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Laminated composites based on polyacetylene and Al–Mg alloy negative electrode materials for Li rechargeable batteries

O.N. Efimov, D.G. Belov, G.I. Kozub, L.I. Tkachenko, L.P. Krinichnaya, G.N. Petrova

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

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Abstract

The procedures of the preparation of laminated polyacetylene (PA)–Al–Mg and PA–microporous polypropylene (PORP) composites are developed. The electrochemical behaviour is studied under the conditions of Li^+ intercalation. It is shown that PA application on a metal surface facilitates the formation of Li–Al–Mg alloy. The composites can be used as materials for negative electrodes in Li batteries.

Keywords: Polyacetylene; Alloy; Electrodes; Lithium; Batteries; Composites

1. Introduction

Because of poor cycleability of the Li electrode and possible shortings caused by dendrite growth, Li alloys or materials based on conducting polymers, namely, polyacetylene (PA) and poly(*p*-phenylene) (PPP) [1], were suggested as materials for a negative electrode in Li rechargeable power sources (batteries). However, the electrodes become brittle and destroyed because of a dimensional instability of Li alloys [2], and PA and PPP have a relatively low capacity as compared with Li electrode. Shacklette et al. [3] developed composite electrodes composed of a dispersion of Li alloy and conducting polymers, thus eliminating shortcomings inherent to negative electrodes based on Li and its alloys.

In our work we use the same approach, but the main goal is the design of laminates, in which the conducting coating over the Li electrode or its alloy performs as a thin selective membrane with Li^+ conductivity. This avoids electrolyte decomposition and dendrite growth since the direct electrode–electrolyte contact is excluded in this case. On the other hand, a high capacity of the Li electrode is maintained. In addition, PA film applied on Li alloy acts as a protective layer which prevents the mechanical destruction of the electrode.

2. Experimental

2.1. Preparation of laminated PA–Al–Mg composite [4]

An Al–Mg foil was used as a substrate. According to Auger spectroscopy data its rough surface layer contained (at.%): Al, 67.0; O, 23.0; Mg, 5.5; C, 3.0; Ca, 1.5. A foil surface was wetted by a viscous catalyst solution, prepared by mixing polyisobutylalumoxane (PIBA) (5×10^{-3} mol, m.w. 900) with tetrabutoxytitanium (5×10^{-3} mol) under argon without using any solvent. Acetylene polymerization was carried out for 15 min at −78 °C under 700 Torr. An intact PA coating was very adherent to the Al foil surface. Coating thickness constituted $(15–25)\times10^{-6}$ m. The sample was washed with toluene and dried under vacuum.

2.2. Preparation of laminated Al–Mg–PA–microporous polypropylene (PORP) and Li–PA–PORP composites

The method of preparation of a skeletal PA–PP composite as film by polymerization of PA in a microporous polypropylene film 'PORP' (material analogous to Celgard) was developed for improving physical-mechanical properties of PA coating and its application directly onto the Li electrode. PORP has a thickness of 20×10^{-6} m, 53% porosity, effective pore diameter 0.03×10^{-6} m and is used as a separator in Li batteries. PORP film was impregnated with Shirakawa catalyst [5] and acetylene polymerization was carried out for 15–20 min at room temperature under 500–600 Torr. PA was formed both inside the pores and on the surface of PORP. The resulting film was washed with toluene and dried in vacuum. PA content in PORP film was 10–45 wt.%, depending on catalyst concentration and polymerization duration. PA–PP film was more elastic as compared with pure PA film and it was pressed directly onto both sides of an Al–Mg or Li electrode.