ABSTRACT. Using small-amplitude potential step technique for the study of the graphitic stage 2 (LiC_{12}) to stage 1 (LiC_{6}) transition, 5 distinct domains with different current vs. time relationships were found. The most interesting was a linear increase of current at the beginning of domain II and a decrease in current (with time) within domain IY. This was identified with slow nucleation of stage 1 into stage 2, their growth and further coalescence with the formation of the continuous moving boundary. The characteristic parameters of both these processes were evaluated on the basis of the models proposed.

Introduction

Small-amplitude potential step technique is known to be a very useful technique to observe and quantitatively describe the initial stage of electrodeposition of metals on foreign metallic substrates, namely, the appearance and growth of nuclei of the new phase [1-3]. Another type of electrochemical systems in which nucleation and growth mechanism plays an important role is the formation of intermetallics, which is, in fact, a special case of the heterogeneous solid-phase electrochemical reactions [4,5]. The formation of Li-Al alloy by electrodeposition of Li on Al [8] may serve as a typical example. In this case the phase transformation is accompanied by a change in the rate-determining step, causing a complicated shape of potentiostatic transients related to such processes [4].

Electrochemical insertion of active metal ions (e.g. Li^{+}, Mg^{2+}) into appropriate inorganic hosts may proceed via the formation of solid solutions or first-order phase transitions. In the latter case nucleation phenomena can be observed experimentally. For instance, phase transitions during electrochemical Li-ion insertion into graphite [6-8], Li_{x}Mn_{2}O_{4} spinel [9] or Mg-ions insertion into Mg_{x}Mo_{6}S_{8} Chevrel phase [10]) start with a slow growth of nuclei of a new (more rich in ions content) phase in the bulk of the old one (which is more diluted). This was identified by characteristic rising current transients in response to potential steps, similar in shape to current transients related to both cases of electrocrystallization of metals from liquid electrolyte solutions or the formation of intermetallic alloys. However, to the best of our knowledge, only brief, qualitative descriptions of current transients related to nucleation processes during intercalation of ions into host materials, appear in the literature.

In a series of recent papers [11,12] we presented the results of careful measurements and modeling of the chronoamperometric responses of lithiated graphite electrodes at different temperatures which describe the nucleation of stage 1 (LiC_{6}) in the bulk of the stage 2 (LiC_{12}), and the formation and further advancement of the moving boundary between the two-coexisting phases. Potentiostatic current transients related to LiC_{12} → LiC_{6} phase transition at four different temperatures were analyzed by the use of appropriate models for nuclei growth and moving boundary between the two phases which are formed during intercalation of Li into LiC_{12}. The lateral growth velocity of the nuclei and the velocity of the moving boundary as well
Experimental

Highly resolved potentiostatic intermittent titration (PITT) data for ions intercalation electrodes can be obtained with the use of thin composite electrodes of relatively small mass. Coin-type cells are very convenient for electroanalytical characterizations of ion-insertion electrodes (IIEs). The cells were standard 2032 coin-type cells (NRC, Canada), containing a composite graphite working electrode (of a geometric surface area of 1.5 cm$^2$), Li counter and reference electrodes. The separator was a Cellgard Inc. polypropylene membrane placed between the Li counter- and reference electrodes (CE and RE, respectively), whereas a thin sheet of glassy paper separated the working (WE) and the reference (RE) electrodes. A thin strip of Li RE was pressed onto a Ni wire and was isolated from both the electrodes and the stainless steel framework by a thin polypropylene tape (for details see refs. [6]). The preparation of thin composite graphite electrodes has been described previously [6,7]. The electrodes contained ~1.8 mg of graphite powder (KS-15 from Timrex Inc.) and 10% (by weight) of PVdF binder. The cells were constructed under a highly pure argon atmosphere in VAC Inc. glove boxes, and were hermetically sealed by a standard crimping device (NRC, Canada) and were additionally isolated from atmospheric contaminants with epoxy glue. The cells were thermostated at required temperatures.

The electrolyte solution was 1M LiPF$_6$ in a mixture of ethylene carbonate (EC) + dimethylcarbonate (DMC) 1:1 (Li-battery grade from Merck, KGaA).

PITT was applied using a computerized potentiostat-galvanostat Model 20 Autolab, from Eco Chemie, Inc., which included a FRA module. The collection of data was controlled by the GPES Version 4.9 Eco Chemie B.V. Software (Utrecht, The Netherlands).

The potentiostatic titration of graphite electrodes was performed by potential step from 0.085 to 0.080 V (vs. Li/Li$^+$) during 10 hours, in which LiC$_{12}$ (stage 2) is quantitatively converted to LiC$_6$ (stage 1).

Results

Figure 1 shows a typical chronoamperometric response obtained from a composite graphite electrode at the beginning of stage 2 to stage 1 transition. Typically, five different domains are clearly seen in this figure. In the first, short-time domain denoted as I, the current drastically decreases, reaching a minimum, and then increases strictly proportional to time (domain II). A broad maximum of current is observed at the boundary between the domains II and III, and then the current starts gradually to decrease in domain III. This decrease continues within domain IV, marked by an increase in $-dI/dt$, and finally, the current drops to a very small value at longer times, when the electrode reaches complete equilibrium with Li ions in the solution at the applied potential of 0.080 V (domain V marked by a decrease in $-dI/dt$). Domains I, II and III are well-separated (by minimum and maximum in current, respectively, see Fig. 1), whereas the boundaries between domains III, IV and V were obtained from the application of a moving boundary model, as was previously reported.

The initial decrease in current in domain I can be only partially ascribed to the double-layer charging due to the potential step, since the usual time constant related to
double layer charging, is of the order of a few milliseconds, whereas the duration of
domain I is much longer, about 220 s. Hence we assumed that the initial phase, stage
2 (i.e. LiC_{12}) is first saturated with the inserted Li-ions, so that nuclei with a
subcritical size may form after this saturation. These subcritical size nuclei have a
limited probability to be formed. Then, they coagulate to form larger size,
supercritical nuclei. The current in domain I reflects this scenario and thereby
decreases relatively slowly as the subcritical LiC_6 nuclei reach the maximal
concentration that stage II can contain.

We suggest that the growth of the supercritical nuclei, accompanied by an
increase in their surface area is the reason for the increase in current measured in
domain II (see Fig. 1). These supercritical nuclei are formed in the electrode near its
boundary with the electrolyte solution, gradually increase in their size, overlapping
with each other, and finally, form a continuous phase (stage I). This phase is located
between the contact of the electrode with the electrolyte solution and the boundary
between the two co-existing stages 1 and 2 in the electrode bulk. We should mention
that Li-graphite electrodes are never bare in non-aqueous Li salt solutions. They are
covered by surface films which comprise solution reduction products (insoluble Li
salts, and, apparently, polymeric species). The latter boundary changes in time, thus it
is, in fact, a moving boundary. As Li insertion proceeds, the interphase boundary
moves into the interior of the particle's bulk, while stage 2 is transformed into stage I.
The related changes of current in time are represented by domains IV and V. The
formation of the moving boundary (from nuclei of the new phase) is believed to occur
in the vicinity of the maximum current in the chronoaamperometric curve in Fig. 1, i.e.
starting from the boundary between the domains II and III and continuing into domain
III.

Since the current within domain II was proportional to time we used the
common electrocrystallization model for growing cylindrical nuclei [1,4] (far from
their overlapping within the graphite particles):

\[ I = \frac{2nFbA}{M}(\pi N_o a^2)t \]  

where \( n, F, A \) and \( M \) are the number of electrons, participating in the insertion
reaction, the Faraday number, active surface area of the electrode and atomic mass of
the inserted Li, respectively. \( N_o \) is the total number of nucleation sites in the
"nucleation layer" of the electrode, and \( a \) is the lateral growth velocity (in cm s⁻¹). The
physical meaning of \( b \) requires special consideration. This quantity defines a mass per
surface unit characteristic of the first insertion layer of Li ions, proportional to its
thickness \( h \) and to the specific density of Li ions in stage 1, \( \rho_{Li/1} \), and can be readily
obtained from chronocoulometric data:

\[ b = \frac{V}{A} \rho_{Li/1} = \frac{\Delta Q M}{nFA} \]  

Combination of Eqs. 1 and 2 results in estimation of the product \( N_o a \) whereas
an additional assumption on the calculation of \( a \) allows for separation between \( N_o \) and
and \( a \), and in addition, provides information about the characteristic nucleation time
constant \( \tau_n \) and the thickness of the layer, \( d_1 \) in which nucleation and growth of the
nuclei take place. Front view of growing cylindrical nuclei is presented in Fig. 2a
whereas the thickness of this layer, resulting finally in the development of a
continuous phase boundary is shown in Fig. 2b.

The characteristic nucleation time constant (at 30°C) was found to be \( \tau_n = 990 \)
s; the density of nucleation sites is \( N_o = 2.5 \times 10^8 \) cm⁻², the velocity of the lateral
growth of cylindrical nuclei is $a = 3.6 \times 10^{-8} \text{ cm s}^{-1}$ and the thickness of the nucleation layer is $d = 0.36 \mu m$. These values are not too far (by orders of magnitude) from similar parameters for the deposition of CdSe from Cd(II)-selenosulfite solution [13]: $1920 \text{ s}, \sim 10^{10} \text{ cm}^2$, $(1 - 4) \times 10^{-9} \text{ cm s}^{-1}$ and $0.025 - 0.08 \mu m$, respectively. The lower number of the successful supercritical nucleation clusters, characteristic of the phase transition in the graphite electrodes, than that for the classical deposition reactions from liquid solutions, can be tentatively ascribed to a highly ordered structure of the host matrix of the graphite particles.

**Conclusion**

Using simple electrodeposition models we were able to estimate for the first time the parameters of the nucleation and growth process during first order phase transitions in ion-insertion electrodes. Further studies should be important to refine the mechanisms of nucleation and moving boundary formation in the case of ion-insertion electrodes. This may be closely related to the improvement of cycling ability of such electrodes since the nucleation and growth processes are repeatable each cycle.

**REFERENCES**

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Fig. 1. A typical chronoamperometric response of a graphite electrode (30° C), related to the LiC₁₂→LiC₆ transition (stages 2→1), due to the application of a potential step from 0.085 to 0.080 V (vs. Li/Li⁺). Five characteristic domains are indicated. The division is explained in the text.

Domain II: instantaneous nucleation and growth of stage 1 in the bulk of stage 2 via cylindrical clusters

Moving boundary (compatible with the Cottrellian approach?)

Fig. 2. Front view (a) and view from the side (b) of growing nuclei (other details are shown in the figure).