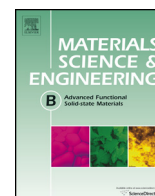




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Highly conductive cathode materials for Li-ion batteries prepared by thermal nanocrystallization of selected oxide glasses

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ABSTRACT

Glassy analogs of two important cathode materials for Li-ion cells: V_2O_5 and phosphoolivine $LiFePO_4$ were heat-treated in order to prepare nanocrystallized materials with high electronic conductivity of up to $7 \times 10^{-2} \text{ S cm}^{-1}$ and ca $7 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , respectively. There is a clear correlation between the crystallization phenomena and the increase in the electrical conductivity for both groups of glasses. Electrochemical tests of heat-treated glasses of the V_2O_5 – P_2O_5 system, used as cathodes in lithium cells confirm their good gravimetric capacity and reversibility. Heat-treatment of glasses of the Li_2O – FeO – V_2O_5 – P_2O_5 system also leads to a high increase in the conductivity and to formation of nanocrystalline grains in the glassy matrix, evidenced by HR-TEM images. The temperature dependence of the conductivity of these materials follows the Arrhenius formula. The presented results indicate that the overall increase in conductivity in nanocrystallized materials is due to good charge transport properties of their interfacial regions.

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1. Introduction

Li-ion batteries, today's most important power sources for portable electronics [1], with prospects of massive use in electric cars [2,3], have been present in the world market since early 1990s. Despite a long period of their usage and intensive research work meanwhile, Li-ion batteries still need improvement in their performance, safety, longevity, economic competitiveness and reduction of the impact of used-battery wastes on the environment [4]. One of key challenges on the road to better Li-ion batteries is the improvement of the cathodes [5,6]. Some of today's leading cathode materials (e.g. $LiFePO_4$, $Li_3V_2(PO_4)_3$) despite their satisfactory electrochemical performance [7,8] exhibit very poor electric conductivity at RT, as low as ca $10^{-9} \text{ S cm}^{-1}$ for $LiFePO_4$ [9] and ca $2 \times 10^{-8} \text{ S cm}^{-1}$ for $Li_3V_2(PO_4)_3$ [10]. The most common and so far the most successful method to circumvent that deficiency consists in carbon coating of the grains of the synthesized active materials (e.g. [11]). Another ways to better conducting cathode materials include: (i) their synthesis in nanostructured forms (e.g. [12]) or (ii) aliovalent doping of the pristine active materials (e.g. [13,14]).

In recent years, we have proposed and investigated an alternative route to the conductivity enhancement, namely a thermal nanocrystallization of glassy analogs of the important crystalline cathode materials, such as: V_2O_5 [15,16], $LiFePO_4$ [17,18] and $Li_3V_2(PO_4)_2F_3$ [19]. The advantages of our approach to produce active cathode materials include the absence of carbon additives and simplicity and straightforwardness of synthesis, which consists of two stages only: (i) glass preparation by melt-quenching and (ii) thermal treatment of the glass to induce its nanocrystallization. Our experience with that method has shown that one can, by the appropriately chosen heat-treatment conditions, achieve a huge (even by a factor 10^9) and irreversible conductivity enhancement. We have also shown that this effect is closely related to changes in the microstructure – namely to appearance of nanoscale crystalline grains, with dimensions going down even to a few nanometers, embedded in the glassy matrix [18]. Taking into account this correlation we have postulated that the conductivity enhancement is caused mainly by the presence of interfacial regions around newly formed nanograins. The defective nature of such interfaces can provide good conditions for small polaron hopping, which is a main electronic transport mechanism in systems like V_2O_5 [20,21], $LiFePO_4$ [22] or $Li_3V_2(PO_4)_3$ [23,24].

In this paper, we present results of our recent studies on effects of thermal nanocrystallization of the glasses of the systems V_2O_5 – P_2O_5 and Li_2O – FeO – V_2O_5 – P_2O_5 on their electrical conductivity, microstructure and electrochemical properties.

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2. Experimental

2.1. Preparation

2.1.1. V_2O_5 – P_2O_5 glasses

Glassy samples of nominal composition $90V_2O_5$ – $10P_2O_5$ were prepared by a standard melt quenching technique. Appropriate amounts of starting chemicals: V_2O_5 (Aldrich, 99.6%) and $(NH_4)H_2PO_4$ (POCh – Polish Chemicals, 99.5%) were mixed in an agate mortar and placed into alumina crucibles, which were transferred into an electric furnace heated to $1300^\circ C$. The molten mixtures were held at that temperature for 60 min in air. Then they were rapidly poured out onto a stainless-steel plate held at room temperature and immediately pressed with another identical plate.

2.1.2. Li_2O – FeO – V_2O_5 – P_2O_5 glasses

Four series of glasses were prepared by a standard melt quenching technique. The nominal compositions of those series are listed in Table 1.

Appropriate amounts of precursors: Li_2CO_3 (Aldrich, 99.9%), $Fe_2O_4 \cdot 2H_2O$ (Aldrich, 99.9%), $(NH_4)H_2PO_4$ (POCh – Polish Chemicals, 99.5%) and V_2O_5 (Aldrich, 99.6%) were mixed in a mortar and annealed under flow of nitrogen (purity 99.999%) in two steps: (i) at $300^\circ C$ for 2 h and (ii) at $570^\circ C$ for next 2 h. Subsequent stages of the synthesis of the glassy materials involved second mixing in a mortar, melting at $1250^\circ C$ and a rapid quenching, according to the procedure described in more detail in our earlier paper [18].

2.2. Experimental methods

Samples of the above listed materials were investigated using several experimental methods, including: X-ray diffractometry (XRD), differential thermal analysis (DTA), impedance spectroscopy (IS) and transmission electron microscopy (TEM). X-ray diffraction patterns were collected using a Philips X'Pert Pro apparatus equipped with a copper anode and a Ni filter and set in the Bragg–Brentano configuration. The $CuK\alpha$ radiation of wavelength $\lambda = 1.542 \text{ \AA}$ was used in the experiments. Diffraction patterns were acquired at room temperature before and after the heat-treatment stages. XRD measurements confirmed amorphousness of all as-prepared materials and provided information about the state of crystallinity, phase composition, and estimated size of crystalline grains of the heat-treated samples. DTA measurements were carried out to determine the temperatures of glass transition (T_g) and crystallization (T_c), and to help in setting maximum temperatures of heat-treatment stages leading to optimum nanocrystallization. The DTA experiments' conditions were as follows: heating rate of $1^\circ C \text{ min}^{-1}$, a pure argon atmosphere (flow) and the maximum temperature of $750^\circ C$. Samples were placed in open alumina pans. The measurements were done using a SDT Q600 setup (TA Instruments).

The conductivity was determined from impedance spectroscopy measurements carried out on heating and cooling ramps. Before these measurements, platinum electrodes were applied onto opposite faces of the samples by *dc* sputtering. Impedance spectra were

Table 1
Nominal compositions of glassy materials of the Li_2O – FeO – V_2O_5 – P_2O_5 system under study.

Label	Composition	Li:Fe:V:P:O proportions
G08	$25Li_2O$ – $40FeO$ – $2V_2O_5$ – $25P_2O_5$	1:0.8:0.08:1:4
G10	$25Li_2O$ – $37.5FeO$ – $2.5V_2O_5$ – $25P_2O_5$	1:0.75:0.1:1:4
G15	$25Li_2O$ – $31.25FeO$ – $3.75V_2O_5$ – $25P_2O_5$	1:0.625:0.15:1:4
G20	$25Li_2O$ – $25FeO$ – $5V_2O_5$ – $25P_2O_5$	1:0.5:0.2:1:4

acquired in the 10 mHz–30 MHz frequency range. The measuring setup was based on a Solartron 1260 Gain Phase/Impedance Analyzer integrated with an oven and a module for temperature programming and stabilization (Eurotherm 2404). The electrical conductivity was measured during heating and cooling ramps. An impedance spectrum at each temperature was acquired after the temperature had been stabilized for at least 40 min. Transmission electron microscopy (TEM) images were acquired using a Titan Cubed 80–300 instrument at the Institute of Physics, PAS. This microscope was used mainly in High Resolution mode (HR-TEM), but also sometimes in Scanning Transmission Electron Microscopy (STEM) mode. Additionally, there were several experiments on local elemental analyses, using an Energy Dispersion Spectroscopy (EDS) module.

Some samples of the highly conducting nanocrystallized $90V_2O_5$ – $10P_2O_5$ glasses were tested as cathodes in laboratory-made rechargeable lithium cells, which were assembled in a MBraun glove box in an oxygen- and moisture-free atmosphere (<0.01 ppm) in gas-tight Swagelok-type holders. Batches (ca 5 g) of the powdered glasses were first heated to $550^\circ C$ in a tube furnace, with the temperature program similar to the one used in the electric measurements. Then they were ball-milled in a Retch PM100 planetary mill. The cathodes for the discharge/charge tests were prepared using 70 wt% active material (i.e. nanocrystallized $90V_2O_5$ – $10P_2O_5$), 20 wt% carbon black and 10 wt% binder (PVDF – polyvinylidene difluoride). To prepare the cathode layer a slurry was made by mixing these materials in N-methyl-2-pyrrolidone. The suspension was spread on an aluminum current collector using a doctor blade. After the evaporation of the solvent in an oven at $70^\circ C$ for 24 h, disks of 12 mm in diameter containing active cathode material were cut. Anodes were cut in form of disks of the same size from Li metal ribbons in an oxygen-free atmosphere in a glove box. The electrolyte was a 1 M $LiPF_6$ solution in 1:1 EC/DEC solvent. Discharge/charge cycles of these cells were done using an Arbin BT-2043 Battery Test System. The cell was discharged/charged at rates of: C/20 – initially, then at C/10 and finally at C/5 rate with fixed cut-off voltages of 1.5 V and 4.5 V.

3. Results

3.1. $90V_2O_5$ – $10P_2O_5$ glasses/nanomaterials

Materials of this composition were selected because they can be prepared in a glassy form by a standard melt-quenching and can be readily turned into a nanostructured material by an appropriate heat-treatment. In contrast, pure V_2O_5 crystallizes, at least partly, when melt-quenched [16]. We chose them also because there is a renewed interest worldwide in studies on vanadate-based cathode materials for Li-ion batteries (e.g. [25,26]).

The electrical conductivity of the $90V_2O_5$ – $10P_2O_5$ glass as a function of temperature is shown in Fig. 1. Initially modestly conducting ($\sigma = 7 \times 10^{-5} \text{ S cm}^{-1}$ at RT) glassy material upon heating becomes more and more conductive. Up to ca $280^\circ C$, i.e. to approx. crystallization temperature T_{c1} (cf. the inset in Fig. 1) the conductivity increases according to the Arrhenius formula, with a single activation energy of $E = 0.34 \text{ eV}$. Near $270^\circ C$ the increase becomes faster and at ca $350^\circ C$ the activation energy discernibly decreases. After reaching a maximum temperature of ca $550^\circ C$, the sample was cooled down at a very slow rate. The conductivity decrease in the cooling stage follows the Arrhenius formula with a single activation energy of ca 0.13 eV down to room temperature. The conductivity values at given temperatures on cooling are much higher than those on the heating ramp. The electrical conductivity at room temperature of the sample after the heating-cooling cycle is $7 \times 10^{-2} \text{ S cm}^{-1}$, what means that it is ca. 1000 times higher than the conductivity of

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