M.Sc. Eng. Artur Frąckowiak

Department of Inorganic and Analytical Chemistry

Faculty of Chemical Technology and Engineering

West Pomeranian University of Technology in Szczecin

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Abstract of the doctoral thesis

"Synthesis and properties of solid solutions with the structure of $M_8V_{10}W_{16}O_{85}$ phases, where M = Fe and Al"

The ever-increasing number of portable electronic devices and hybrid or electric cars is causing a rapid increase in demand for high-capacity, low-weight energy sources. These requirements are best met by lithium batteries today, which however are not free from defects. For this reason, work is constantly being carried out to improve the properties of commercialized active components of electrodes and new materials for their production are being sought. One of the potential groups of materials for the production of anodes are block-structured phases, also known as Wadsley-Roth phases. Their structure contains tunnels, which are paths of rapid lithium diffusion in the crystal lattice. Currently, block-structured phases containing in the crystal lattice niobium or niobium and additionally elements such as vanadium, tungsten, titanium and iron are intensively studied. Studies on ternary oxide systems M_2O_3–V_2O_5–WO_3 (M=Fe, Al) have led to the discovery of phases with the general formulas $Fe_8V_{10}W_{16}O_{85}$ (Fe8) and $Al_8V_{10}W_{16}O_{85}$ (Al8), a solid solution of limited solubility of the $Fe_8V_{10}W_{16-x}Mo_xO_{85}$ type where $0 \leq x \leq 4$ and a continuous solid solution $Fe_{8-x}Al_xV_{10}W_{16}O_{85}$, $0 \leq x \leq 8$. All the mentioned phases crystallize in the tetragonal system and the similarity of their unit cell parameters and powder diffraction patterns to those characteristic of the isostructural phases of $(W_{0,35}V_{0,65})_2O_5$ and M-Nb_2O_5 with a block structure allows us to assume that the phases of the $M_8V_{10}W_{16}O_{85}$ type are isostructural with $(W_{0,35}V_{0,65})_2O_5$ and M-Nb_2O_5 and belong to the phases with a block structure. The literature review showed that until the beginning of the research for this doctoral dissertation, the structure of the Fe8 and Al8 phases had not been solved or refined by the Rietveld method. Moreover, the Fe8 and Al8 phases had not been studied as potential active materials for the production of electrodes in lithium batteries. Some properties of these phases, which may be of significant importance in the case of their use as active materials for electrodes in batteries, were not known. Therefore, the aim of this work was to refine the structure of the Fe8 and Al8 phases by the Rietveld method, search for other phases with this structure and comprehensively investigate their properties.

In the first stage of the research, the structure of the Fe8 and Al8 phases was refined using the Rietveld method, assuming the initial model of the structure of the M-Nb_2O_5 and $(W_{0.35}V_{0.65})_2O_5$ phases. Due to the different multiplicity of positions occupied by metal ions in the M-Nb_2O_5 structure (two positions with a multiplicity of 8 and one 16) and the different formal oxidation state of ions building the structure of the studied M8 phases (3+, 5+ and 6+), it was necessary to develop an appropriate research procedure in order to determine the method of filling the individual crystallographically independent positions with ions. It assumed conducting literature

studies on the method of filling nonequivalent crystallographic positions by different ions in the structure of block phases and performing studies using XPS spectroscopy and in the case of the Fe8 phase, Mössbauer spectroscopy. The results of the studies conducted using the XPS method showed that in the Fe8 phase structure only Fe^{3+}, V^{5+} and W^{6+} ions occur and in the Al8 structure only Al^{3+}, V^{5+} and W^{6+} ions. In turn, using the Mössbauer spectroscopy method, it was established that Fe^{3+} ions occupy three positions in the Fe8 crystal lattice in octahedral coordination, which differ significantly in the degree of deformation. Moreover the occupancy rate was estimated. This allowed for the preparation of an equation balancing the mass and charge of ions in the M8 phase structure. The solutions for the Fe8 phase selected during this procedure were refined using the Rietveld method. Good values of the discrepancy factors R and acceptable bond lengths and angles between bonds confirmed the correctness of the obtained solutions. Then, the structure of the Al8 phase was refined using the Rietveld method, assuming the structure model obtained as a result of the refinement of the Fe8 phase structure. In this case, good values of the discrepancy factors and acceptable bond lengths and angles between bonds in polyhedra were also obtained. Based on the determined bond lengths and angles between them and the results of the tests obtained using IR and Mössbauer spectroscopic methods, the degree of deformation of the octahedra building the structure of the Fe8 and Al8 phases was compared.

In the next stage of the research it was shown that M8 type phases can be obtained by the solution method, the solid-phase reaction method using oxides activated in high-energy mills or the solid-phase reaction method using reagents such as vanadates or tungstates of the appropriate metals. In all presented cases pure phases were obtained after the heating stage in the temperature range of 650-800°C. The NIR spectroscopy method was used to study the mechanism of synthesis of Fe8 and Al8 phases by the solution method. It has been shown that by the method of solid-phase synthesis with the use of oxides, it is not possible to obtain M8 phase analogues containing gallium, chromium, zinc, nickel or titanium instead of iron or aluminum. On the other hand, a series of solid solutions with limited solubility such as $Al_{8-x}M_xV_{10}W_{16}O_{85}$, $Fe_{8-x}M_xV_{10}W_{16}O_{85}$, were obtained, where some aluminum or iron ions are replaced by gallium or chromium ions, and a solid solution of $Al_8V_{10}W_{16-y}Mo_yO_{85}$ where some tungsten ions were replaced by molybdenum ions. In addition, solid solutions of the type $Al_{2-x}Fe_x(WO_4)_3$, $Fe_{2-x}Al_xWO_6$ and $Al_{1-x}Fe_xVO_4$ were obtained, which were then used as substrates for the synthesis of M8 solution phases. The solubility ranges of these solid solutions as well as melting points were determined. After the indicator of their powder diffractograms, the parameters of their elementary cells were determined. In addition, the IR spectra of the obtained solid solutions were recorded and analysed.

In the next stage of the research, the values of the mean linear coefficients of thermal expansion of the Fe8 and Al8 phases and selected samples of the solid solution $Fe_{8-x}Al_xV_{10}W_{16}O_{85}$ were determined by means of a diffractometric method. The analysis of the obtained research results indicates a very strongly marked anisotropy of thermal expansion of the Al8 crystal lattice and solid solution samples. In the case of the smallest parameter of elementary cells, with a length of approximately 3.8Å, rare negative values of thermal expansion coefficients were obtained. Using the available literature data and the results of this work, a comparison of changes in the size of unit cells caused by temperature increase (thermal expansion), chemical expansion associated with ion substitution in the crystal lattice and expansion associated with the introduction of lithium into the crystal lattice of the active components of the electrodes was compared.

In the last stage of the study, Fe8 phase lithiation tests were performed. They were preceded by tests of the electrical conductivity of Fe8 and Al8 by EIS. XRD and SEM microscopy were used to identify and characterise the properties of Fe8 and Al8 as well as graphene, acetylene black and PVdF nanoflakes used to make electrodes for electrochemical research. XRD and SEM methods were then used to evaluate the efficiency of grain crushing of M8 phases using a manual agate mortar and a high-energy ball mill. Based on the results of these tests, a Fe8 sample was selected for electrochemical tests, crushed in an agate mortar for 5 minutes, containing crystallites with sizes from 1 to 80 μm and a sample ground for 15 minutes in a ball mill and containing grains of 0.1-0.3 μm. Electrochemical tests have shown that in the case of a sample crushed in an agate mortar (grains of 1-80 μm), after the first intercalation, a capacity of 260 mAh/g was recorded, while the calculated theoretical value is equal to 284 mAh/g. However, this value dropped to 110 mAh/g after the second intercalation cycle and stabilized at 80 mAh/g after the 15th lithiation cycle. Despite the much higher degree of grain size reduction of Fe8 used to prepare the second electrode (0.1-0.3 μm), very similar results of electrochemical tests were obtained. The results of the XRD test have also shown that after the first intercalation of lithium, Fe8 amorphization occurs.

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A. Filipczuk