The Electrode Material for Hybrid Supercapacitor Based on the Nanostructured Iron-Substituted Lithium-Manganese Spinel

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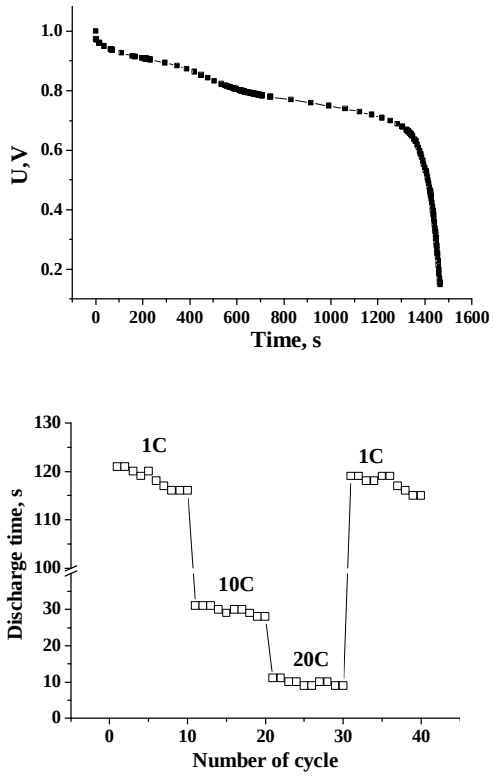

Fig.1. Typical discharge curve cycling characteristics of supercapacitor based on the AC and $LiMn_{1.95}Fe_{0.05}O_4$ spinel

Modern electronic devices and electric transport demand new energy sources with high specific power, capacity and energy. The hybrid supercapacitors (HSC) combine advantages of carbon and Faraday's electrodes and are the most perspective alternative of lithium power sources. We investigated the electrode material of HSC based on the $LiMn_{1.95}Fe_{0.05}O_4$ spinel in $LiNO_3$ and Li_2SO_4 water electrolytes.

The carbonated and activated carbon (specific surface area about 670 m^2/g, average mesopores and micropores sizes are 8 and 1.7 nm, respectively) were used as a polarized electrode. Lithium-manganesespinel was synthesized by sol-gel method without autoburning. As the initial precursors we used $Mn(NO_3)_3 \cdot 6H_2O$, $LiNO_3 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$. The electrochemical studies were performed by the galvanostatic cycling and cyclic voltammetry. The diffusion coefficient was calculated by galvanostatic intermittent titration method.

The monophase $LiMn_{1.95}Fe_{0.05}O_4$ spinel with the Fe^{3+}cations substitution in the octahedral sites has been obtained (XRD and Mosssbauer spectroscopy data). The average particle sizes (calculated by Scherrer equation) were about 10-12 nm. The measurement of conductivity's frequency dependencies (impedance spectroscopy data) indicates the presence of the conductivity percolation mechanism in the 10^3 - 10^5 Hz range due to electrons jumps between the iron cations in the the spinel lattice. The obtained values of DC conductivity (about 10^{-3} Sm/m) are significantly higher than typical characteristic of unsubstituted lithium manganese spinel. Discharge curves (current density 1C) are characterized by a lateral region in 0.9-0.8 V range (Fig. 1a). Redox peaks were observed at the CVA curvesin the same voltage range so it's an evidence of lithium intercalation in the spinel structure. Calculated diffusion coefficient vary in 10^{-9}-10^{-10} cm^2/s range. Such comparatively high values are associated to high conductivity of spinel grains. The model capacitor specific capacitance decrease with the current density enlarging to 10 C and 20 C (Fig. 1b), however system are reversible even after high current cycling. The specific power of model capacitors was about 700 W/kg.

[1] B.I. Rachiy, B.K. Ostafiychuk, I.M. Budzulyak, V.M. Vashchynsky, R.P. Lisovsky, V.I. Mandzyuk, The effect of thermochemical treatment of carbon materials on their electrochemical properties, *Journal of Nano- and Electronic Physics* **6**(4) (2014) 040311-040316.