

Synthesis and Electrochemical Behavior of Superdense LiC₂ Prepared by Ball-milling

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Introduction

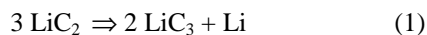
Superdense lithium carbon intercalation compounds (GIC) Li_xC₆, with x as high as 3, are usually prepared (1) under rather drastic temperature and pressure conditions (300°C, 50 kbars). The compounds are metastable and tend to decompose after pressure release following a rather complex path that ends with formation of LiC₆. Electrochemical de-intercalation of lithium from LiC₂ under the usual conditions found in lithium-ion batteries results in a theoretical capacity three times higher than that of LiC₆: 1115 mAh/gr computed on the graphite weight (2). This capacity is not recovered during the following cycles because, under normal electrochemical conditions, only LiC₆ is formed.

In this paper the synthesis by insertion of lithium into graphite by direct ball milling is described. The products have been characterized by ⁷Li NMR, X-ray diffraction and density measurements (3). A preliminary electrochemical investigation as anode in lithium-ion batteries is also presented.

Results and discussion

A planetary mill Retsch, mod. PM 400 equipped with stainless steel vials and balls, has been used to ground mixtures of natural graphite (Ceylon type by Alfa) and lithium powder under different experimental conditions. The best results have been obtained by milling for 12 hours a mixture of Li and carbon in molar ratio 1 : 2 at a rotation rate of 200 rpm. The product is a yellow powder with slight greenish brightness stable for months (see below) at ambient conditions if protected from atmospheric contamination.

Density measurements performed using a pycnometer with water-free oil as dispersing medium results in a density value of 1.85. This value, is very close to 1.93: i.e. the theoretical density that may be computed for a mixture of LiC₃ and Li resulting from a reaction of the type



The result clearly indicates that the milling process leads to a superdense phase.

The X-ray pattern of a ball-milled powder of formal composition LiC₂ results in a spectrum in which all the reflections are indexable in the hexagonal unit cell of LiC₆ with an a parameter of 430 pm and c = I_c = 370 pm (4). No reflection relative to metallic lithium is observed.

⁷Li NMR spectroscopy has been performed at different temperatures. The spectra, can be interpreted in terms of formation of a mixture of LiC₆ and of a superdense phase such as Li₈C₂₄ (LiC₃). Integration of the area under the peaks gives an 8:1 ratio between LiC₃ and LiC₆ consistent with an equation of the type



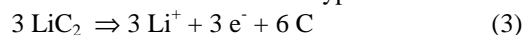
for which the calculated density is 1.83, very close to the

one measured by pycnometry. Equations (1) and (2) are not in contradiction as ⁷Li NMR (5, 6) shows the presence of LiC₆ and allows a better description of the powder. Free lithium is not detected from the NMR because it is probably present in aggregates of nanometric size.

Electrochemical results

The electrochemical performances of ball-milled compounds of formal composition LiC₂ have been tested by galvanostatic charge/discharge and slow scan rate cyclic voltammetry.

Fig. 1 shows the first galvanostatic deintercalation-intercalation cycle (current rate 100 μA) together with the differential capacity curve (dq/dE vs.E). The deintercalation capacity in the first cycle is of the order of 950 mAh/gr very close to the theoretical value for an overall electrochemical reaction of the type



During the successive intercalation roughly only 1/3 of the capacity delivered during the first cycle is obtained, which is consistent with formation of first stage LiC₆.

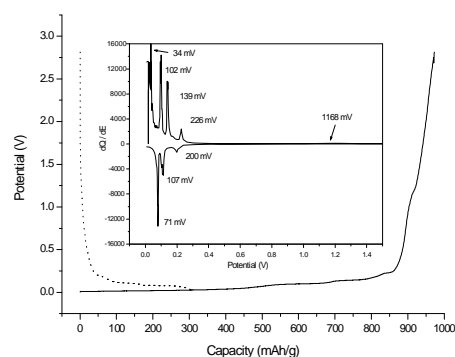


Fig. 1 . Galvanostatic deintercalation (—) intercalation (···) profiles of an electrode of formal composition LiC₂ prepared by ball milling. The insert shows the differential capacity curve.

The behavior is the same found for high pressure prepared LiC₂ (2). No evidences are present in the galvanostatic curves for SEI formation. The wave, at about 1.1 V, has been proved to be connected with some kind of contamination of the compound by the glove-box atmosphere (presence of O₂ or N₂).

Most of the lithium is deintercalated at potentials below 50 mV (see peak at 34 mV in the insert). This deintercalation corresponds to desorption of lithium aggregates or better to deintercalation of some kind of superdense 2D lithium layers. The other peaks on the deintercalation curve and the corresponding three peaks on the reverse process occur at the potentials found during staging transitions from LiC₆ to graphite and reverse.

References

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