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## Characterization and Electrochemical Properties of Nanostructured Zr-Doped Anatase TiO<sub>2</sub> Tubes Synthesized by Sol–Gel Template Route

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A series of nanostructured Zr-doped anatase TiO<sub>2</sub> tubes with the Zr/Ti molar ratio of 0.01, 0.02, 0.03, and 0.09 were prepared by a sol–gel technology on a carbon fiber template. The electrochemical performance of Zr-doped anatase TiO<sub>2</sub> as anodes for rechargeable lithium batteries was investigated and compared with undoped titania. Tests represented that after 35-fold charge/discharge cycling at C/10 the reversible capacity of Zr-doped titania (Zr/Ti = 0.03) reaches 135 mA h g<sup>-1</sup>, while the capacity of undoped titania (Zr/Ti = 0) yielded only 50 mA h g<sup>-1</sup>. Based on the results of the physicochemical investigation, three reasons of improving electrochemical performance of Zr-doped titania were suggested. According to the scanning electron microscopy and transmission electron microscopy, Zr<sup>4+</sup> doping induces a decrease in nanoparticle size, which facilitates the Li<sup>+</sup> diffusion. The Raman investigations show the more open structure of Zr-doped TiO<sub>2</sub> as compared to undoped titania due to changing of the unit cell parameters, that significantly affects on the reversibility of the insertion/extraction process. The electrochemical impedance spectroscopy results indicate that substitution of Zr<sup>4+</sup> for Ti<sup>4+</sup> into anatase TiO<sub>2</sub> has favorable effects on the conductivity.

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### 1. Introduction

Conventional carbonaceous anode materials for Li-ion batteries (LIBs) are characterized by availability and moderate structural deformation (9%–10%) during cycling. Their practical capacity is quasi-equal to theoretical value of 372 mA h g<sup>-1</sup>. However, the charged anode Li<sub>x</sub>C<sub>6</sub> (C<sub>6</sub> + xLi<sup>+</sup> + xe<sup>-</sup> ↔ Li<sub>x</sub>C<sub>6</sub>, 0 < x < 1) is a highly reducing agent and it can react with electrolyte. Li<sub>x</sub>C<sub>6</sub> has a low potential (<0.3 V vs. Li<sup>+</sup>/Li), hence, at high-rate charge Li-metal can be deposited on the surface of anode. This can lead to Li dendrite formation, making battery unsafe. The safety problem of LIB is especially critical for large, multi-cell modules that are applied in the hybrid and electric vehicle applications, unmanned underwater vehicles, emergency uninterruptible power supplies, energy storage technologies for renewable power systems, etc.<sup>[1–5]</sup>.

Nanostructured titania in the anatase crystallographic modification is a promising anode material for safer LIB designs<sup>[6–8]</sup>. Indeed, the reaction between lithium ions and TiO<sub>2</sub> occurs at electrochemical potentials, which are considerably higher (>1 V vs. Li<sup>+</sup>/Li) than that of lithiated graphite. It is good for practical applications, because it improves the safety, which is associated with the electrolyte solution reactivity and the possibility of the metallic lithium deposition. Moreover anatase TiO<sub>2</sub> has a small volume expansion ratio (<4%) during insertion/extraction of Li<sup>+</sup> ions and good cycle reliability<sup>[9,10]</sup>. The theoretical specific capacity of TiO<sub>2</sub> in the anatase crystallographic modification (TiO<sub>2</sub> + yLi<sup>+</sup> + ye<sup>-</sup> ↔ Li<sub>y</sub>TiO<sub>2</sub>, 0 < y < 1) reaches 335 mA h g<sup>-1</sup>. The major drawbacks for anatase TiO<sub>2</sub> are slow solid state diffusion of Li<sup>+</sup> (10<sup>-15</sup>–10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup>) and poor electrical conductivity (10<sup>-12</sup>–10<sup>-7</sup> S cm<sup>-1</sup>)<sup>[11,12]</sup>. Recently, it has been shown that a number of anatase titania nanostructures, such as nanotubes, nanospheres, nanofibers, nanorods are promising morphologies as anode materials for LIBs<sup>[13–16]</sup>. Despite the variety of synthesized nanostructured TiO<sub>2</sub> materials, an acceptable alternative to a conventional graphite anode has still not been found.

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A literature overview showed that the doping of anatase TiO<sub>2</sub> with aliovalent cations (Ni<sup>2+</sup>, V<sup>5+</sup>, Nb<sup>5+</sup>, Fe<sup>3+</sup>, Mo<sup>6+</sup>, Ti<sup>3+</sup>, etc.) is the promising way to prepare the safe, reliable, highly capacitive and powerful anode material<sup>[17–25]</sup>. Indeed, the incorporation of metallic ions into the titania crystal structure leads to the charge redistribution in the lattice and creates vacancies, that improves material conductivity<sup>[24]</sup>. In addition, doping induces a decrease in particle size, which facilitates lithium diffusion due to the short path and enhances energy density because of better Li<sup>+</sup> accommodation at the boundary of the nanoparticles<sup>[19]</sup>. On the other hand, structural properties of crystal lattice play a significant role for ionic transport through TiO<sub>2</sub> nanostructure<sup>[26]</sup>. At the same time, the ionic radius of most reported dopants are close to one of Ti<sup>4+</sup> that results in insignificant TiO<sub>2</sub> lattice distortion after doping.

In the present work, an inexpensive template sol-gel method for synthesis of nanostructured TiO<sub>2</sub> in the anatase crystallographic modification doped with Zr<sup>4+</sup> cations as a promising anode material for LIB is reported. Note that until now the interest in Zr-doped TiO<sub>2</sub> mainly connects with enhancing the photocatalytic activity of TiO<sub>2</sub> as a result of Zr<sup>4+</sup> doping. The electrochemical behavior of the nanostructured titania doped with Zr<sup>4+</sup> ions as a potential anode material for LIB has not been investigated previously by anybody. Furthermore, as opposed to Ti<sup>4+</sup> substitution by metallic ions with different valences, the doping of TiO<sub>2</sub> with isovalent cations (Hf<sup>4+</sup>, Zr<sup>4+</sup>) in point of view of its electrochemical performance has not yet reported. To optimize the dopant concentration, different Zr/Ti molar ratios of 0.01, 0.02, 0.03, and 0.09 have been investigated.

## 2. Experimental

### 2.1. Synthesis

Zr-doped anatase TiO<sub>2</sub> was synthesized by stepwise slow hydrolysis in aqueous solutions of the inorganic precursors of titanium and zirconium accompanied with deposition on the template surface (pH 7–8)<sup>[27–30]</sup>. To optimize the zirconium concentration into titania crystal lattice, different Zr/Ti molar ratios of 0.01 (ZT-1), 0.02 (ZT-2), 0.03 (ZT-3), and 0.09 (ZT-4) were maintained. In the synthesis process, the following precursors were used: TiCl<sub>4</sub>, ZrOCl<sub>2</sub>, and Busofit T055 carbon fiber manufactured at the Belogorsk Chemical Fibers Plant (Belarus) as a template. The specific surface of the carbon fiber was determined using a Micrometrics ASAP 2020 V3.04 H (USA) spectrometer from isotherms of low-molecular adsorption of nitrogen by the BET method. It was equal to 960 m<sup>2</sup> g<sup>-1</sup>. The porosity distribution was evaluated using the original density functional theory. The major part of the surface (780 m<sup>2</sup> g<sup>-1</sup>) is formed by micropores of a diameter of 2 nm. The template removal was carried out through slow annealing at a temperature of 500 °C under air atmosphere for 2 h (preventing active combustion of the carbon). Since the original carbon fiber contains about 0.01% silicon as impurity, the preliminary autoclave treatment with NH<sub>4</sub>HF<sub>2</sub> at 130 °C was carried out. As a result, the silicon content in the sample decreases by 30 times. For the comparison, undoped anatase TiO<sub>2</sub> (ZT-0) was also synthesized under the same conditions without the presence of ZrOCl<sub>2</sub>.

### 2.2. Characterization

The Zr/Ti molar ratio was determined by energy-dispersive X-ray analysis (EDX) on Shimadzu EDX 700 (Japan) spectrometer. The X-ray tube was operated at 40 kV and 50 mA. The particles morphology and size were observed by scanning electron microscopy (SEM) using Hitachi S5500 (Japan) and transmission electron microscopy (TEM) on Carl Zeiss Libra 200FE (Germany). TEM was operated under an acceleration voltage of 200 kV. The samples for SEM were pre-

pared by spreading the undoped or Zr-doped anatase TiO<sub>2</sub> on the sticky conductive adhesive tape. To investigate the crystal structure of materials the X-ray diffraction (XRD) and Raman spectroscopy were used. In the case of both methods the samples were additionally heat treated at 550–700 °C under air for 30 min. Stoe Stadi P (Germany) diffractometer with CuK<sub>α</sub>-radiation was applied for XRD measurements. Raman studies were conducted on Bruker RFS-100/S (Germany) spectrometer equipped with a Ge detector. As the excitation source an Nd:YAG laser with a wavelength of 1064 nm was applied. CHNS elemental composition of materials was determined using a Eurovector EA3000 (Italy) analyzer. The conductivity was evaluated by electrochemical impedance spectroscopy (EIS) with a two-electrode cell at the room temperature using Solartron 1260 (UK) impedance/gain-phase analyzer. For EIS measurement undoped or Zr-doped anatase TiO<sub>2</sub> was pressured into a pellet with polytetrafluoroethylene at a weight ratio of 80:30. The ZView software v. 3.3b (Scribner Associates Inc.) was applied for data handling of the Nyquist diagrams.

### 2.3. Electrochemical measurements

The working electrode consisted of active material (undoped or Zr-doped anatase TiO<sub>2</sub>), electroconductive additive (Super P carbon black), and binder (polyvinylidene fluoride) at a weight ratio of 80:10:10. The mixture was homogenized in *N*-methylpyrrolidone solvent on IKA C-MAG HS 7 magnetic stirrer (China) for 12 h at a rate of 250 rpm to prepare uniform viscous slurry. The slurry was spread on a copper current collector by the doctor blade technique using MTI AFA-I (USA) instrument. The electrode sheet was dried at 60 °C for 24 h in MTI DZF-6020-110P (USA) vacuum oven. Finally, MTI T06 (USA) tool was applied for manually operated cutting of round disks from electrode sheet. The mass of the active material was equal to approximately 2 mg cm<sup>-2</sup>. The thickness and geometrical area of the working electrode were 70 μm and 1.75 cm<sup>2</sup>, respectively.

The half-cell was assembled in Plas-Labs 890-NB (USA) glove box under dry argon atmosphere. A Swagelok-type MTI STC-19 (USA) two-electrode cell was used to test the electrochemical performances. A lithium metal disk of a thickness of 0.1 mm was used as both counter and reference electrode. One molar solution of LiBF<sub>4</sub> salt in the mix of propylene carbonate and dimethoxyethane at a volume ratio of 3:1 was used as an electrolyte. To prevent short circuit, a polypropylene separator was used. Relaxation of half-cell was performed for at least 5 h to stabilize the open-circuit potential (OCP).

The electrochemical performance was investigated using Solartron 1470E potentiostat/galvanostat (UK). The parameters were measured by the galvanostatic charge/discharge in the potential range from 3 to 1 V at cycling rates of C/10, whereas C is equal to 335 mA g<sup>-1</sup>. In this work, due to the half-cell applying the discharge stands for lithiation process, while the charge for delithiation. The half-cell impedance was studied by EIS at OCP with an AC amplitude of 10 mV over the frequency (*f*) range from 10 mHz up to 1 MHz. All the spectra were recorded at room temperature. The results were analyzed using ZView software v. 3.4c from Scribner Associates Inc. (USA/Canada) to fit the experimental data. The chi-square ( $\chi^2$ ) value did not exceed 10<sup>-3</sup> for the EIS data in the work. The measurements were carried out on at least six half-cells for each test.

## 3. Results and Discussion

### 3.1. Morphology and composition

The SEM micrographs (Fig. 1) for as-synthesized ZT-0, ZT-1, ZT-2, ZT-3, and ZT-4 represent the dependence of Zr-doped anatase TiO<sub>2</sub>

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