ELECTROCHEMICAL LITHIATION OF THE BINARY COMPOUND TiSb

Kordan V. M., Fedak T. A., Tarasiuk I. I., Zelinska O. Ya., Pavlyuk V. V.
Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
6 Kyryla i Mefodiya St., 79005 Lviv, Ukraine
kordan50@gmail.com

The sample with the composition $Ti_{50}Sb_{50}$ was synthesized by arc melting of the pressed mixture of pure metals with further annealing in evacuated silica tube at 400 °C for two months. The X-ray phase analysis (diffractometer DRON-2.0M, Fe *Kα*-radiation) confirmed the formation of TiSb (structure type NiAs, space group $P6_3/mmc$) as a major phase and negligible amount of antimony as a minor phase.

Electrochemical lithiation of the obtained phase was carried out in the 2-electrode Swagelok-type cell using the powder of synthesized alloy as a negative electrode and a powder of $LiCoO_2$ (structure type $NaFeO_2$, space group $R\bar{3}m$) as a positive electrode. The electrodes were isolated by separator on the basic of pressed cellulose soaked in electrolyte (1M solution of $Li[PF_6]$ in 1:1 ethylenecarbonate / dimethylcarbonate). All electrochemical investigations were carried out in galvanostatic mode (charge and discharge at 1.0 mA/cm^2) over 50 cycles.

With the intercalation of Li into the octahedral voids of TiSb the lattice parameters of the phase increased because of the formation of Li_xTiSb (1). In the next stage, the partial substitution of Sb-atoms by Li occurred with the formation of $Li_{x+y}TiSb_{1-y}$ phase and binary $Li_{z-y}Sb_y$ phases as by-products (2). The lattice parameters of the major phase decreased. Delithiation of the cathode $LiCoO_2$ occurred by charge process (3). During discharge the Li-atoms returned to the original positions in the channels of the structure.

After 50 cycles of the electrochemical lithiation-delithiation the decreasing of the lattice parameters of the main phase was the following: a = 4.0146(9)–3.9999(7) Å, c = 6.202(1)–6.169(2) Å, V = 86.57(3)–85.48(3) Å^3 ($\Delta V/V$ = 1.26 %). Reversible amount of Li was calculated to be 0.025 Li/f.u. X-ray fluorescence spectroscopy (spectrometer ElvaX Pro) confirmed the smaller content of Sb in the main phase and hence the partial substitution of Sb by Li. During the study of the topology and morphology of the sample surface after lithiation by scanning electron microscopy (microscope Tescan Vega3 LMU) the formation of nano-particles with the size of 50-70 nm was observed on the porous aggraded grains. The electrochemical reactions at the electrodes were the following:

$$TiSb + xLi^+ + x\bar{e} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_xTiSb \quad (1)$$

$$Li_xTiSb + zLi + \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_{x+y}TiSb_{1-y} + Li_{z-y}Sb_y \quad (2)$$

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} x\bar{e} + xLi^+ + Li_{1-x}CoO_2 \quad (3)$$

Due to significant electronegativity of antimony, the reaction of substitution in this case is more typical than the reaction of inclusion. That is why the value of reversible amount of Li is lower than it could be only at the inclusion.

Funding for this research was provided by the Ministry of Education and Science of Ukraine (grant No. 0117U007192).