

ELECTROLYTIC MOLYBDENUM OXIDES IN PRIMARY AND SECONDARY LITHIUM POWER SOURCES

*E. Shembel¹, P. Novak¹, V. Tysyachy^{1,2},
A. Markevich³, R. Apostolova³, I. Kirsanova³*

¹Ener1, Fort Lauderdale, Fl 33309, USA
E-mail: eshembel@ener1.com

²National Metallurgical Academy of Ukraine,
Dnipropetrovsk, Ukraine

³Ukrainian State Chemical Technology
University, Dnipropetrovsk, Ukraine

Molybdenum oxides are used as cathode materials for lithium batteries due to high specific energy [1,2], which value is considerably depends on a production method. In this work we study the molybdenum oxide materials for chemical power sources produced by the electrochemical deposition method on a current-conducting substrate. Peculiarity of this technology is a possibility to apply films with the thickness and composition variable in a wide ranges. This allowed producing thin-layer non-ballast electrodes for primary and rechargeable lithium power sources [3].

Comparison of the specific and rate characteristics of the experimental prototypes based on the proposed materials with the analogues products of Panasonic and Ultralife has shown the good prospects of the proposed materials. Using stoichiometric MoO_3 as a cathode material for primary cells is of special interest. Its specific efficiency at the currents up to 2 mA/cm^2 remains at $260 \div 200 \text{ Ah/kg}$, which is 1.5 times higher than with the compared prototypes. The cathode based on electrochemically synthesized non-stoichiometric Mo_4O_{11} has shown high specific discharge capacity ($\sim 180 \div 200 \text{ Ah/kg}$) and cyclability (over 150 cycles).

OCV-intercalation degree curves and cyclic voltammograms obtained at low potential scan rates (up to $20 \mu\text{V/s}$) confirm stoichiometry of lithium intercalation/ deintercalation in MoO_3 . The first cycle is followed by two phase transitions. The next cycles occur at one stage. Discharge and charge of non-stoichiometric Mo_4O_{11} can be considered as one-stage process in the range of 2.5-1.3 V.

Electrochemical behavior of synthesized materials has been studied at the first and the subsequent cycles by the method of impedance spectroscopy with the help of VoltaLab equipment. It has been established the influence of intercalation degree on the coefficient value

of lithium chemical diffusion to the investigated materials at discharge and charge, which ranged from 10^{-9} to $10^{-11} \text{ cm}^2/\text{S}$ for the thermal sprayed material and was by the order of magnitude higher for electrolytic oxide.

The connection of the obtained dependences with the cyclic voltammetry curves by the method [4] has been analyzed. The rate constants of Li^+ transfer through the electrode/electrolyte interface which values for the investigated materials is in the range of $10^{-7} \div 10^{-8} \text{ cm}^2/\text{S}$ have been determined.

It has been studied the influence of thickness and discharge rates of the cathode layers from the proposed materials on the values of specific capacity and energy. Recommendations concerning application of MoO_3 layers in primary cells and electrochemically deposited Mo_4O_{11} in rechargeable lithium batteries have been proposed.

References

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