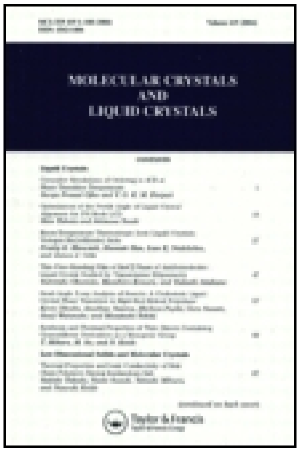

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Intercalation of lithium hydride into graphite and electrochemical behavior

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The lithium hydride does not intercalate by itself, on the contrary, the reaction of hydrogen in LiC_6 leads to a mixture of LiH and high stages lithium intercalated compounds. However, in the presence of a heavy alkali metal (potassium or cesium), LiH intercalates to give quatenary phases M_2LiHC_{8s}, s being the stage. Those compounds contain large amounts of intercalated metal per carbon atom ($M/C = 3/8s$) and may be interesting as electrode material for secondary batteries.

Keywords : Alkali hydrides; Intercalation; Electrochemistry

INTRODUCTION

The compounds based on lithium are of some interest for the possibility to use them as anodes for secondary batteries instead of pure lithium metal which tends to form lithium dendrites during the charge-discharge cycles. Those dendrites are responsible for short-circuits [1].

Many studies can be found in the literature aimed to increase the capacity of carbon anodes in lithium batteries. The amount of intercalated lithium can reach up to LiC_2 when the metal is intercalated under high pressure but LiC_2 readily reacts in lithium containing solvents. This limits[2] to LiC_6 the maximum amount of lithium that can be electrochemically intercalated-deintercalated in graphite. The lithium amount and the corresponding capacity of anodes can be increased by using high specific area disordered carbons in which the graphene layers are built as a card house [3]. Once more, the intercalation is not reversible and the passivation layer becomes very important. This is probably connected to the presence of impurities (i.e. H_2) which favors the intercalation but inhibits reversibility [4].

We have prepared very rich metal content compounds by co-intercalation of LiH and potassium : K_2LiHC_{8s}, with the stage s = 1 to 4. It was very exiting to try to use such compounds as anodes for secondary batteries [5]. On the other hand, such quaternary phases can be obtained with cesium in place of potassium.

EXPERIMENTAL

The hydrogen reacts at 100°C with the first stage MC_8 compounds with M = K or Rb and leads to ternary second stage phases $MH_{2/3}C_8$ in which the metallic layer migrates in half of the planes and superimposes. When the metal is cesium, there is no reaction, which accounts for a higher stability of CsC_8 [6]. The compound LiC_6 reacts with hydrogen at room temperature and leads to a mixture of LiH and high stage lithium intercalated into graphite [7].

This is due to the very high heat of formation of LiH compared to that of the other alkali metal hydrides, as shown in table 1.

Table 1 : Enthalpy of formation of the different alkali metal hydrides[8]

	LiH	NaH	KH	RbH	CsH
ΔH_f (kcal/mol)	-44	-13.94	-14.11	-12.08	-13.48

The intercalation process involves a first step in which the alkali metal (coming from the partial decomposition of the hydride) intercalates alone and leads to binary phases. The second step consists in the intercalation of both alkali metal and hydride, the final compound being the ternary $MH_{0.8}C_{4s}$ with M, a heavy alkali metal. This first step cannot take place with the lithium hydride LiH since it does not dissociate up to 700 °C. On the contrary, the presence of a heavy alkali metal makes this first intercalation possible and, then, LiH can intercalate, as it was shown with potassium [5]. This "assisted" intercalation of LiH is obtained with cesium and the resulting quaternary phases Cs_2LiHC_{8s} are prepared at 500 °C, in the presence of 43% in weight of cesium. HOPG platelets are "immersed" in a large excess of the cesium (43% in weight) and LiH mixture.

The following table shows the conditions of synthesis with potassium and cesium.

Table 2 : Synthesis conditions of quaternary phases with potassium and cesium

	Temperature (°C)	M/LiH % (weight)	M/LiH % (atomic)	Stage
Potassium	420 - 500	35	1/9	1-4
Cesium	500	43	1/22	2, 3

The fact that one needs for cesium a lower amount than for potassium is in good agreement with the relative affinities towards graphite.

The chemical compositions were determined by weight uptake, chemical analysis and confirmed by x-rays. They correspond to the general formula M_2LiHC_{8s} s being the stage : 1 to 4 with potassium, 2 or 3 with cesium.

The XRD show interplanar distances of 8.92 Å and 10.03 Å respectively, values close to that of the corresponding ternary phases : 8.53 Å for $KH_{0.8}C_4$ and 10.03 Å for $CsH_{0.8}C_4$ [9]. The unit cell, hexagonal with a = 4.95 Å, c = $2*I_c$ = 17.84 Å for the first stage with potassium, is very large with cesium : orthorhombic with a = 17.91 Å, b=27.07 Å and c = 13.38 Å for stage 2.

ELECTROCHEMISTRY

Previous studies of potassium intercalation compounds dealt with the test of KC_8 as precursor of an improved graphite electrode for lithium-ion batteries[10-11]. It was demonstrated that KC_8, upon polarization toward positive potentials, irreversibly deintercalates potassium leaving a "graphite-like" electrode that, on subsequent cycles performs as natural graphite with the advantages of an improved kinetic. One of the surprising property of KC_8 derived electrodes is the absence of any evidence for the irreversible capacity loss characteristic of the first cycle of graphite electrodes and connected with formation of the so called Solid Electrolyte Interface (SEI)[2].

The maximum theoretical capacity of KC_8 electrodes in lithium-ion cells depends on the type of cathode used. The limiting capacity that may be obtained when using a lithium-free cathodic material, such as V_2O_5, is 279 mAh g^{-1}, i.e. the capacity associated with the initial potassium deintercalation process. The possibility to exploit all the available graphite capacity requires the use of a cathodic material containing enough lithium to compensate for the different stoichiometry of KC_8 and LiC_6, i.e. 1/3 lithium excess (referred to 1 mole of KC_8)[10].

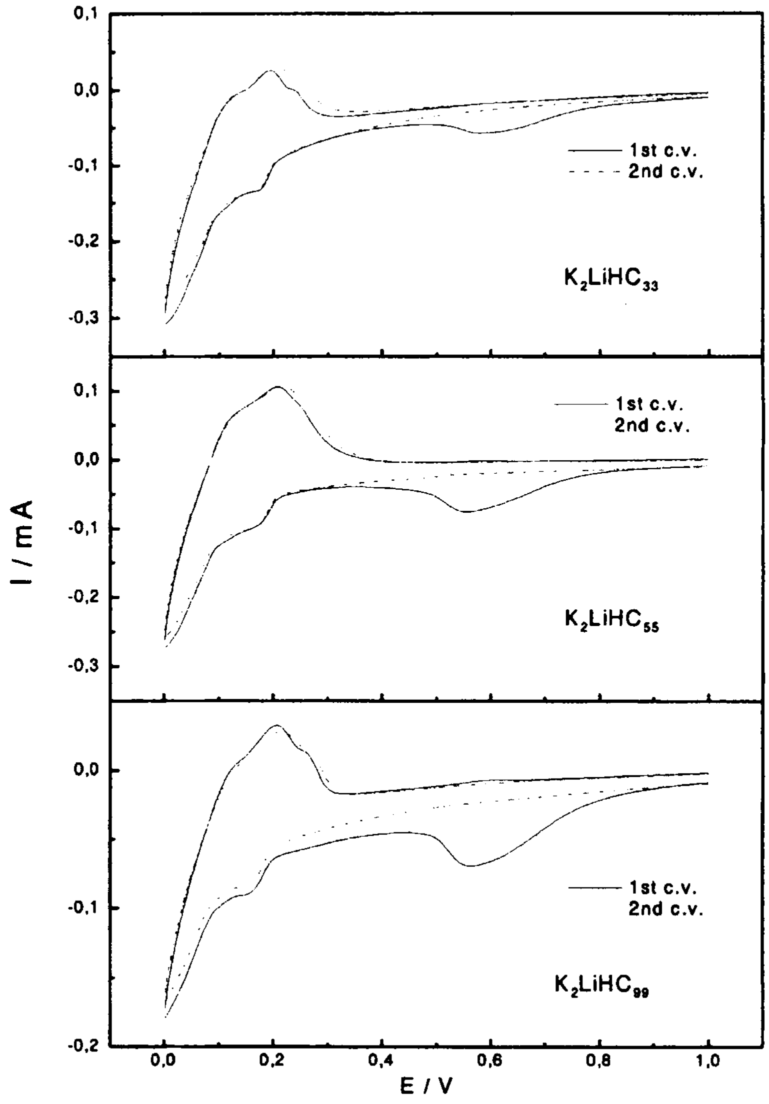

Fig.1- Cyclic voltammograms of different compounds. Scan rates 1 mV/s.

Because of the high metal content, in the attempt to increase the available capacity, it seemed attractive to check the potassium compounds K_2LiHC_{8s} as secondary battery electrode. Two types of experiments have been performed : slow scan rate cyclic voltammetry and galvanostatic charge-discharge cycles. In all cases the electrolyte was a 1 M $LiClO_4$ solution in ethylene carbonate : dimethyl carbonate (1:1 weight ratio) using lithium metal as reference and counter electrodes. The cyclic voltammetric experiments were performed using a Pt button (3 mm diameter) electrode onto which the compound of interest was attached by rubbing. For galvanostatic studies a pellet electrode was obtained by pressing the compound at 5 ton cm^{-2} onto a copper current collector. The pellets was inserted into a spring-loaded button cell using Celgard 2400 from Hoechst as separator.[10]

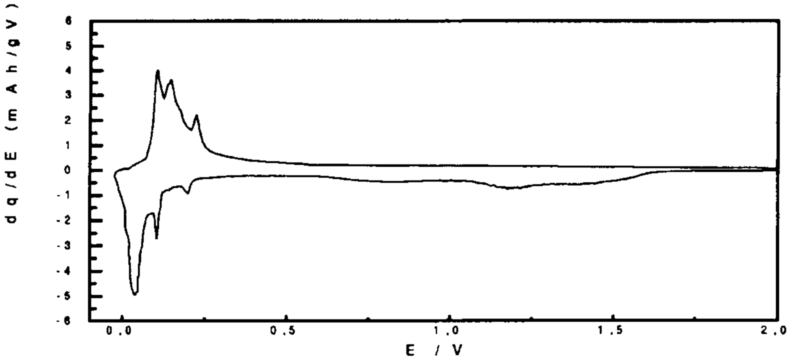

Fig. 2- dq/dE plots for the first charge-discharge cycle of a K_2LiHC_{33} electrode in 1M $LiClO_4$ EC-DMC electrolyte

Fig. 1 shows three cyclic voltammograms relative to K_2LiHC_{8s} compounds having nominal composition : K_2LiHC_{33}, K_2LiHC_{55} and K_2LiHC_{99}, respectively. Only the potential range 0-1V is shown because the voltammograms above 1 V do not show any significant feature. The first cycles (full line) show an irreversible reduction wave around 0.6 V vs Li that, by comparison with the corresponding cyclic voltammograms on pure graphite[2], is likely to be due to formation of the solid electrolyte interface. The relative intensities of the waves increase with decreasing metal content, consistently with an electrode that becomes more graphite like in going from K_2LiHC_{33} to K_2LiHC_{55} and K_2LiHC_{99}. The fact that decreasing metal content corresponds to a more graphite like electrode is also consistent with the open circuit voltage vs Li of freshly prepared electrodes that increase in the order KC_8 (0,3-0.4 V)[10], K_2LiHC_{33} (1-1.1 V), K_2LiHC_{55} (1.3-1.4 V) and K_2LiHC_{99} (2.3-2.4 V).

The reversible waves, in the potential region 0-0.2 V vs Li, are due to lithium intercalation. Because of the relatively high scan rate the staging peaks are not well resolved. Staging, as well as SEI formation, results more clearly from Fig. 2 that shows the differential capacity curve (dq/dE vs E) obtained from the first galvanostatic charge-discharge curve of a K_2LiHC_{33} electrode (nominal capacity calculated on the bases of a LiC_6 phase and of the graphite content : 1.5 mAhr, discharge rate 100 µ A). No electrochemical evidence for deintercalation of potassium, as was the case for KC_8, is apparent from the first cyclic voltammograms dq/dE curves. However, the capacity to intercalate lithium on the first cycle is about 50% of the theoretical and increases with the number of cycles to reach values close to 80%. This means an increase of the amount of graphite available for lithium intercalation and seems to be a signature of a progressive deintercalation of the initial potassium and lithium hydride upon extended cycling.

New experiments are in progress in order to confirm these preliminary results, which looks interesting from a practical point of view : the battery application.

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