Kinetics of Lithium Ion Intercalation/ Deintercalation Process Into Manganese Dioxide

Elena Shembel*, Vladislav Tysyachny#, Nataly Globa*, Nelya Zaderey#, and Peter Novak*

* Ener1 Inc. 550 W Cypress Creek Road, Suite 120, Fort Lauderdale 33309, FL, USA.
E-mail: eshembel@ener1.com
Chemical Power Sources Research Laboratory, Ukrainian State Chemical Technology University, 8 Gagarin Ave., 49005, Dnipropetrovsk, Ukraine.
E-mail: shembel@onil.dp.ua

The work is devoted to the problem concerning production of effective cathode material for lithium-metal secondary power source. The developed by the authors of the paper chemically synthesized manganese dioxide (MnO_2) characterized by a high bulk density (up to 2.9 g/cm^2), high discharge capacity at the first cycle (up to 270 mAh/kg), stable cyclability (up to 170-200 mAh/g) is the promising material.

Experimental strategy

- Influence of the synthesis conditions and thermal treatment on the structure and chemical properties of synthesized MnO_2 has been investigated using XRD and TGA.
- Electrochemical investigations were carried out using CV-metry, EIS, and galvanostatic cycling.
- Kinetics regularities of intercalation / deintercalation process have been determined.
- Investigations and testing of the actual prototypes of lithium-metal secondary power sources were carried out in the systems with liquid nonaqueous electrolyte with use of special stabilizing additives.

Experimental results and discussion:

The synthesized cathode material has a good rechargeability in non-aqueous electrolyte (Fig 1). At the same time, from the point of view of classical electrochemistry, the system is irreversible as evidenced by a great difference between the potentials of cathode and anode peaks. At the initial stages of cycling the structure changes resulting in the potential displacement of cathode and anode peaks are observed. It is connected with a small rate of hardly reversible phase transformations. With decreasing potential scan rate (cycling voltammetry) or current value (cycling galvanostatics) the intercalation process is possible within one phase.

The further analysis of the experimental data was carried out using the proposed in the literature [1-3] quantitative characteristic of interaction between the intercalation particles. Some cases concerning repulsion, attraction and unavailability of interaction between the intercalated particles were considered. The particularities of lithium intercalation in LiV_3O_8 and MnO_2 have been compared.

The analysis performed show the unavailability of phase transformations at lithium ions intercalation into investigated chemically synthesized MnO_2 This can explain a high cyclability of the cathodes based on the given type of MnO_2 (Fig.2).

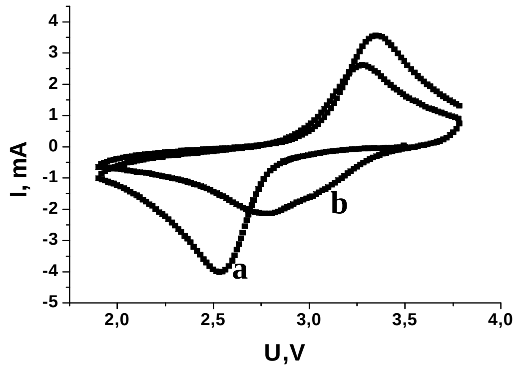

Fig.1 Cyclic voltammograms of MnO_2.
Electrolyte: PC, DOL, 1M $LiN(SO_2CF_3)_2$
Potential scan rate (V/s): $5\cdot10^{-4}$
A - the 1st cycle; b – the 2nd and 3d cycles

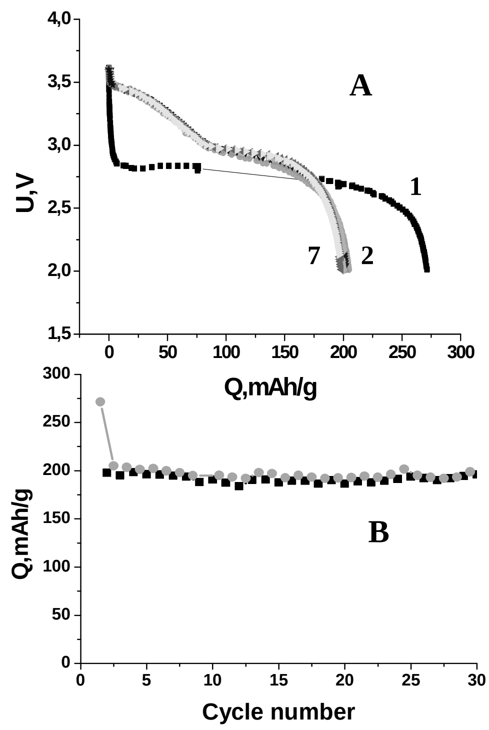

Fig. 2 Charge-discharge cathode characteristics of Li-MnO_2 cell (A) and the change of specific discharge capacity at cycling (B).
Discharge capacity value is denoted relative to MnO_2 (2325 cell). I_{disch}- 0.35 mA. I_{ch} – 0.2 mA.
Electrolyte: PC, DOL, $LiN(SO_2CF_3)_2$
Numerals on curves indicate cycle numbers.

References

1. Voinov M.U. // Electrochemica Acta, (1981), v.26, N 10, p.p.1373-1376.
2. West K., Jacobsen T., Zachau – Christiansen B., and Albung S. // Electrochemica Acta (1983), v.28, .p.97.
3. Armand M.B. in Marphy D. W., Steele B. C. N. (Edc) Materials for Advanced Batteries, Plenum Press New Jork and London, 1980, p.145

Acknowledgments

Financial support of the work was provided within the framework of IPP Thrust 1 Program No. 323130AF-1, STCU Project No. 656, and CRDF Project No.UCO-1207.