

POTENTIAL STEP STUDY OF INTERCALATION PROCESSES

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Intercalation processes are the processes with strong nonlinearities of their thermodynamic and kinetic parameters. That's why a method of intercalation processes study must be adaptive to these features. In this regard, potential step method [1] has many preferences. By means of each step chronoamperometric curve analysis one can obtain potential – composition relation in differential or integral forms. In additional, there is an opportunity of calculation of diffusion coefficient – potential dependence.

We used potential step method to the study of lithium intercalation in ferritic-carbon alloys from acetonitrile 1M LiBF₄ electrolytes, cathodic hydrogen insertion in titanium alloys, intercalation processes, which accompanying cathodic dispergation of platinum in alkaline electrolytes, anodic oxidation of nickel and nickel oxide powders.

In generally, data treatment scheme is showed on fig. 1. By integrated of each step current-time dependence, one can obtained coulombic - potential function, Q(E) and its differential form, dQ/dE. As Q is proportional to intercalation stoichiometry, x, in M_xA, differential form is sensitive to the specific points of intercalation process. From j(t) function it is possible to obtain insertion particle diffusion coefficient of each potential step, using a well-known equation: $i(t) = Q\sqrt{D/\pi \cdot t}$.

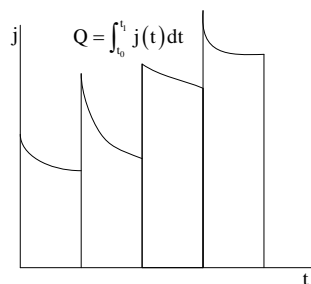


Fig.1 Data treatment scheme of potential pulse study.

The coulombic – potential differential form (fig. 2a) has several separate region, which is connected with energy of host deformation and intercalated particle repulsion [2]. These regions are different for different hosts.

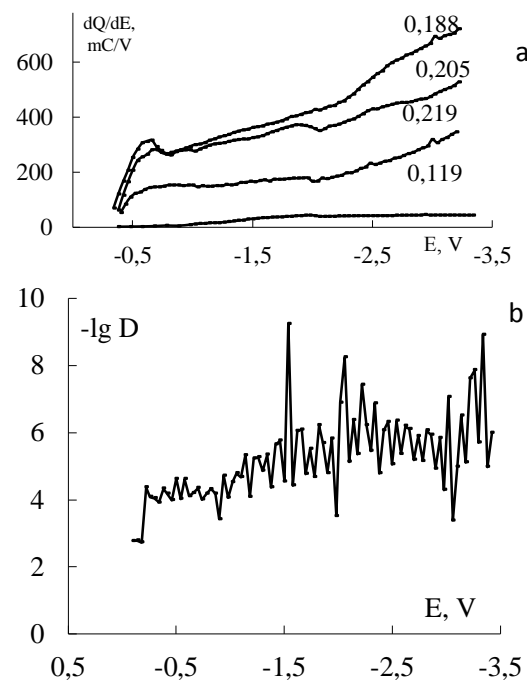


Fig. 2 A results of data treatment of lithium intercalation in carbonaceous steels with different carbon content (numbers near the curves) from acetonitrile 1M LiBF₄ electrolyte: a - coulombic – potential differential form; b – diffusion coefficient versus potential curve. Each potential step was 40mV and 60s long.

A diffusion coefficient-potential function (fig. 2b) is, typically, complex-periodical dependence. This form of function means, that in intercalation process stages of transport in electrolyte, solid phase and vacancy transport periodically replace to each other.

Thus, potential step study of intercalation processes, is a technique of both thermodynamic and kinetic investigation of intercalation study.

1. A.H. Thompson , Phys.Rev.Let. 40 (23) (1978) 1511-1514.
2. Michel Armand , Philippe Touzain, Graphite intercalation compounds as cathode materials, Materials Science and Engineering, 31 (1977) 319-329.