
SUMMARY OF THE 2004 A.N. FRUMKIN
AWARD WINNING PAPER

Electro and Photo-Induced Diffusion and Migration Processes in Nonstoichiometric Lithium Compounds

K. I. Pridatko^z, A. V. Ivanishchev, and V. A. Zobenkova

Saratov State University,
ul. Astrakhanskaya 83, Saratov, 410012 Russia

Received December 8, 2004

Studying the transport processes in solid intercalation electrodes represents a pressing problem in the solid-state electrochemistry and is simultaneously a prerequisite for the further improvement of lithium-ion and lithium-polymer batteries. The aim of this work is consisted of studying basic laws for kinetic and diffusion processes that occur during the electrochemical intercalation of lithium into carbon and titanium dioxide by means of the development of model electrode systems and the application of a complex of electrochemical methods. In this work there were used such electrochemical methods as potentiostatic and galvanostatic intermittent titration at small concentration perturbations [1–5], cyclic voltammetry [4, 6, 7], electrode impedance spectroscopy [6, 7], and photoelectrochemistry [7, 8]. The objects under investigation were thin-film model electrodes that contained no binding or electroconducting additives.

It was established that the experimentally obtained chronoamperograms and chronopotentiograms satisfy equations of theory of diffusion with a surface control [9], thus demonstrating the validity of its application for describing transport processes in intercalated materials. A detailed study of the way the chemical diffusion coefficient for lithium D depends on the electrode potential E was performed. It was established that, for the lithium-carbon intercalation compounds, the concentration D, E dependence exhibits an extremum character with a minimum in the region of transition from intercalation compounds of a first step to the intercalation compounds of a second step, which corresponds to a maximum of the intercalation capacity of the material. The correspondence between the extremes in two curves was explained in terms of the Frumkin isotherm. The lithium concentration in the intercalate was shown to hardly effect its own diffusion coefficient in the region of compositions reach in lithium and to have a considerable effect at in the region of dilute phases.

It was established that the appearance of the temperature dependence of the lithium diffusion coefficient in carbon varies with the lithium concentration in the intercalate. However, we stress that the temperature

effect on D is virtually nonexistent at compositions that lie in the vicinity of the extremum in a D, E curve. This potential region corresponds to the “plateau” exhibited by a charge-discharge curve where there take place successive transients between intercalation steps.

The polarization dependence of a kinetic current through the Li_xC_6 electrode, which was measured for the first time ever, is fully determined by ion-conducting properties of a surface solid-electrolyte interface (SEI) and obeys the same typical regularities of an ohmic-injector current, which had been established for a passivated lithium electrode in [10]. The concentration and mobility of mobile charge carriers in SEI were determined and found to be dependent on the lithium concentration in the intercalate.

Typical peculiarities of frequency spectra for titanium dioxide electrodes made it possible to reliably identify steps basic for the electrochemical transport of lithium. The first step is the transport of lithium ions through the electrode/electrolyte interface, then the ions pass through a SEI, and the ultimate step is the diffusion of intercalated lithium through the electrode matrix, onto which additionally imposed is the electron transport at the expense of the intrinsic conduction of the matrix. These processes are reflected in the frequency dependences of impedance. The proposed equivalent circuits satisfactorily model impedance spectra for the electrodes studied.

The photosensitivity of a lithiated titanium dioxide electrode was studied, spectral characteristics of the photocurrent and its potential dependence are obtained, and the flat-band potential determined. The photocurrent is maximum in the ultraviolet spectrum range and corresponds to an internal photoeffect at the expense of own absorption of titanium dioxide. The photocurrent emerges also under the action of light quanta with energies below that of the band gap energy and exhibits a characteristic exponential spectral dependence. Weakly doping titanium dioxide with lithium exerts no fundamental effect on its photoelectrochemical behavior and manifests itself chiefly in a decreased quantum efficiency. Inserting considerable lithium amounts makes semiconducting properties of material weaker and photosensitivity disappears. The

^z Corresponding author, e-mail: pridatko@chem.sgu.ru

reverse process of electrochemical extraction of the inserted component leads to the recovery of initial characteristics of the photoeffect. That the photocurrent depends on the electrode potential results from two effects acting in concert, specifically, that the photocurrent depends on the electrode potential and that the material photosensitivity alters at the expense of electrochemical restructuring of titanium dioxide in Li_xTiO_2 .

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research, project no. 02-03-32642; the Russian Federation Agency for Education, projects nos. UR.05.01.035, A03-2.11-390, and A04-2.11-17; and project no. 45166 of the program "Development of High Education Potential".

REFERENCES

1. Churikov, A.V., Volgin, M.A., and Pridatko, K.I., *Electrochim. Acta*, 2002, vol. 47, p. 2857.
2. Churikov, A.V. and Ivanishchev, A.V., *Electrochim. Acta*, 2003, vol. 48, p. 3677.
3. Churikov, A.V., Volgin, M.A., Pridatko, K.I., Ivanishchev, A.V., Gridina, N.A., and L'vov, A.L., *Elektrokhimiya*, 2003, vol. 39, p. 591.
4. Pridatko, K.I., Churikov, A.V., and Volgin, M.A., *Elektrochim. Energ.*, 2003, vol. 3, p. 184.
5. Ivanishchev, A.V. and Churikov, A.V., *Elektrochim. Energ.*, 2003, vol. 3, p. 174.
6. Churikov, A.V., Zobenkova, V.A., and Pridatko, K.I., *Elektrokhimiya*, 2004, vol. 40, p. 67.
7. Zobenkova, V.A. and Churikov, A.V., *Elektrochim. Energ.*, 2004, vol. 4, p. 29.
8. Churikov, A.V., Zobenkova, V.A., and Gamayunova, I.M., *Elektrokhimiya*, 2004, vol. 40, p. 115.
9. Churikov, A.V., *Elektrokhimiya*, 2002, vol. 38, p. 120.
10. Churikov, A.V., *Elektrokhimiya*, 2001, vol. 37, p. 202.