



Extending the hydrogen storage limit in fullerene



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ABSTRACT

Li_6C_{60} has been chosen as the most representative system to study the hydrogenation mechanism in alkali-cluster intercalated fullerides. We present here a muon spin relaxation (μSR) experiment that hints the chance to achieve a higher storage capacity on fullerene with respect to the values suggested in literature. Moreover, a linear relationship between the muonium adduct radical hyperfine frequency and the level of C_{60} hydrogenation was found and it can be exploited to probe the C_{60} hydrogenation level, giving more credit to this technique in the field of hydrogen storage materials.

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1. Introduction

Hydrogenated fullerenes are mostly studied for their ability to store large quantities of hydrogen, available under mild conditions of temperature and pressure. Recently, they have also been exploited as fluorophores in light emitting diodes, being their energy gap tuneable with the number of chemisorbed hydrogens [1]. Alkali cluster intercalated fullerides recently demonstrated to be fascinating materials for their use in the field of reversible hydrogen storage [2–7]. In these compounds, hydrogen is absorbed through a complex chemisorption process, involving the dissociation of hydrogen molecules operated by the intercalated alkali clusters. The majority of such hydrogen atoms promptly react with the fullerene molecules, thus forming hydrogenated C_{60} (hydrofullerene); subsequently, a minor fraction reacts with the clusters, promoting the partial segregation of a phase of metal hydride as a by-product. It is worth noting that this process is a limiting factor for the hydrogenation of these systems, since the nuclearity of the alkali cluster is reduced, as well as its catalytic activity towards hydrogen dissociation. However, the production of hydride is not completely detrimental, since the de-hydrogenation process

surprisingly appears to be completely reversible, already at moderate thermodynamic conditions. Here, we consider Li_6C_{60} as a model system to investigate the hydrogen absorption properties in this class of compounds. This compound shows a face centred cubic (*fcc*) crystal symmetry, where the octahedral interstices are filled by Li alkali clusters. Li_6C_{60} is able to absorb about 5 wt% H_2 after a 10 h isotherm at 350 °C and 100 bar H_2 (corresponding to about 40 hydrogen atoms per formula unit), with an onset temperature of ~140 °C, virtually reaching the plateau at 5.2 wt% H_2 (about 42 hydrogen atoms per formula unit) for longer isotherm [6,8]. The complete hydrogen desorption is characterized by an endothermic peak, corresponding to a dehydrogenation enthalpy of about 63 kJ/mol H_2 , with an onset temperature of ~270–306 °C, depending on the synthetic route [8,9]. The *in situ* neutron powder diffraction (NPD) study on Li_6C_{60} under deuterium pressure, suggested the initial formation of a stable $\text{Li}_6\text{C}_{60}\text{D}_y$ single phase ($y \approx 8$) starting at around 140 °C. This is followed by the partial segregation of LiD above 200 °C. The subsequent increase of hydrogen chemisorbed on C_{60} brings to a structural transition of the hydrofulleride to a bcc lattice [6].

This experimental behaviour is in contrast with the theoretical model proposed by Wang et al. for the hydrogenated Li_6C_{60} , where the Li atoms should be coordinated to C_{60} pentagons, either inward (*i.e.* near the internal surface) or outward the hydrofullerene molecule, and some of them should be able to bond hydrogen atoms [10].

The absorption kinetics inevitably slows down when Li ions that

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belong to intercalated clusters begin to form the hydride but can be significantly improved by adding small amounts of Pt and Pd to Li_6C_{60} . For the undoped C_{60} , the catalyst promotes the hydrogenation, but the process is not reversible [11]. However, in the alkali doped compound the transition metal catalyst facilitates the H_2 dissociation process, originally driven by the Li clusters, even when their nuclearity is largely reduced due to Li conversion into LiH. The gravimetric storage capacity is related to the number of hydrogen atoms bound to C_{60} and to the amount of metal hydride formed at the expenses of the intercalated Li, following the equation $\text{Li}_6\text{C}_{60} + \frac{y}{2}\text{H}_2 \rightleftharpoons \text{Li}_{6-\alpha}\text{C}_{60}\text{H}_{y-\alpha} + \alpha\text{LiH}$. The hydrogen chemisorption by fullerene occurs through the saturation of the carbon sp^2 hybrid orbitals and the subsequent formation of C–H bonds. Thus, in principle, only an even number of hydrogen atoms can be bound to C_{60} [12]. If lithium did not react with hydrogen, forming LiH (*i.e.* $\alpha = 0$), the hydrogenation degree on C_{60} would lead to $y \approx 42$ (5.2 wt% H_2) and to $y \approx 48$ when Pd is added as catalyst (~ 5.9 wt% H_2).

However, both NPD and nuclear magnetic resonance (NMR) suggest that about 2 M fractions of LiH are formed in Li_6C_{60} following the hydrogenation (*i.e.* $\alpha = 2, y = 40$) [6,13]. In the case of Pt– Li_6C_{60} , whether or not the hydrogenation proceeds with additional segregation of LiH remains unclear. A complete reaction of lithium with hydrogen would lead to $\text{C}_{60}\text{H}_{42} + 6\text{LiH}$. However, the temperature dependence of the NMR spin-lattice relaxation rate ($1/T_1$) in $\text{Pt}_x\text{Li}_6\text{C}_{60}\text{H}_y$ allowed us to estimate $\alpha = 3$, suggesting the formation of $\text{Li}_3\text{C}_{60}\text{H}_{45} + 3\text{LiH}$ (manuscript in preparation). Although as minor species, hydrofullerene molecules with higher hydrogen content, such as $\text{C}_{60}\text{H}_{48}$, have been detected by Teprovich et al. during the study of Li_6C_{60} , [8] suggesting that the hydrogenation extent can be further improved in these systems.

Beyond hydrogen absorption kinetic measurements, muon spin relaxation (μSR) spectroscopy has successfully been exploited to study fullerides and turned out to be a powerful technique to study hydrogen storage materials, other than being particularly suitable to insight the hydrogen chemistry in carbon nanostructures [14–17]. In a μSR experiment, a beam of spin polarised positive muons (μ^+) is implanted in the sample and their spin evolution is measured, as a function of its residence time, by the detection of the outgoing positrons, the latter emitted after the ~ 2.2 μs muon mean life time. During this process, parity conservation is violated causing the positrons to be preferentially emitted in the direction of the muon spin at the time of its decay. Hence, muons act as microscopic probes of the local magnetic fields.

When a positive muon thermalizes into materials having low electronic density, it can bind to an electron forming a light isotope of hydrogen, known as muonium (Mu), which can be hosted in the lattice interstitial spaces, as well as forming a chemically bound species, *i.e.* a Mu adduct radical. Generally, Mu reacts with fullerene forming C_{60} -Mu adduct radicals or endohedral muonium ($\text{Mu}@\text{C}_{60}$, *i.e.* a Mu trapped at the centre of C_{60} icosahedron, showing nearly-free hydrogen features) [18]. A different muon-electron spin hyperfine coupling allows to identify and differentiate these species from an experimental point of view. For a saturated hydrofullerene, the formation of radicals is no longer expected, whilst the existence of $\text{Mu}@\text{C}_{60}$ has not been investigated so far.

In this study, we aim to verify the hydrogenation limit of fullerene by measuring the formation of Mu radical species, exploiting the unique power of μSR technique for the study of hydrogen-storage materials. In particular, we found that μSR signal can be also sensitive to the C_{60} hydrogenation extent, through the modulation of the muon hyperfine interaction with the unpaired electron. Eventually, we show that the reduction of the C_{60} aromaticity upon hydrogenation gradually increases this interaction.

2. Methods

C_{60} (99.95% purity) and C_{60}H_x (where $x \approx 39$, as average of a distribution of hydrofullerenes) powders were purchased from M.E.R. Corporation. Lithium metal (99% purity), platinum (99.99%), and palladium (99.98%) were purchased from Sigma Aldrich. Li_6C_{60} , $\text{Pd}_x\text{Li}_6\text{C}_{60}$, and $\text{Pt}_x\text{Li}_6\text{C}_{60}$ were synthesized by mixing C_{60} and lithium (or the respective LiM_x alloys, where $M = \text{Pd}, \text{Pt}$ and $x = 0.17$ and 0.07 respectively) in a high-energy ball milling (Fritsch Mini-Mill Pulverisette23), as described elsewhere [9]. The non-identical transition metal stoichiometries depend on the different capabilities of Li to give liquid azeotropic mixtures with Pt and Pd metals, however we did not observe a relevant dependence of these stoichiometries on the maximum H_2 absorption values. Hydrogenated Li_6C_{60} , $\text{Pd}_x\text{Li}_6\text{C}_{60}$, and $\text{Pt}_x\text{Li}_6\text{C}_{60}$ were obtained by heating the synthesized compounds at 350°C ($5^\circ\text{C}/\text{min}$ rate, 10 h isotherm) under 100 bar H_2 , in a PCTPro-2000 manometric instrument by Setaram. In order to obtain intermediate levels of hydrogenation on C_{60} , Li_6C_{60} underwent two partial hydrogenations at 190°C (60 bar H_2) and at 280°C (100 bar H_2). X-ray powder diffractions were carried out by means of a Bruker D8 Discover instrument ($\text{Cu-K}\alpha_1$ radiation), working in Debye-Scherrer geometry and equipped with an area detector (GADDS). In case of partially hydrogenated $\text{Li}_6\text{C}_{60}\text{H}_y$ the measurements were carried out on a Xenox Nano-inXider small angle and wide angle diffractometer equipped with an area detector. Glass capillaries were filled with powder and sealed in Ar. The measurements were performed while spinning, collecting data for several hours per frame. The μSR experiments were carried out at the ISIS-Rutherford Appleton Laboratory (Didcot, UK). The 100% spin-polarized pulsed beam of this facility is optimized to study the muon spin evolution over long time-scales. Pt and Pd doped compounds were measured on the Argus spectrometer at the RIKEN-RAL Muon facility. The total experimental muon polarization asymmetry was established to be 23.10(15) %, estimated on a separate transverse field (TF) experiment on pure silver. The baseline, due to muons stopping outside the sample, was measured to be 5.76(11) % of the total polarization at zero field (ZF), whereas its longitudinal field (LF) dependence was measured applying a field in the range 0–3.8 kG and was considered in order to extract the repolarization data. The semi-hydrogenated compounds of Li_6C_{60} were measured on the EMU spectrometer. In that case, the total experimental asymmetry and baseline were estimated to be 23.48(3) and 7.34(5) % respectively. About 200–400 mg of sample was pressed and sealed in an air-tight silver-coated aluminium cell, capped by a kapton window. The muon polarization was followed by plotting the asymmetry function, expressed as $A(t) = \frac{N_b(t) - \alpha N_f(t)}{N_b(t) + \alpha N_f(t)}$, where $N_{b/f}$ is the backward/forward collected counts and α is a geometrical parameter, calibrated for each temperature by fitting the oscillation observed under the application of a 20 G transversal field. Time dependent polarizations were analysed by means of the WiMDA software [19], after correcting for the double-pulsed structure of the muon beam.

3. Results and discussion

The hydrogen absorption runs of $\text{Pt}_x\text{Li}_6\text{C}_{60}$ and $\text{Pd}_x\text{Li}_6\text{C}_{60}$ samples at 350°C and 100 bar H_2 yield to achieve about 5.8 (1) wt% H_2 for both the samples, as shown in Fig. 1(a) and (b) respectively. These values are in agreement with the ones previously reported for Pt and Pd doped Li_6C_{60} [9]. The full hydrogenation of Li_6C_{60} (350°C , 100 bar H_2) is reported elsewhere and leads to 5 wt% H_2 absorbed [9,13]. The hydrogenation of Li_6C_{60} at 190°C and 60 bar H_2 leads to about 1.7 wt% H_2 stored after 10.5 h (Fig. 1(c)), while the hydrogenation at 280°C and 100 bar H_2 allows to achieve about

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