MATHEMATIC MODELS AND EXPERIMENTAL STUDY OF LITHIUM ION INTERCALATION IN ELECTROLYTIC VANADIUM OXIDE

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Electrochemical intercalation of lithium ions in V_2O_5 as the thin-layer cathodes of lithium secondary batteries is determined by the transport properties of lithium ions, discharge rate, structure and thickness of electrodes [1-3]. Film electrodes without binder and carbon (or black) are the convenient object for checking of mathematical model identity of lithium ions intercalation by actual discharge process [4]. In the work diffusion models are used for description of discharge processes in V_2O_5 films at galvanostatic mode and potential relaxation when a current switched off. The films are produced by anodic deposition on a stainless steel and then dried at $18°C$ as described in detail elsewhere [5-7].

The main assumptions accepted at the consideration of mathematical models, assume the unavailability of phase transformations at lithium ion intercalation, constancy of Li^+ chemical diffusion coefficient ($\tilde{D}_{Li}$), insignificance of chemical polarization and migration.

According to the equations obtained, the specific charge, returned by electrode in the case of $\tilde{D}_{Li} \tau / l^2 \geq 1$ (τ - time of discharge completion, l - electrode thickness), decreases linearly with discharge current increase. Connection between the values of discharge capacity, electrode thickness in the form acceptable for the determination of the optimal thickness of film at the given values of discharge rate and diffusion coefficient of Li^+ has been established. Potential relaxation equation after discharge current switching off has been obtained. In accordance with the equation potential rate increase is proportional to current switching off and inversely proportional to a film thickness. It is presented in the form acceptable for the calculation of Li^+ diffusion coefficient and evaluation of equilibrium potential change depending on the degree of intercalation.

Theoretically obtained dependence was checked on the actual thin-layer electrodes produced of V_2O_5. Values of the chemical diffusion coefficients of Li^+, optimal electrode thickness at the given discharge rates, as well as the values of the derivative dependence (E_{eq}/dx) of equilibrium potential (E_{eq}) on the intercalation degree (x) have been determined. The value of dE_{eq}/dx is in a close agreement with the data obtained by the direct differentiation of the experimental curve of OCV-x $(x= 0.3-0.7)$. $\tilde{D}_{Li}$ value equal to $1.5*10^{-11}$ cm^2/c, corresponds to the value presented in [4,5].

References
[1] J. Sato, T. Asado, H. Tokugawa, K.Kobayakawa, J. Power Sources 68 (1997) 674.
[2] X.Zhang and R. Frech, J. Electrochem. Soc. 145 (1998) 847.
[3] N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Grouft, J. Appl. Electrochem. 28 (1998) 41.
[4] T.Kudo, M.Hibino, Electrochem. Society Proceeding. - 95-22 (1995) 31.
[5] E. M. Shembel, R. D. Apostolova, V. M. Nagirny, D. Aurbach, B. Markovsky, J.Power Sources 81/82 (1999) 480.
[6] E. Shembel, R. Apostolova, V. Nagirny, D. Aurbach, B. Markovsky // Power Sources, 80, P. 90 (1999).
[7] R.Apostolova, E.Shembel, V.Nagirny. J Appl. Chemistry, 36 (2000) 41 (In Russian).