Opportunities for Real-World Applications. Electrochem. Soc. Interface 2008, 17, 53–57.
[3] Liu, C.; Li, F.; Ma, L.-P.; Cheng, H.-M. Advanced

[3] Liu, C.; Li, F.; Ma, L.-P.; Cheng, H.-M., Advanced Materials for Energy Storage. Adv. Mater., 2010, 22, E28–E62.

[4] Zhang, L. L.; Zhao, X. S. Carbon-Based Materials as Supercapacitor Electrodes. Chem. Soc. Rev. 2009, 38, 2520–2531.

[5] Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. Nat. Mater. 2008, 7, 845–854.

[6] Lang, X.; Hirata, A.; Fujita, T.; Chen, M. Nanoporous Metal/Oxide Hybrid Electrodes for Electrochemical Supercapacitors. Nat. Nanotechnol. 2011, 6, 232–236.

[7] Nyholm, L.; Nyström, G.; Mihranyan, A.; Strømme, M.Toward Flexible Polymer and Paper-Based Energy Storage Devices. Adv. Mater. 2011, 23, 3751–3769.