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SYNTHESIS, MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES OF TiO₂ MICROSPHERES

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A method for the synthesis of TiO₂ microspheres is presented, and their morphology is characterized. Electrochemical tests in sample Li||TiO₂ cells reveal that the specific capacity delivered upon discharge is lower than the theoretical value due to the presence of the amorphous phase. A decrease in the specific capacity upon current loading is explained by diffusion limitations in microspheres and by hydraulic resistances in the pores to the transfer of charge carriers in the electrolyte.

Keywords: titanium oxide, microspheres, electrochemical properties

INTRODUCTION

Nanostructured titanium dioxide in the form of wires, ribbons, rods, sheets, tubes, spheres is prospective for transformation of the energy of light to electricity, photocatalytic destruction of volatile organic compounds, sensors, electrodes of lithium ion batteries [1, 2]. Samples consisting of spherical TiO₂ particles obtained by various methods based mainly on the hydrolysis of organic derivatives of titanium are extensively probed as photocatalysts and electrode materials in lithium-ion batteries [3–10]. The spherical form of titanium dioxide seems to be the most common since numerous varieties of this substance including nanorods [4] and nanosheets [10] tend to self-organize forming microspheres. Such a tendency is natural from the point of view of the minimum surface energy of a spherical particle [4, 9].

The synthesis of TiO₂ nanoforms often requires hydrothermal conditions [10–13]. In this paper, a novel method for the synthesis of TiO₂ microspheres in «mild» conditions, viz., in solutions of moderate concentration, at medium temperature and ambient pressure is presented, and morphology and electrochemical properties of the material obtained are described. Following our previous work [14] and unlike other approaches [1–13], we use TiCl₄ instead of organic derivatives of titanium as a raw material.

EXPERIMENTAL

The synthesis of microspheres has been carried out as follows. First, a solution of the peroxo complex of Ti(IV) has been obtained from a hydrochloric solution of TiCl₄, hydrogen peroxide, and ammonia. Then, hydrous oxide-peroxide of titanium has been precipitated by adding 5 % solution of NaOH, the reaction mixture has been transferred into a one-liter two-necked flask and heated on an oil bath at 130 °C for 6 h upon stirring. It should be mentioned that an analogous approach using Ti(OC₄O₉)₄ as a raw material [11] leads to TiO₂ nanowires.

Microspheres obtained have been washed with 0.01 M HCl and distilled water, dried at 160 °C for 4 h and annealed in air at 400 °C for 4 h. Just this regime is considered optimal and prevents aggregation of particles, see Ref. [14] and references therein.

The morphology of the material has been studied by means of X-ray diffraction (XRD, DRON-4-07, CuK α -radiation) and scanning electron microscopy (SEM, JEOL JSM6700F). Specific surfaces, pore volumes and pore radii distributions (BJH method) have been found by nitrogen adsorption-desorption isotherms (Quantachrom NOVA 2200e).

Electrochemical investigations have been carried out on an automated testing device in galvanostatic, voltammetric, and combined (constant current – constant voltage, CCCV)

regimes in model coin type cells of the 2016 size. The working electrode has been prepared with the TiO₂ powder, SFG6 graphite, carbonized soot, and poly(vinylidene difluoride) as a binder in the mass ratio of 80:6:6:8; N-methyl pyrrolidone has been used as a solvent. A suspension prepared on a high-speed stirrer and an ultrasonic disperser has been cast on an aluminum current collector by means of a laboratory doctor blade. After the removal of the solvent under an IR radiator the quantity of TiO₂ in a dried remainder was ~3.5 mg/cm². The electrode has been rolled so as to decrease the thickness of the layer from 85 to 35 μm. Model cells have been assembled in a glove box filled with high-purity argon (H₂O content less than 1 ppm). Before assembling, half-cells with working electrodes have been vacuum dried at 120 °C for 24 h. Lithium metal have served as a counter and reference electrode. To divide cathode and anode compartments, two Celgard separators of 12 μm thickness impregnated with 1M solution of LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) taken at 1:1 mass ratio have been used.

RESULTS AND DISCUSSION

XRD data signify that the microspheres have the structure of anatase, cf. JCPDS, Card # 21-1272 (Fig. 1). The calculation of the mean crystallite size according to the Scherrer formula gives $r_{\text{cryst.}} = 5\text{--}6$ nm.

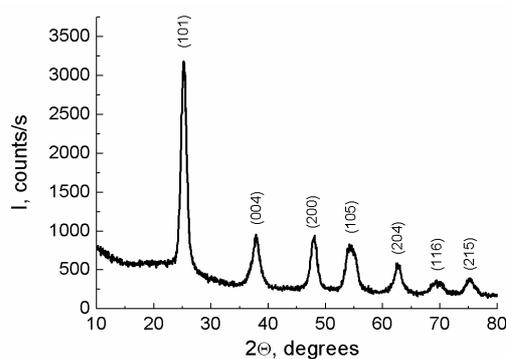


Fig. 1. XRD pattern of TiO₂ microspheres

SEM micrographs reveal that the microsphere diameters vary within the range of $d_{\text{part}} = 380\text{--}600$ nm (Fig. 2). The roughness of the surface fully corresponds to the size of crystallites, hence the microspheres should be considered as agglomerates of nanocrystals.

Surface characteristics and porosity of the TiO₂ microspheres are shown in Fig. 3. Nitrogen adsorption-desorption isotherms can be assigned to

the IV type of the IUPAC classification [15] and correspond to capillary condensation in pores. Using the adsorption branch of capillary condensation, one obtains the differential pore distribution curve according to which the dominating pore radii lie in the range of $r_{\text{pore}} = 1.7\text{--}2.3$ nm. This means that the microspheres are mesoporous. Distances between them are too great to produce any other peak on the pore size distribution in the region of macroporosity.

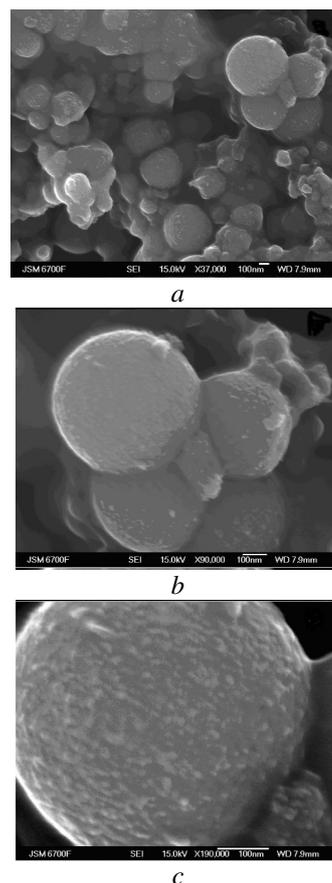


Fig. 2. SEM micrographs of TiO₂ microspheres. Magnification is equal to 37000 (a), 90000 (b) and 190000 (c)

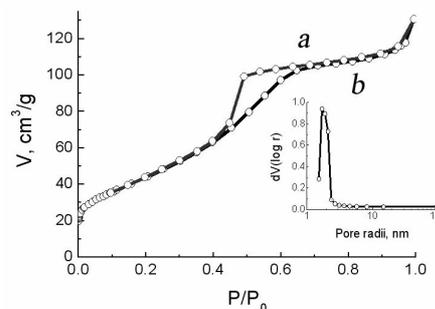


Fig. 3. Nitrogen adsorption-desorption isotherms (a) and pore distribution curves (b) for TiO₂ microspheres

The specific surface of the microspheres is $166 \text{ m}^2 \cdot \text{g}^{-1}$, and the pore volume equals to $0.20 \text{ cm}^3 \cdot \text{g}^{-1}$. Based on this data and using the gapped gapless packing model [16], one can find the particle size $d_{\text{part}} = 9 \text{ nm}$ and pore radius $r_{\text{pore}} = 2.4 \text{ nm}$ in a good agreement with the estimates of d_{cryst} and r_{pore} by the Scherrer and BJH methods, respectively. Furthermore, the model [16] allows for characterizing the packing density in microspheres ρ which appears to be equal to 0.56 being far enough from the limiting value ($\rho = 0.76$), thus signifying good permeability of spheres.

It is known that according to the reaction $\text{TiO}_2 + 0.5\text{Li}^+ + 0.5\text{e}^- = \text{Li}_{0.5}\text{TiO}_2$, 1 mole of TiO_2 of the anatase structure can reversibly insert 0.5 mole of Li^+ [17]. The theoretical capacity delivered in this process equals to $167.7 \text{ mA} \cdot \text{h/g}$. Electrochemical studies have been performed in the potential range of 2.75–1.5 V. Several cycles have been registered up to the complete coincidence of the charge/discharge curves, and the data obtained have been considered stationary. The 1C notation corresponds to the specific current of $167.7 \text{ mA} \cdot \text{g}^{-1}$.

In Fig. 4, the charge/discharge characteristics of model Li|LiTiO_2 cells with cathodes prepared with

the TiO_2 microspheres are displayed. Charging has been performed in the CCCV regime. The 0.2C, 0.5C and 1.0C constant current has been applied up to the cut-off voltage of 1.5 V; additional charging has been carried out by means of exposure at the 1.5 V constant voltage up to the residual current of 0.1C. The galvanostatic discharge has been performed with the 0.2C, 0.5C or 1.0C current to the cut-off voltage of 2.75 V.

Fig. 4 b signifies that upon growing the current the length of the galvanostatic region decreases; at the same time, the duration of the additional charging increases. Upon five times increasing the current density (from 0.2C to 1.0C) the charge capacity decreases insignificantly, from 139 to 130 $\text{mA} \cdot \text{h/g}$, whereas the discharge capacities remain equal to the charge capacities and signify that the coulombic efficiency is close to 100%. However, the charge-discharge capacity upon cycling with the smallest currents (0.2C) appears smaller than the theoretical one by 27 $\text{mA} \cdot \text{h/g}$. For further explanation of this phenomenon voltammetric studies of a set of model cells have been carried out.

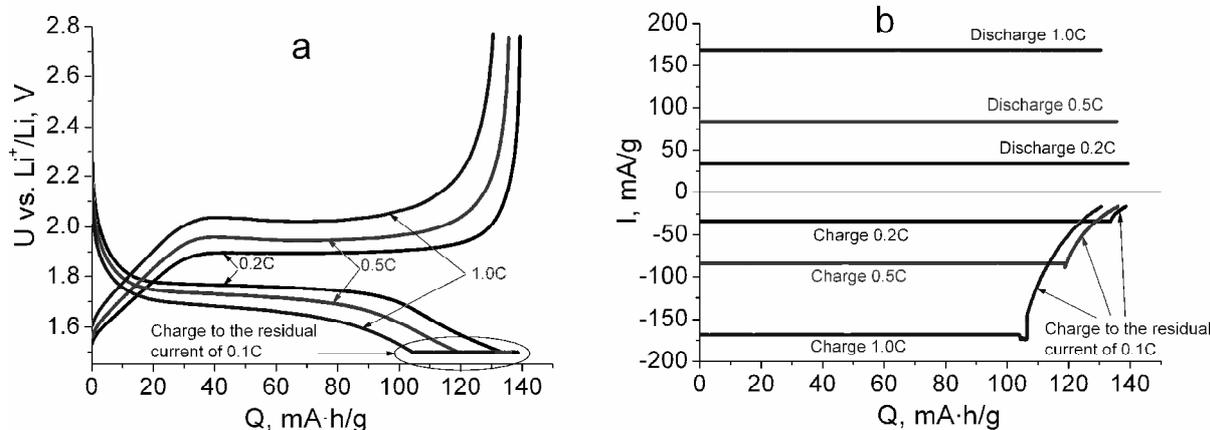


Fig. 4. Stationary charge-discharge curves for Li|LiTiO_2 cells in CCCV regime at various charge currents and additional charge at 0.1 C and various discharge currents in $U=f(Q)$ (a) and $I=f(Q)$ (b) coordinates

In Fig. 5, voltammetric curves obtained at the scanning speed of 0.1 mV/s are shown. These are registered in the range from 2.6 V to various cut-off voltages (1.65, 1.6, 1.5, 1.4, 1.3, 1.2, and 1.0 V). As in Ref. [14], except the main cathode and anode processes occurring at 1.7 and 2.0 V, respectively, washed-up peaks of insertion and desinsertion of lithium to and from amorphous TiO_2 are visible as noticed in Fig. 5 by arrows. This

implies incomplete crystallization of the sample in the course of its annealing. Based on the ratio of experimental and theoretical specific capacities, one can estimate the percentage of amorphous TiO_2 in the sample as 16%.

Inset demonstrates that should the charging process be performed up to the end of lithium insertion into the amorphous phase of TiO_2 (the cut-off potential of $\sim 1.25 \text{ V}$), the discharge

capacity close to the theoretical value would be obtained upon discharging. It is known, however, that lithium insertion into TiO₂-based electrodes at voltages lower than 1.5 V causes the degradation of the anatase structure upon cycling. Such degradation is apparent as a right-hand shift of anodic peaks of the main intercalation process, which reflects the growth of the internal resistance of the electrode and the capacity loss from cycle to cycle.

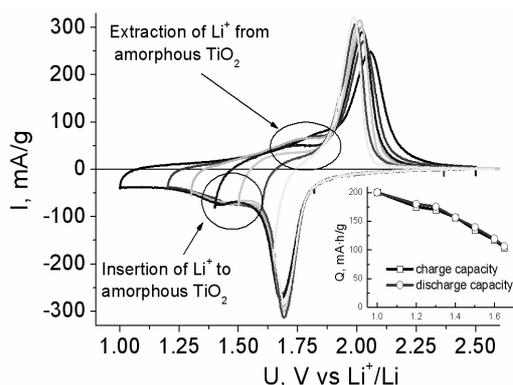


Fig. 5. Voltammetric curves for Li|TiO₂ cells at various charge cut-off voltages. The scanning speed is 0.1 mV/s. Inset shows the dependence of the specific capacity of TiO₂ on the charging cut-off voltage

In order to prevent the degradation of the electrode, further electrochemical tests have been performed within the 2.75–1.5 V voltage range. In Fig. 6, stationary discharge curves are collected as obtained in the galvanostatic mode at the current densities of 1C, 2C, 4C, 6C, 8C, and 10C. Charging has been carried out in the CCCV regime with the 1C charge and 0.1C surcharge currents; charge curves are omitted in Fig. 6. One can see that if the current density grows from 1C to 10C, the discharge capacity decreases from 122 to 39 mA·h/g. Upon growing the current density significant polarization is showing up, in particular, since the 6C currents a horizontal part of the discharge curve disappears. Such a decrease in the capacity and a growth of polarization upon current loading indicates that the electrical resistance of the TiO₂ microspheres is quite high.

The dependence of capacity retention on the current rate is compared in Fig. 7 with the results of our previous studies [14] of nanosized (15–20 nm) non-aggregated TiO₂. Examining these data one can conclude that the non-aggregated samples have much better electrochemical properties than the microspheres.

Insufficient values of the capacity retention of the material studied upon current loading may be caused by several reasons. Although the microspheres of titanium dioxide, as follows from XRD and SEM data, are formed by nanocrystals,

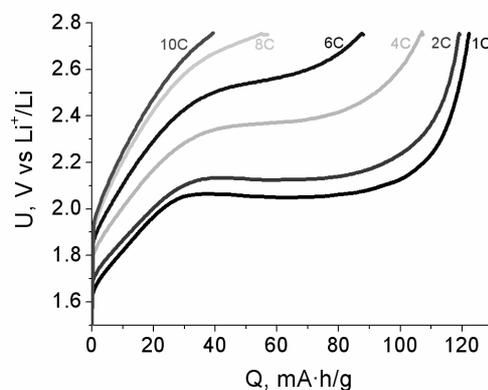


Fig. 6. Stationary discharge curves for Li|TiO₂ cells at various current densities

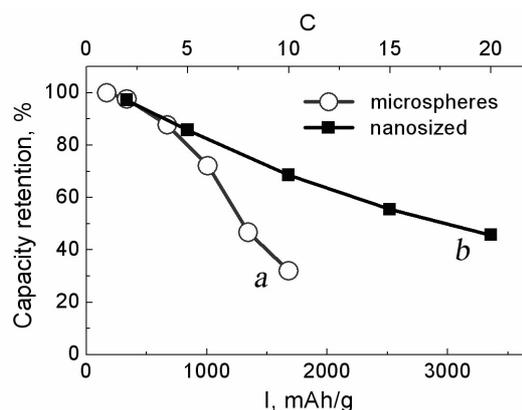


Fig. 7. Dependence of the capacity retention on the current rate for microspheres (a) and nanocrystalline non-aggregated TiO₂ (b)

the size of the spheres themselves, as well as the diffusion path of the lithium cations from the surface of the sphere to its center are of the micron size. This may influence the properties of the electrode due to limitations caused by the Li⁺ diffusion speed in the anatase structure, which is not so high [18, 19]. Another, even more sensible explanation may be based on the insufficient permeability of the pore structure of the microspheres by the electrolyte. A rough estimate based on the density of solvents (1.321 cm³/g for EC and 1.063 cm³/g for DMC [20]) gives their cross-sections as ca. 0.5 nm. This means that the size of charge carriers (solvated lithium cations

and, especially, anions) is commensurable with the pore diameter determined in porosity studies (3.4–4.6 nm, see above), and great hydraulic resistances should be overcome so as to ensure charge transfer in existing channels. From this point of view, smaller TiO₂ spheres having greater pore radii should be more advantageous for electrochemical applications.

CONCLUSION

A method for the synthesis of TiO₂ microspheres under «mild» conditions, viz., in solutions of moderate concentration, at medium temperature and ambient pressure is presented. The particles obtained are of 380–600 nm diameter and

consist of anatase crystallites of 5–6 nm size. Their specific surface area and pore volume are equal to 166 m²·g⁻¹ and 0.20 cm³·g⁻¹, respectively, and pore diameters are of 3.4–4.6 nm. Electrochemical tests in sample Li||TiO₂ cells reveal that the specific capacity delivered upon discharge is lower than the theoretical value due to the presence of amorphous titanium oxide. A decrease in the specific capacity upon current loading may be caused by great hydraulic resistances in the pores to the transfer of charge carriers in the electrolyte. This means that smaller TiO₂ spheres having greater pore radii should be more advantageous for electrochemical applications.

Синтез, морфология и электрохимические свойства микросфер TiO₂

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Представлен метод синтеза микросфер TiO₂ и охарактеризована их морфология. Электрохимические испытания элементов Li||TiO₂ свидетельствуют о том, что удельная емкость при их разряде оказывается меньшей, чем теоретическая, в связи с присутствием аморфной фазы. Уменьшение удельной емкости при токовой нагрузке объяснено диффузионными ограничениями в микросферах и гидравлическим сопротивлением переносу носителей заряда в порах.

Ключевые слова: оксид титана, микросферы, электрохимические свойства

Синтез, морфологія та електрохімічні властивості микросфер TiO₂

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Представлено метод синтезу микросфер TiO₂ та охарактеризовано їх морфологію. Електрохімічні випробування елементів Li||TiO₂ свідчать про те, що питома ємність при їх розрядженні виявляється меншою, ніж теоретична, в зв'язку з присутністю аморфної фази. Зменшення питомої ємності при навантаженні струмом пояснено дифузійними обмеженнями у микросферах і гідравлічним опором перенесенню носіїв струму в порах.

Ключові слова: оксид титану, микросфери, електрохімічні властивості

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