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ScienceDirect
Progress in Solid State Chemistry 36 (2008) 213–222
Progress in Solid State Chemistry
www.elsevier.com/locate/pssc

Overview on the intercalation reactions of lithium alloys into graphite

Nicolas Emery [a], Claire Hérold [a,*], Philippe Lagrange [a,b]

[a] *Laboratoire de Chimie du Solide Minéral – UMR CNRS UHP 7555, Université Henri Poincaré Nancy I, B.P. 239, 54506 Vandœuvre-lès-Nancy Cedex, France*

[b] *Ecole Européenne d'Ingénieurs en Génie des Matériaux, Institut National Polytechnique de Lorraine, 6, rue Bastien Lepage, B.P. 630, 54010 Nancy Cedex, France*

Abstract

Lithium intercalates easily into graphite either by chemical way or by electrochemical way. This well-known reaction leads to the first stage LiC_6 binary compound. However, it is more difficult to prepare a ternary compound by intercalation of a lithium alloy. This is mainly due to thermodynamical causes.

Nevertheless, it has been observed that a few well-chosen alloys (Ca–Li and Eu–Li) are able to intercalate into graphite. Calcium and europium have been used for well defined reasons. Although in these alloys both metals present are able to intercalate by themselves, the intercalated sheets are poly-layered. This observation is entirely original, but it can be easily explained.

On the other hand, it has been established that, using well-chosen lithium alloys, calcium and europium can also intercalate alone into graphite, leading to the corresponding binary phases. In these occasions, lithium appears essentially as a factor able to promote the melting of the second metal and its intercalation by a preliminary spreading of the graphene planes.

Keywords: Lithium; Calcium; Europium; Graphite intercalation compounds; Crystal structure; Superconductivity

Contents

* Corresponding author.
E-mail address: Claire.Herold@lcsm.uhp-nancy.fr (C. Hérold).

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doi:10.1016/j.progsolidstchem.2008.07.002

1. Introduction

The reaction between lithium and graphite was observed for the first time in 1955 by Hérold [1]. Heated under vacuum at 500 °C with lithium, natural graphite platelets became gold yellow and the as-formed product reacted with water leading to a release of acetylene and hydrogen. The precise formulas of the graphite intercalation compounds of lithium were given 10 years later by Juza and Wehle [2], in particular that of the first stage LiC_6. Finally its crystal structure was determined in 1975 by Guérard and Hérold [3]. The 1990s showed a large expansion of the research on lithium–carbon systems in the field of electrochemistry in order to use these materials as negative electrodes in the Li-ion batteries.

Among the alkali metals, lithium is quite different from the others and its ability to intercalate into graphite too. In contrary to sodium and heavy alkali metals, lithium leads to ternary compounds only with a few elements.

In this paper we show the particularities of lithium as a metal and as an intercalate into graphite too. It is then possible to explain almost partially the difficulties to synthesise ternary compounds containing lithium.

2. The particularities of lithium among the alkali metals

Lithium, as numerous heads of columns of the periodic table, is quite different from the other elements following it in its column. Indeed, the lithium atoms are very small, and especially the lithium cations whose ionic radius is close to 60 pm. This value is less than half of the corresponding one for potassium. Besides, it is the lightest element among the solid ones. There are more than 80 °C between its melting point and that of sodium, the following element in the column, whereas the difference between the melting points of two following elements belonging to this column never exceeds 35 °C. Concerning its chemical properties, its reactivity with nitrogen is specific to lithium among the alkali metals. Its ability to react with graphite is also quite different.

3. The originality of lithium–graphite intercalation compounds

Heavy alkali metals intercalate into graphite leading easily to first stage binary graphite intercalation compounds MC_8 [4]. With sodium, only high stage compounds can be prepared [5]. The case of lithium is different since first stage compounds can be synthesised either by chemical or electrochemical way. Besides the formula of this compound is LiC_6. This fact can