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Synthesis and characterization of mixed sodium and lithium fullerides for hydrogen storage

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ABSTRACT

We herein report on the synthesis of mixed alkali cluster intercalated fullerides $\text{Na}_x\text{Li}_{y-x}\text{C}_{60}$ ($y = 12$; $x = 1-6$) by a two-steps mechanochemical reaction of fullerene with sodium and lithium. These compounds crystallize in the cubic lattice of C_{60} displaying a contracted lattice parameter with respect to the Na_6C_{60} parent structure. The analysis of the hydrogen sorption behaviour shows a slight decrease in the dehydrogenation enthalpy for $y = 12$ with respect to the sodium free member. Raman spectroscopy highlighted a partial electron transfer from alkali metals to C_{60} , suggesting the presence of charged sodium/lithium clusters. Finally, we applied muon spectroscopy to understand the different hydrogenation mechanisms in $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$ and $\text{Na}_x\text{Li}_{12-x}\text{C}_{60}$ and explain their different performance.

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Introduction

Intercalated fullerides have gained renewed interest in the field of energy storage for their performance as hydrogen-absorbing materials [1–5]. Sodium (Na) or lithium (Li) doping of Buckminster fullerene C_{60} in a molar ratio greater than four (i.e. A_xC_{60} , $x > 4$. $\text{A} = \text{Na}, \text{Li}$) results in a face-centred-cubic (fcc) arrangement of C_{60} molecules with alkali ions occupying the large interstitial sites of the fullerite structure. For each fullerene, the fcc lattice hosts two tetrahedral (TH) sites and an octahedral one (OH), virtually allowing a maximum doping of

$x = 3$. However, the OH site is large enough to host a small alkali cluster. Examples include $\text{Na}_{10}\text{C}_{60}$ and $\text{Li}_{12}\text{C}_{60}$ [6,7], where a bcc and an fcc cluster of Na/Li are formed respectively. For such high doping levels, the number of alkali ions exceeds the maximum amount of electrons that can virtually populate the lowest degenerate unoccupied molecular orbital (LUMO) on fullerene, the latter being able to host six electrons, but the metal clustering can overcome this instability. $\text{Na}_{10}\text{C}_{60}$ and $\text{Li}_{12}\text{C}_{60}$ can reversibly absorb up to 3.0 and 5.2 wt% H_2 with a relative dehydrogenation enthalpy of about 66 and 52 kJ/mol H_2 , respectively [8,9]. The absorption process leads to a partial

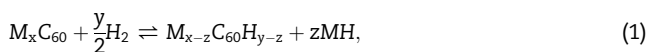
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segregation of NaH or LiH, achieved after hydrogenation of the fullerene molecule.



where $M = \text{Na, Li}$. Overall, the Na intercalated compounds show lower absorption capacity with improved kinetics, working temperature, and desorption enthalpies [8]. On the other hand, Li has the advantage to be lighter than Na and higher levels of absorption can be achieved when it is intercalated. Recently, we managed to find an optimal sorption performance by synthesizing mixed Na and Li doped fullerides with composition $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$. These phases have demonstrated better performance with respect to Li_6C_{60} for $x < 2$, reaching a full absorption at 553 K and 100 bar H_2 , with 44 kJ/mol H_2 desorption enthalpy [10]. With this paper, we extend the study of the Na–Li mixed phases for the high-stoichiometric compounds $\text{Na}_x\text{Li}_{12-x}\text{C}_{60}$, hereby reporting on the synthesis, structure, Raman spectroscopy, hydrogen sorption analysis, and muon spectroscopy of these novel fullerides.

Materials and methods

All the synthetic procedures and handling of materials were carried out by operating under vacuum or inside He or Ar filled glove boxes (O_2 and H_2O levels < 1 ppm). $\text{Na}_x\text{Li}_{12-x}\text{C}_{60}$ samples were synthesized in a two-steps procedure through high-energy ball milling (Fritsch Mini-Mill P23; ZrO_2 bowl with 5 balls). In the first step, C_{60} powder (M.E.R., 99+%) and the relative molar ratio of Na (Alfa Aesar, 99.95%) were milled at 30 Hz for 1 h (3 times 20 min each, separated by a 5 min break). The so-obtained black powder was subsequently milled under the same conditions with a stoichiometric amount of Li (Sigma-Aldrich, 99% granular), previously cut in small flakes. Each sample is then pelletized under 1.5 tons (9 mm diameter pellets, about 150 mg each), placed in stainless-steel cylinders closed with a screw cap, and sealed in borosilicate vials under high vacuum ($p < 10^{-5}$ mbar). Thermal annealing was carried out in static vacuum at 673 K for 5 days. $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$ samples were synthesized as previously reported [10]. X-ray powder diffraction (XRPD) was carried out on 0.7 mm diameter and 0.01 mm wall-thickness capillaries using a Xenocs Nano-inXider diffractometer, operating in wide-angle X-ray scattering mode (WAXS). Raman spectroscopy was carried out at room temperature by means of a Bruker Senterra Raman microscope operating with $20\times$ or $50\times$ objective. Powders in the capillaries were analysed using 785 nm and 532 nm laser wavelengths at relatively low power density (< 200 W/cm²) and short acquisition time to avoid radiation damage on the specimen. Hydrogen absorption investigations were performed on the as-prepared samples in a PCTPro-2000 manometric instrument (Hy-Energy & Setaram). About 300 mg of each sample was heated from room temperature up to 553 K at 5 K/min under 100 bar H_2 and a 10 h isothermal step was appended at the end of the ramp. H_2 -desorption kinetic measurements were performed by heating the samples at 673 K under 0.5 bar of hydrogen and appending 10 h of isotherm. Four sorption cycles were performed for each

sample to verify the cycling ability of the samples. Coupled calorimetric-manometric measurements were performed by connecting the high-pressure stainless-steel cell of a Sensys high-pressure DSC (Setaram) with the PCTPro equipment. About 30 mg of the samples hydrogenated in the first charging run were dehydrogenated by heating from room temperature up to 673 K at 0.5 bar of H_2 in dynamic mode (heating rate of 5 K/min). The uncertainty for the H_2 ab/de-sorption wt% values and for the desorption enthalpies are in the order of ± 0.3 wt% and ± 2 kJ/mol H_2 respectively. Muon spin relaxation (μSR) experiments were carried out at the ISIS Facility, RAL (Didcot, UK), on the EMU spectrometer. The 100% spin-polarized pulsed beam of this facility is optimized to study the muon-spin evolution over long time-scales. The total experimental muon polarization asymmetry was estimated on a separate transverse field (TF) experiment on pure silver. The baseline, due to muons stopping outside the sample, was measured to be 3% 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. For each sample, about 300–400 mg of powder was pressed and sealed in an airtight silver-coated aluminium cell, capped by a kapton window. The muon polarization is followed by plotting the asymmetry function, expressed as $A(t) = (N_b(t) - \alpha N_f(t)) / (N_b(t) + \alpha N_f(t))$, 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 transverse field. The time-dependent polarization was analysed by means of the WiMDA software [11].

Results

Diffraction

XRPD patterns for $\text{Na}_x\text{Li}_{12-x}\text{C}_{60}$ samples for $x = 0, 1, 2, 3$, and 6 are reported in Fig. 1. Synthesized samples appear as single phases characterized by an apparent high symmetry. Diffraction patterns showed broad lines, ascribed to disorder in the fulleride structure. Data were analysed by means of Le Bail pattern decomposition using the fcc cell of C_{60} . Similar to the parent low-stoichiometric compounds $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$, we expect a disordered occupation of Na and Li sites, as well as the presence of rotational disorder for C_{60} molecules [10,12]. The emergence of the 400 peak intensity at around 25.4° with the increase of x suggests a higher occupancy of Na in the $4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and $8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) sites, rather than in the $32f$ (x, x, x) positions. This observation is also in agreement with the smaller lattice expansion of $\text{Na}_6\text{Li}_6\text{C}_{60}$ ($a = 14.244$ (2) Å) as compared to Na_6C_{60} ($a = 14.380$ Å [13]) and $\text{Na}_{10}\text{C}_{60}$ ($a = 14.590$ Å [6]), where the $32f$ sites are occupied by Na forming a tetrahedral (Na_6C_{60}) or bcc ($\text{Na}_{10}\text{C}_{60}$) cluster in the OH interstice. Specific values for the lattice parameters are reported in Table S11. The relatively high contraction of the unit cell is also found in Li_6C_{60} and $\text{Li}_{12}\text{C}_{60}$, where the strong electrostatic interaction between Li ions and the negatively charged fullerene molecules shrinks the lattice volume [7].

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