Nanowhiskers for lithium battery anode

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Abstract. The paper presents the prospect of using copper oxide nanowhiskers as an anode material in a lithium-ion battery. Technology for the synthesis of copper oxide nanowhiskers by electrochemical deposition and thermal oxidation was developed. The stress state of CuO nanowhiskers under lithiation/delithiation was considered. A test was carried out of lithium batteries with anodes containing copper oxide nanowhiskers with various binders.

1. Introduction

The key trend of our time is the transition to alternative energy sources. Some countries use wind, sun, and water energy as a resource. An important problem is the storage of electricity; this requires high-capacity batteries that are stable at high and low operating temperatures, as well as capable of withstanding a large number of charge-discharge cycles. The lithium-ion battery is the most popular and efficient energy storage device, but it has a limited lifespan and does not withstand critical temperatures. In addition to the usual usage of lithium-ion batteries in portable devices, they are also used in electric vehicles and as energy storage devices in the smart home, which will solve environmental and economic problems. Therefore, research is being carried out on new materials for electrodes. The use of nanowhiskers as part of the anode in a lithium battery is promising since this can lead to an increase in the capacitive characteristics of the battery due to the large surface of the active mass of the substance, as well as to an increase in recharge cycles due to the mechanical properties of the material; also, nanowhiskers provide a short path for the diffusion of lithium ions. During the passage of the charge-discharge cycle, such materials do not experience a change in volume and the electrolyte does not recover on their surface with the formation of passive films. For research, we have chosen copper oxide due to its low cost, ease of production, strength, electrical properties, and high theoretical capacity [1].

A nanowhisker is a one-dimensional nanomaterial, the length of which significantly exceeds the other dimensions, which do not exceed several tens of nanometer. Nanowhiskers are highly durable, flexible, and resistant to aggressive environments. In this work, the use of copper oxide nanowhiskers as a material for lithium-ion batteries was considered. Batteries with high-performance characteristics will solve environmental problems: reduce the use of natural resources for energy generation, reduce environmental pollution [2].

The main components of a lithium-ion battery are the cathode, anode, electrolyte, separator, and current collector. Typically, carbonaceous materials such as graphite are used as the base of the anode materials. However, graphite anodes are prone to various types of degradation, such as structural damage to the surface during cycling [3], a decrease in capacity [4, 5], and delamination due to joint intercalation of solvents [6]. To solve these problems, research is being carried out on composite
materials (for example, nanowhiskers and carbon) to improve the mechanical and electrical properties of graphite anodes.

There are several methods for the synthesis of CuO nanowhiskers, they include “wet” chemical [7], electrochemical and hydrothermal methods [8], as well as methods of thermal and plasma oxidation [9-12]. Thermal oxidation is one of the most widely used methods for producing CuO nanowhiskers due to its simplicity, mass production, and relatively low cost.

2. Experimental

In this work, for the synthesis of copper oxide nanowhiskers, the method of electrochemical deposition from an aqueous solution followed by thermal oxidation was chosen. The ratio of the compounds of electrolyte, the deposition time, and the annealing temperature noticeably affect the size and structure of the synthesized CuO nanoparticles.

To prepare the electrolyte, distilled water and 250 g/l of CuSO₄·5H₂O was used with constant stirring and heating. To increase the electrical conductivity of the electrolyte, as well as dissolve the salt, 90 g/l of H₂SO₄ was added to the electrolyte. All reagents were used with an analytical grade at least.

The steel mesh (type AISI 304) was used as the cathode. The mesh is preliminarily cleaned in distilled water, then in an ultrasonic bath, after which it is dried and placed in an electrolyte solution opposite the anode - a copper plate, between them there is a copper reference electrode. The electrochemical cell was connected to the potentiostat (Ellins P45) and then an overvoltage of 100 mV was applied, the deposition time was 40 minutes. After the electrodeposition process, the mesh with copper coating was washed in distilled water and dried. The samples in the form of mesh with copper coating are placed in a muffle furnace for 4 hours at a temperature of 400°C. Thermal oxidation of copper leads to the growth of CuO nanowhiskers.

3. Results and discussion

Scanning electron microscope investigation shows that the deposited copper particles have pentagonal symmetry (figure 1), which means they contain disclination-type defects, the average particle size is 10 μm.

Thermal oxidation of copper leads to the growth of CuO nanowhiskers. Figure 1b shows that the particles have lost their faceting and have a spherical shape; nanowhiskers with a length of up to 5 μm and up to 100 nm in diameter have formed on their surface.

Presumably, the formation of CuO nanowhiskers occurs as a result of a reaction at the CuO / Cu₂O interface, which creates compressive stress in the CuO layer and leads to forced diffusion of copper ions outward along the CuO grain boundaries [13].

In [14] was described and tested batteries with anodes based on copper oxide nanowhiskers with various binders as sodium carboxymethylcellulose (CMC) and polyvinylidene fluoride (PVDF). After 100 charging-discharging cycles, the electrode containing CMC maintains a stable capacity of at least 200 mAh/g, and in the electrode with PVDF, the capacity drops to 60 mAh/g. Presumably, the CMC binder has better adhesion to the surface of Cu₂O/CuO nanowhiskers, adjusting to volumetric expansion during cycling.

Let us consider in more detail the chemical processes taking place on the electrodes. As lithium ions flow into the CuO nanowhiskers, the concentration distribution is continuous, so the transformation strain also varies continuously with position. The central core of the nanowhisker has tension during lithiation.

Lithium ions diffuse in or out of the electrode during charging or discharging. For dilute solutes within the nanowhiskers, the lithium-ion concentration is governed by the diffusion equation:

$$\frac{\partial C}{\partial t} = D \nabla^2 C = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \right)$$

(1)
Figure 1. Micrographs of copper particles deposited on a steel mesh (a) and nanowiskers grew on particles after annealing (b), (c).

where $C$ is the molar concentration, $D$ is the diffusion coefficient of the lithium-ion.

It should be noted there are two possible ways of operating a battery: potentiostatic or galvanostatic regimes: In the first case the electrode is surrounded by a constant lithium-ion concentration. At galvanostatic regime, the current, thus the ionic flux at the surface of the electrode, is a constant. In our studies [14] the battery is charged/discharged with a constant current density $J$. Hence, the ionic flux at the surface of the electrode is constant. We assume the initial lithium-ion concentration inside the electrode is $C_0$ and the concentration at the center is finite. The appropriate boundary and initial conditions to solve the diffusion equation can be written as

\[
\begin{cases}
C(r,0) = C_0 \\
D \frac{dC(r,t)}{dr} \bigg|_{r=R} = \frac{J}{F}
\end{cases}
\]  

where $F$ is Faraday’s constant.

The diffusion equation (1) can be non-dimensionalized. Concentration-distance curves in non-dimensionalized forms, plotted from the numerical solution of equation (1) are shown in figure 2.

Figure 2. Concentration distribution of lithium ions in the CuO nanowiskers for constant flux $\frac{J}{F}$ at the surface. The numbers on curves are the value of $\frac{D\tau}{R^2}$. 
Diffusion-induced stresses can cause the nucleation and growth of cracks, leading to mechanical degradation of the active electrode materials.

The stress state of nanowhiskers during lithiation/delithiation can be written using the analogy between thermal stresses [15]:

\[
\begin{align*}
\epsilon_r - \frac{\Omega}{3} C &= \frac{1}{E} \left( \sigma_r - \nu(\sigma_\theta + \sigma_z) \right) \\
\epsilon_\theta - \frac{\Omega}{3} C &= \frac{1}{E} \left( \sigma_\theta - \nu(\sigma_r + \sigma_z) \right)
\end{align*}
\]  

(3)

where \(E\) is Young's modulus, \(C\) is the molar concentration, and \(\Omega\) is the partial molar volume of the lithium ion, \(\sigma_r\), \(\sigma_\theta\), \(\sigma_z\) are radial, tangential, axial stresses, \(\epsilon_r\) and \(\epsilon_\theta\) are radial and tangential strains.

In our case, nanowhiskers electrodes were long whiskers grown on a substrate and thus one of the ends of the whiskers is always attached to the substrate. Such long nanowhiskers with a fixed end are under the generalized plane strain condition.

Atomic diffusion in solids is a much slower process than elastic deformation; mechanical equilibrium is established much faster than that of diffusion. So, mechanical equilibrium one can be treated as a static equilibrium problem:

\[
\frac{d\sigma_r}{dr} + \frac{\sigma_r + \sigma_\theta}{r} = 0
\]

(4)

For infinitesimally small deformation, the radial and tangential strain of cylindrical particles can be related to radial displacement. There is no displacement at the center, furthermore, the radial stress has to satisfy mechanical equilibrium at the surface. Using these conditions, the stress components in dimensionless form were plotted and shown in figure 3.

The radial stress at the center initially increases, reaches a maximum 0.35, and then remains constant until the electrode reaches the saturation concentration. The radial stress is always tensile while tangential stress is tensile at the center and compressive at the surface. The magnitude of tangential stress is the same at the center of the whisker. The tangential stress maximum occurs at the surface at time zero. It should be noted the equation system is symmetric concerning lithiation and delithiation, and mirror opposite conclusions (i.e., replacing tensile stress by compressive stress).
Figure 3. Radial (a) and tangential (b) stresses inside whisker at different radial locations and times of lithiation/delithiation.

4. Conclusions
Copper (II) oxide nanowhiskers were synthesized by the method of electrochemical deposition of copper with subsequent thermal oxidation. These materials are used as active components of anodes of lithium-ion batteries.

The analysis of stress, strain, and strain energy in nanowhiskers electrodes, can be used to optimize the nanowhiskers size depending upon the properties to maximize the battery life.

Such CuO nanowhiskers can accommodate large strain without degradation in size. The previous experiment [14] also confirms the better behavior of nanowhiskers electrodes than bulk electrodes.

Acknowledgments
The authors are thankful to the Russian Science Foundation (Grant No. 19-72-10112) for support of this work.

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