

Electrochemical Behavior of Intermetallic Compounds during Insertion/Dissolution of Lithium

Guterman Vladimir,¹ Lee Sang Mock¹ and Ozeryanskaya Viktoria²

¹Samsung Advance Institute of Technology
SAIT, Box 111
Suwon 440-600
Korea

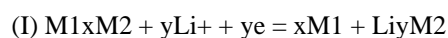
²Department of Electrochemistry, Rostov State University
Zorge street, 7
Rostov-on-Don 344090
Russia

Recently intermetallic compounds (IMC) are considered as perspective components of multiphase anode materials for secondary lithium batteries. Systems, which have a vital importance for practical use, obviously, must show strong structural relationship between a parent structure and its lithiated product. Nevertheless, division of IMC into different "structural" groups can be amplified with other types of classification. For consideration of the possibility of different phase transformation, it is convenient to classify two-component IMC into three groups by the nature of components: group-I - "reagent 1 - reagent 2" (reagent is the metal, which can form Li compounds), group-II - "reagent - inactive metal" and group-III - "inactive metal 1 - inactive metal 2".

We studied kinetics of Li insertion and dissolution while in the process of phase transformations of IMC electrodes, which composed with Group-I (InBi, In2Bi) and Group-II (Mg2Sn, Al2Cu, AlNi, Al3Mg2, Cu5Cd8, MgCd, MgCd3, Mg2Zn3, MgZn2) in nonaqueous solutions of lithium salts. New data, showing the influence of composition and nature of IMC to the lithium diffusivity into primary solid solutions, are obtained as continuous of our previous results.

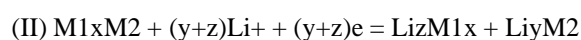
Initially, lithium insertion, limited by solid phase diffusion, is accompanied by formation of solid solution of lithium into IMC surface layer. Lithium diffusivity (DLi) reduces more than one order for Al3Mg2 compare to AlNi and Al2Cu1. Among studied Cd intermetallic compounds, MgCd shows the lowest lithium diffusion rate. But DLi in MgCd3 is higher, than that of both Cd and Mg. Meanwhile, MgZn2 electrode shows quasi-low polarizability during lithium insertion, which differs from that of Zn, Mg and Mg2Zn3.

When lithium supersaturates its solid solutions, a layer of pure lithium is forming on the Mg2Al3, and NiAl cathode surface, however, the reaction of solid-state displacement^{1,2} takes place for the other IMC which we have studied. The solid-state displacement of Group-II yielded lithium-reagent(LiyM2) and inactive metal(M1).



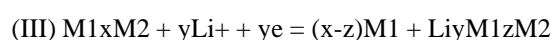
(for CuAl2, Cu5Cd8, MgCd, MgCd3, Mg2Sn, MgZn2 and, sometimes, Mg2Zn3)

For the Group-I IMC, new compounds Li-reagent produced.



(for InBi, In2Bi)

For some IMC, intermediate reactions may take place.:



A possibility of solid phase displacement reactions is de-

termined by hardness of a crystal lattice of initial IMC and volume concentration of a metal- reagent in the IMC. A formation of LiyM2 by lithium insertion into Group-II IMC is more difficult than the same process of corresponding metals-reagents (Al, Sn, Cd or Zn). Reversibility of some reactions with I and II types must protect the "body" of composite anode from reagent dissipation during cycling and must increase conductivity of active electrode material.

The study of Cd and Zn compounds' behavior determines that change of IMC composition can be used for regulation of phase transformations in the M1-M2-Li system. For example, during the lithium insertion into Cu5Cd8 and pure Cd consecutive formation of compounds LiCd3 - LiCd - Li3Cd occurs. But lithium insertion into MgCd3 gives LiCd and Li3Cd and MgCd gives Li3Cd, respectively. Cyclic voltammetry and cronopotentiometry data show that number and intensity of phase transformations of Mg2Zn3-(Li) system is less than those of MgZn2-(Li) alloy.

Efficiency of selective lithium dissolution during discharge depends on the nature of intermetallic parent compounds appreciably. It is related with peculiarities of lithium diffusion into the depth of electrode during preliminary insertion, especially, for the electrodes with thickness of 3 ~ 4 mm. For example, efficiency of lithium dissolution in the first discharge (after electrode charge by Q=0,5 C/sm2) was 30-40% for Cd-(Li), Cu5Cd8-(Li), MgCd-(Li) and only 3-8% for MgCd3-(Li).

With comparison of lithium insertion/dissolution kinetics between IMC and the corresponding their pure metals, the analysis results of phase composition of formed alloys allow us to consider that one of IMC components is the main metal, which determines electrochemical behavior of compound in general. At the same time, some properties of IMC, including an ability to form low concentration lithium compounds appreciably differ from corresponding pure metals. Diffusion penetrability of IMC for lithium can be anomaly high (MgZn2, MgCd3).

A combination of structural variety of IMC, big amount of its possible components, abilities of regulation of their properties, a presence of methods for creation composite materials with dispersed IMC particles, make these alloys perspective materials for lithium batteries.

References

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