

Lithium Polymer Battery with PVDF-based Electrolyte Doped with Copper Oxide Nanoparticles: Manufacturing Technology and Properties

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Abstract. An overview of electrolyte materials for lithium polymer batteries and the prospects for adding metal oxide nanoparticles to the electrolyte are presented in this paper. A procedure for the synthesis of a gel polymer electrolyte based on polyvinylidene fluoride doped with copper oxide nanoparticles is also described, and the ionic conductivity is measured by the electrochemical impedance spectroscopy. Cells with the synthesized electrolyte and LiFePO₄ electrode have been assembled and cycled at different currents. Stable cycling and high capacity have been exhibited by the cell with electrolyte doped with copper oxide nanoparticle (wt. 0.1%).

1. INTRODUCTION

Currently, batteries are widely used to store electrical energy and power various electrical devices and equipment [1]. In addition, hybrid energy such as solar and wind power are being actively developed, but since the sources of solar and wind energy are unstable, batteries are needed to store the resulting energy. Research in this area is important because it can solve the problem of resources scarcity and environmental pollution [2]. The search for new materials for the battery makes it possible to improve its consumer qualities: to stabilize the electrical characteristics, increase the service life, expand the operating range, increase the power density, increase the charge rate, and reduce the cost.

Lithium-ion battery is the most commonly used type of energy storage unit in modern electronic devices. Such batteries consist of two electrodes: an anode and a cathode, the space between which is filled with electrolyte; an electric current occurs when

lithium ions pass from one electrode to another through the electrolyte [3]. Lithium (Li) has a high theoretical specific capacity (3860 mAh/g), a low redox potential (3.040 V vs. a standard hydrogen electrode), and a low density (0.534 g/cm³) [4]. One of the main problems with lithium batteries is the risk of explosion caused by an internal short circuit that occurs when lithium dendrites grow uncontrollably [2].

Basically, the electrolytes used in lithium batteries can be divided into liquid, inorganic ceramic, and organic polymer electrolytes. Liquid electrolytes are usually obtained by dissolving a lithium salt in an organic solvent; they have high ionic conductivity (about 1–10 mS/cm) and good electrode wettability. Ionic conductivity determines how mobile (and available) the ions are for ongoing electrochemical reactions, which partly determines the power of the cell [5]. Commonly used organic solvents for electrolytes include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC). So far, there is no

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solvent that has both high dielectric constant (to dissolve the salt) and low viscosity (to facilitate ion transport) and is stable on the electrodes, so a mixture of solvents is most often used, but they are usually flammable [5]. In Ref. [6] it was shown that EC promotes the formation and growth of lithium whiskers and dendrites, which can pierce the separator and cause a battery short circuit, leading to a fire.

Polymer electrolytes (PE) perform well with lithium batteries and have shown a high ability to inhibit dendritic growth; in addition, such an electrolyte is itself a separator, which simplifies the manufacturing technology [7].

The polarity of the polymer also greatly affects the interaction between ions, for example, polyvinylidene fluoride (PVDF) has a high dielectric constant of 8.3, which contributes to better dissociation of lithium. While the dielectric constant of polyethylene oxide (PEO), which is widely used as a solid electrolyte, is only 5. PVDF has ideal properties as an electrolyte base: mechanical strength, wide voltage window, thermal stability, incombustibility, operating temperature up to 150 °C, decomposition temperature up to 400 °C, high electrochemical stability, no side reactions with other materials [8].

Gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs) must have two main qualities: good compatibility with electrodes to ensure high ionic conductivity and chemical stability during charge/discharge. GPEs have weaker mechanical properties but higher ionic conductivity, while TPEs are mechanically stronger but have low ionic conductivity (less than 0.01 mS/cm). Thus, PE with high ionic conductivity and good mechanical properties is a promising development [9].

The combination of polymer with inorganic materials allows for improved performance as well as improved ionic conductivity. The surface of the metal oxide can act as an additional coordination center for Li⁺ ions, which contributes to a better cation transport [10].

Common inorganic fillers are inert materials (for example, TiO₂, SiO₂, Al₂O₃, etc., which are not conductive fillers) and active ionic conductors (for example, LATP (Li_{1+x}Al_xTi_{2-x}(PO₄)₃ or LLZTO (Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂)) also known as conductive ceramics. These inorganic materials have high hardness and form a composite system capable of improving the mechanical properties of the polymer [8].

The addition of nanoparticles is widely used to improve the properties of lithium-ion batteries [11,12]. Copper oxide nanoparticles (CuO and Cu₂O) are a promising material for batteries [13,14] due to their high theoretical capacity, low cost, ease of preparation, safety, and large surface area.

In this work, we studied the effect of the concentration of copper oxide nanoparticles in a gel polymer electrolyte on conductivity of the electrolyte, as well as on the battery performance characteristics: capacity and Coulomb efficiency.

2. EXPERIMENTAL SECTION

2.1. Synthesis of GPE

PVDF (Sigma-Aldrich, average molecular weight ~180,000) was dried in a vacuum oven at 110 °C for three hours. EC was transferred into a liquid state (melting point 39 °C) in an oven at 80 °C. After preparation PVDF was mixed with a plasticizer and solvents (PC, EC, tetrahydrofuran (THF)) and LiClO₄ salt in mass ratio 2:5:5:1.5:1, copper oxide nanoparticles were also added to the mixture. The composition was mixed on a magnetic stirrer at a temperature of 160 °C. After dissolution PVDF, the electrolyte solution was poured into a Petri dish and left to dry at room temperature for a day. Electrolyte synthesis and gelation were carried out in a glove box (Vilitek VBOX) in a dry argon atmosphere.

Copper oxide nanoparticles were obtained by grinding copper oxide nanowhiskers (the synthesis procedure is described in Ref. [15]) in a planetary ball mill.

2.2. Electrochemical measurements

The ionic conductivity of the electrolyte was measured by the electrochemical impedance method. Stainless steel electrodes in the form of discs 20 mm in diameter were used as blocking electrodes. The impedance of the electrolytes was measured by a potentiostat-galvanostat Electrochemical Instruments P45-X with electrochemical impedance measurement module FRA-24M. The obtained data were processed in the ZView program, where, by extrapolating the data to the intersection with the real component of impedance (abscissa), the bulk resistance of the GPE film was estimated. Based on the average values of the measured resistances, the ionic conductivity of the GPEs was calculated using the formula:

$$\sigma = \frac{L}{RS},$$

where L is the thickness of the GPE film, R is the bulk resistance, and S is the area of electrodes contacting with the GPE film.

The LiFePO₄/GPE/Li (CR-2032) coin cells were assembled in argon-filled glove box. For cyclability

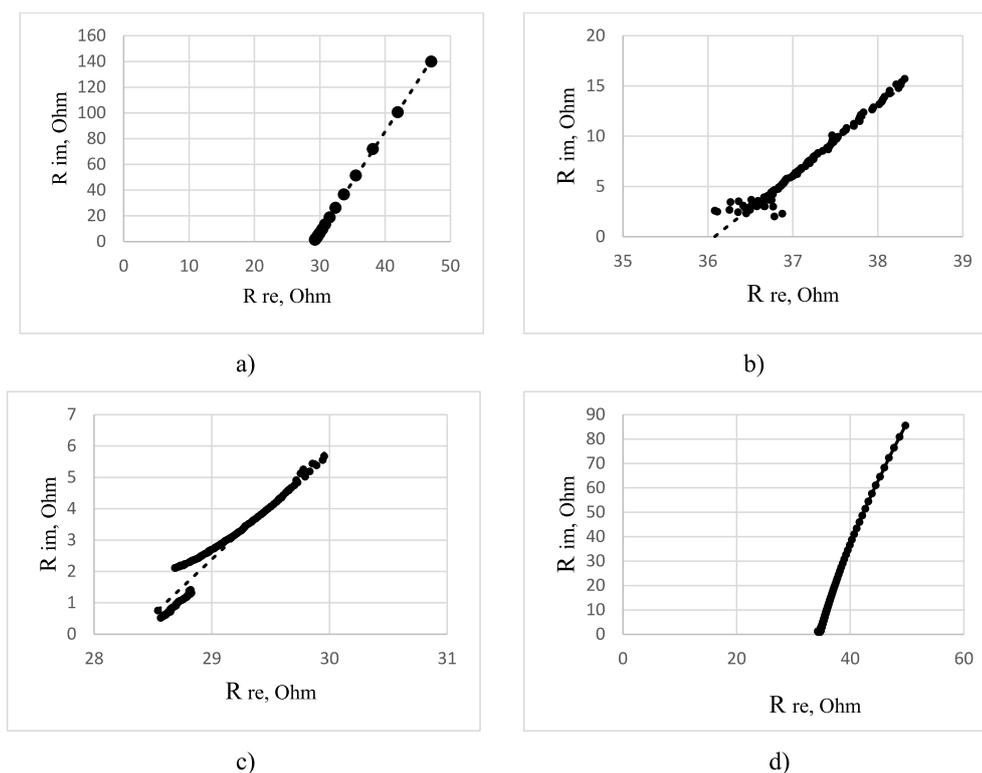


Fig. 1. Nyquist plot of the imaginary part of impedance vs the real part of impedance of GPEs containing copper oxide nanoparticles: (a) – 0.1% wt., (b) – 0.5% wt., (c) – 1% wt., (d) – 2% wt.

tests, the cells were charged/discharged at constant currents from 50 μ A up to 1 mA using a system for testing chemical current sources Coin Cell Battery Tester CT-4008-5V50mA-164.

3. RESULTS AND DISCUSSION

The obtained impedance measurement data (Fig. 1) show that the highest ionic conductivity is observed in the electrolyte containing 2% nanoparticles (Fig. 2). However, at 0.5% or more, cycling problems arose, which are most likely associated with particles

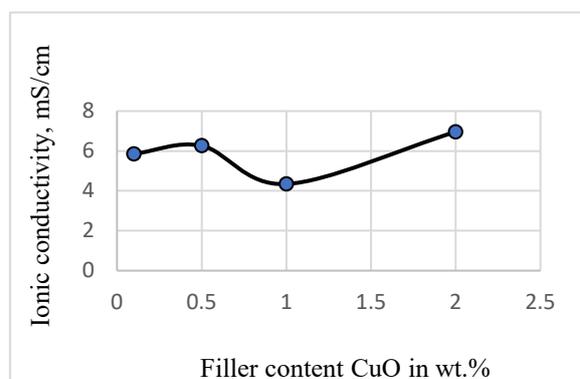


Fig. 2. Dependence of the specific ionic conductivity on the content of CuO nanoparticles in wt.%.

aggregation, that leads to the appearance of electronic conductivity and, as a result, to a short circuit of the cell. It should be noted ionic conductivity alone does not necessarily predict optimal cell performance [5].

Cell with electrolyte containing 0.1% wt. CuO nanoparticles showed good results in cycling. It demonstrates stable operation of more than 100 cycles at a current up to 1 mA, as well as high capacity. The final charge capacity of the battery after 100 cycles was 99.953% of nominal for 1 mA C-rate (Fig. 3).

Figure 4 shows the appearance of the resulting electrolyte and its micrograph obtained by scanning electron microscopy. The micrograph shows that the electrolyte consists of many granules, the average size of which is 15 μ m.

4. CONCLUSIONS

In this work, gel polymer electrolytes based on PVDF with different contents of CuO nanoparticles were synthesized, the resistance was measured by the electrochemical impedance method, and the specific ionic conductivity of the electrolytes was calculated, which for a sample containing 0.1% wt. CuO nanoparticles was 5.85 mS/cm, that is a high value comparable to the specific ionic conductivity of liquid organic electrolytes. The cells were assembled with a LiFePO₄

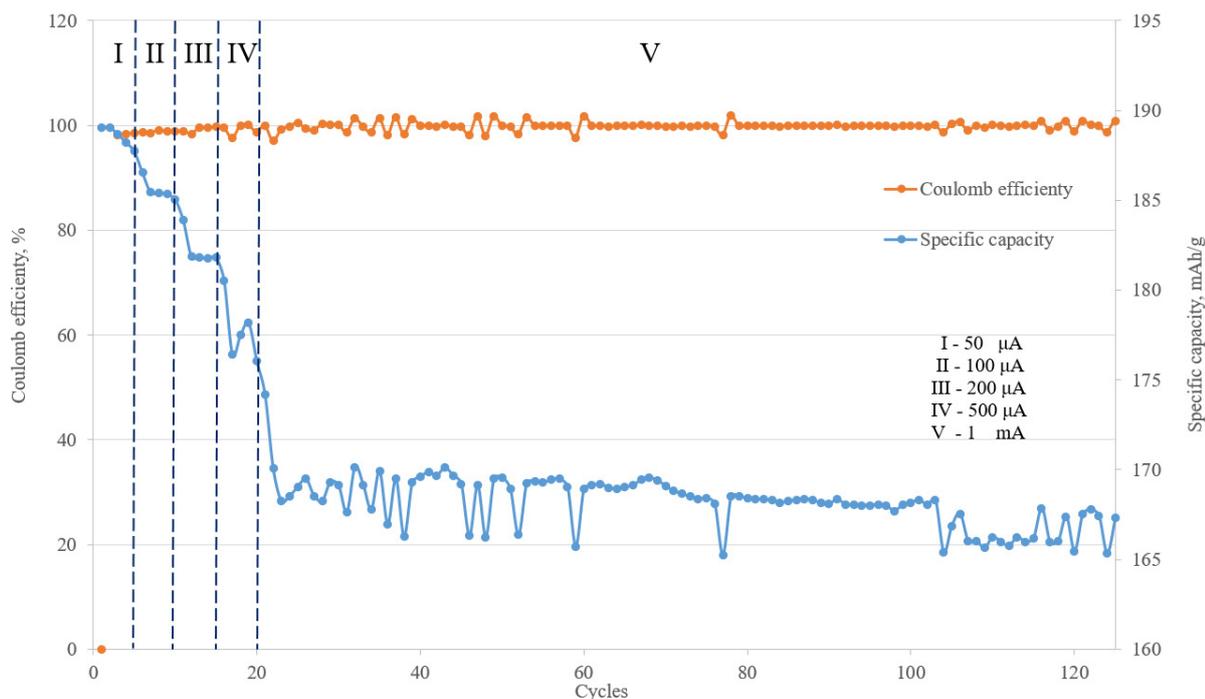


Fig. 3. Dependence of the specific capacity and Coulomb efficiency of the battery charge on the ordinal number of the charge-discharge cycle.

electrode and electrolytes with different content of copper oxide nanoparticles, the cell with GPE (0.1% wt.) showed stable cycling and high capacity. Cells with an electrolyte containing a high concentration of nanoparticles quickly failed, probably due to electronic breakdown between the electrodes. It is shown that the concentration of copper oxide nanoparticles in the electrolyte does not significantly affect the ionic conductivity, but affects the performance of the battery: it increases the service life (the number of charge/discharge cycles while maintaining the capacity level).

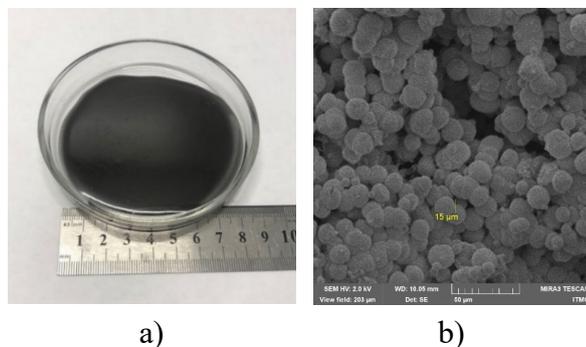


Fig. 4. Gel polymer electrolyte based on PVDF with nanoparticles of copper oxide (a), micrograph of the GPE (b).

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