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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Effect of Ultrasonic Treatment on Electrochemical and Structural Parameters of a MnO_2 Cathode

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Abstract—Original technique for fabrication of nanostructured manganese dioxide cathodes for primary lithium power cells was developed. The technique includes a preliminary ultrasonic treatment of the active paste.

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Lithium power cells (LPCs) are widely used in various fields of industry: radioelectronic devices, communication equipment, warning systems, measureing instruments, and power sources for aeronautical, marine, and space technology [1]. Owing to their high energy parameters, present-day lithium primary systems are beyond any competition with other electrochemical systems as power sources for medical implants, nonvolatile computer memory units, and flash and smart cards. In this case, the reliability, service life, and mass-and-size parameters of these latter are, as a rule, determined by the fabrication quality of a power cell and the amount of chemical power inherent in its design, rather than by the perfection of electronic components. It is also noteworthy that LPCs are among few power cells that possess a huge potential for further improvement of their characteristics and optimization of their manufacture technology. Implementation of this potential can give rise to LPCs of new generation and will considerably expand their application areas.

Today, the lithium–manganese dioxide (Li–MnO_2) system dominates on the world market of primary LPCs. This is so because MnO_2 is inexpensive, technologically convenient, and has a comparatively high diffusion coefficient of lithium ions in the crystal structure of the oxide matrix, which has a direct favorable effect on its electrochemical characteristics [2]. In LPCs, manganese dioxide is reduced by the solid-phase mechanism to give variable-composition phases. In the course of reduction of the oxide electrode occurs topochemical intercalation of lithium ions into the crystal lattice of the cathode material, with the extent and rate of this process determined by parameters of the crystal lattice of MnO_2.

The sweeping development of nanotechnologies forces a fresh look both at technological principles of fabrication of power cell components and at mechanisms of their operation [3]. It is known that the electrochemical characteristics of MnO_2 cathodes are strongly affected by methods used to form the cathode material and by techniques of its synthesis. Transition from bulk crystals to nanosize particles is accompanied by a sharp change in the fraction of defective structures per unit mass and disturbs the equilibrium and symmetry of the electron density distribution. Presumably, use of the nanosize state of the MnO_2 cathode paste can improve electrochemical characteristics of LPCs both by making larger the active reaction zone and by raising the carrier diffusion rate [4]. However, there is no escape, when nanostructuring the electrode, from taking into account one of the most currently pressing obstacles that hinder the development of nanotechnologies in the field of electrochemical power engineering and molecular electronics. This is the problem of stabilization of nanosystems, which is due to the nonequilibrium way in which they are composed.

In this study, it is suggested to make more uniform and stable the structure of a cathode based on a

nanosize active material by using an ultrasonic treatment.

EXPERIMENTAL

Solid-phase cathodes were fabricated by the original method suggested in the study. A nanodispersed MnO_2 powder (manufactured by Tekhnoelektrokhim Research Center, National Academy of Sciences of Ukraine) was mixed in a 85 : 10 ratio with an electrically conducting additive composed of PR-1 pyrographite (Degussa AG) and then impregnated with a 5 wt % solution of a solid-polymer electrolyte (SPE) in dimethylacetamide. The solid-polymer electrolyte is composed of lithium perchlorate (manufactured by Ekotekh Private Company) and polysulfone of PS-1300 brand (Institute of Plastics Open Joint-Stock Company) at a polysulfone : lithium perchlorate mass ratio of 100 : 20 [5]. The solution volume was chosen so as to attach the MnO_2 : PR-1 : SPE ratio of 85 : 10 : 5. Then, the resulting mixture was dried and compacted onto the contact part of the cathode current lead, in one case, and was preliminarily treated with ultrasound on a UZ-1 installation developed at Kriamid Limited-Liability Company, in the other. The compaction was carried out under a pressure of 10 MPa. The finished electrodes were dried in a drying box at a temperature of 100°C in a vacuum for 2 h. The solvent removal was checked by gas chromatography on a Carlo Erba Fractovap series 4160 chromatograph with a 30 m × 0.32 mm × 0.25 μm capillary column and a flame-ionization detector. Further, prior to electrochemical testing, the electrodes were kept in a 6BP1-OS box in dried argon for 24 h. The cathodes prepared using the method described contained no liquid components and had the form of a solid-phase nanocluster system in which the solid-polymer electrolyte composed of a lithium salt dissolved in the polysulfone structure serves as a binder and electrically conducting substance.

A structural analysis of the cathodes was made with a JEOL JGM-7401F field-emission scanning electron microscope. The samples to be analyzed were glued to a Petri dish with a carbon glue and placed in the microscope. The electron microanalysis was supplemented with an X-ray microanalysis. An X-ray spectrum was recorded with an INCA energy-dispersive analyzer with a resolution of 129 eV. The measured intensities were adjusted by taking into account corrections for the atomic number, absorption of the X-ray radiation in a sample, and fluorescence. The composition of the electrode surface was analyzed at eight different points. The dispersity of the components of the solid-phase cathode was monitored by transmission electron microscopy on a JEM-100S microscope.

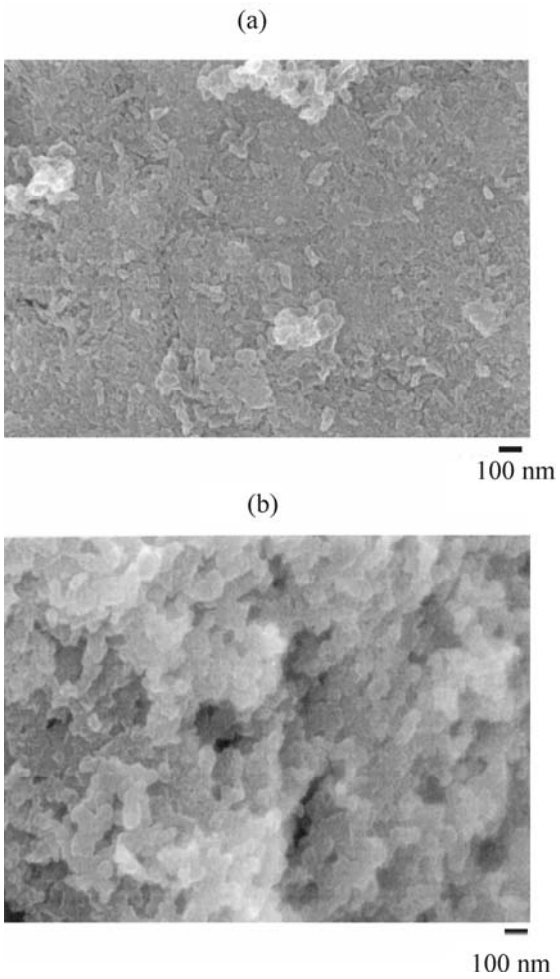

Fig. 1. Surface micrographs of manganese dioxide cathodes (magnification 50000). Agitation: (a) mechanical and (b) ultrasonic.

The electrochemical tests of the electrodes were carried out in a three-electrode poly(propylene) cell at a temperature of 298 K. A cathode under study was placed on the cell bottom and covered with a polymeric electrolyte and lithium foil, with the electrode unit spring-loaded. The working area, active mass, and thickness of the electrodes were 1 cm^2, 0.005 g, and ~0.01 mm, respectively. A Li/Li^+ electrode served as reference. Current was passed through stainless steel rods tightly pressed against the current lead tabs and the body of the reference electrode. The measurements were made with a Solartron SI 1287

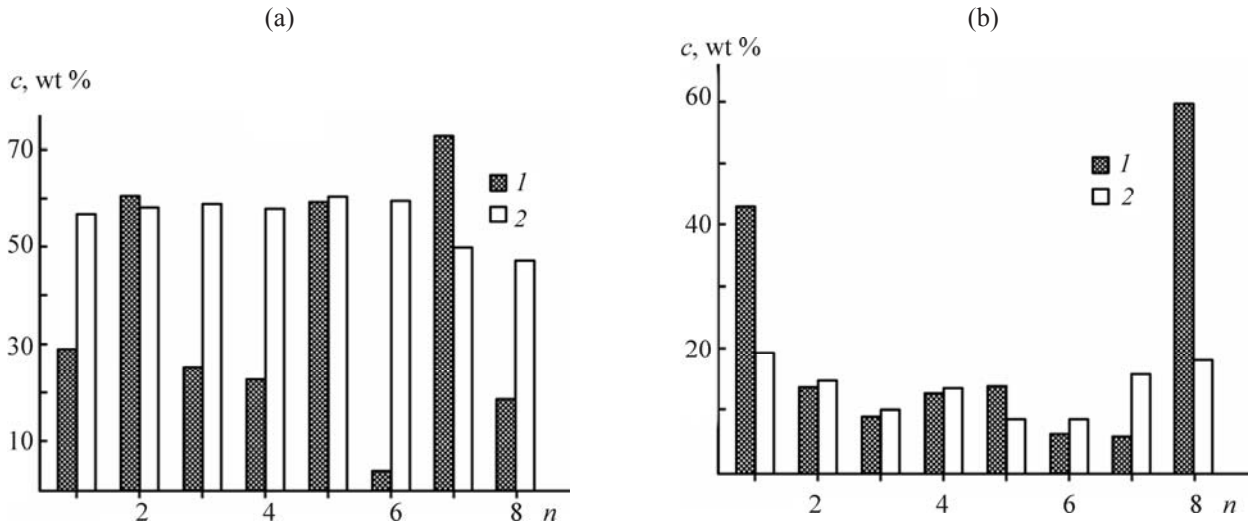

Fig. 2. X-ray microanalysis data on the distribution of (a) manganese and (b) carbon over the electrode surface. (c) Content of an element in the spectrum and (*n*) number of a spectrum. Agitation: (*1*) mechanical and (*2*) ultrasonic.

Electrochemical interface potentiostat in the known three-electrode configuration.

The results of electron-microscopic and X-ray studies are represented by electron micrographs in Fig. 1 and data on the distribution of manganese and carbon in the structure of cathodes (Fig. 2) treated and untreated with ultrasound. A sharp contrast between the states of the surface of the samples and their crystal structure was observed. The surface of manganese dioxide electrodes prepared by the standard technique with mechanical mixing of the active paste components does not exhibit high uniformity over its entire area, but has no block structures or fractures. Attention should also be paid to the presence of a small amount of similar aggregates of nanoparticles with a grain size of about 100 nm. However, the cathode structure obtained cannot be named homogenized: the strong compositional nonuniformity is apparent. An analysis of the element spectra obtained at different points of the cathodes demonstrated that, without an ultrasonic treatment, the maximum deviation of the contents of manganese and carbon from the average over the electrode reaches values unacceptable for providing an effective electronic-ionic transport in the electrode: 98 and 190%, respectively.

Undoubtedly, electrode samples with an ultrasonically treated active paste have a nanostructured nature with nanoparticle sizes of several tens of nanometers. These samples show no aggregation on the micrometer level, the paste is apparently homogenized and constitutes an integrally bound nanosize system. The maximum deviation of the manganese and carbon content from average values does not exceed 8 and 40%, i.e., is substantially smaller than that for the preceding electrodes. In addition, micrographs of ultrasound-treated manganese dioxide cathodes reproduce the effect of bulk nanostructuring manifested as loosening of the compacted mass deeper into the samples, with the resulting sharp increase in their active surface area.

As expected, the best electrochemical parameters in the tests were observed for ultrasound-nanostructured cathodes because of the high uniformity of their structure. The specific capacity of positive electrodes in prototype primary LPCs discharged with a current density of 0.015 mA cm^{-2} was 180 mA h g^{-1} after mechanical agitation and increased to 280 mA h g^{-1} upon an ultrasonic treatment. On raising the discharge current density to 0.25 mA cm^{-2}, the specific capacity of the electrodes somewhat decreased to become 90 mA h g^{-1} upon mechanical agitation and 155 mA h g^{-1} upon agitation with ultrasound.

The energy parameters of the nanodispersed cathodes homogenized and stabilized with ultrasound exceed by approximately 20% those of the widely used macrodispersed cathodes (with MnO_2 particle size of 0.7–2 μm) in the same range of discharge current densities [6]. This energy gain must be primarily due to a transition from bulk crystals to nanosize particles, which is accompanied, as a result of the surface

relaxation effect, by changes in interatomic distances and lattice constants. This disturbs the equilibrium and symmetry in the electron density distribution and leads to changes in the equilibrium interatomic distances, shear deformations, and rounding of vertices and edges of nanocrystals.

The described structural transformation decrease the activation energy of diffusion of the lithium cation, because the process starts to occur via vacancies and interstices, rather than via surface defects as in the case of bulk crystals. In addition, the decrease in the size of active particles in a generally stable system leads to an increase in their integral surface area in the electrode.

It should be mentioned that, without an ultrasonic treatment, the parameters of electrodes based on nanodispersed components are 15% lower than parameters of macrodispersed cathodes and 35% lower than those of ultrasound-stabilized nanodispersed cathodes. The last circumstance is due to a change in the ratio between the gravitational and surface forces in favor of the latter, which occurs as the dispersity of electrode materials increases in the absence of a stabilizing ultrasonic treatment. This disturbs the stability and uniformity of the nanosystem via aggregation of fine particles and formation of a very coarse and nonuniform secondary structure. Such a structure is even coarser and less uniform than a system formed by micrometer surface-inactive particles.

CONCLUSIONS

The energy parameters of nanostructured manganese dioxide cathodes for primary lithium power cells, fabricated using the suggested technology, exceed by 20% the corresponding characteristics of domestic and foreign-made samples.

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