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 <b>MLF Experimental Report</b>	25 June 2011
課題番号 Project No. 2010A0026 実験課題名 Title of experiment Muon States in Nanostructured Carbon Materials 実験責任者名 Name of principal investigator Roderick M. Macrae 所属 Affiliation Marian University, Indianapolis, USA	装置責任者 Name of responsible person Prof. Yasuhiro Miyake 装置名 Name of Instrument/(BL No.) D1 (muon) 実施日 Date of Experiment 26-28 November 2010

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

<p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>All samples were of novel carbonaceous materials: (1) graphite platelet nanofibers (column diameter 50-250 nm), obtained from Aldrich, (2) nanotube forest materials (provided by group of Kenji Hata, AIST), and (3) two samples of starch-derived mesoporous carbon (“Starbon”), one nominally “hydrophilic”, the other “hydrophobic” (see below for clarification), provided by James Clark and Peter Shuttleworth at the Green Chemistry Centre of Excellence at the University of York. All samples were solid powders or flakes as originally provided. Approximately 1 g of each sample was available. For <math>\mu</math>SR experiments, the samples were compressed into pellets of approximately 2 cm in diameter, enclosed in one layer of 16 micron aluminum foil.</p>
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<p>2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)</p> <p>Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.</p> <p>New forms of nanostructured and mesostructured carbonaceous materials are expected to find a variety of technological uses ranging from nanoengineering [1] to spintronics [2] to ultracapacitors [3,4]. Fundamental studies of such materials using a probe which can give some local insight into the physical and chemical properties of the <i>voids</i> are thus of some importance. Muon spin rotation studies have been carried out on diamond [5,6], graphite [7], amorphous carbon [8], fullerenes [9], and nanotubes [10], and are summarized in the recent review by Cox [11]. While in diamond both bond-centered muonium and interstitial muonium are observed [5], in graphite the paramagnetic state formed on muon implantation undergoes rapid spin or charge exchange with the conduction electrons leading to a collapse of the radical line and a temperature-dependent “paramagnetic shift” in the muon Larmor frequency [7]. Insulating amorphous carbon presumably contains a large variety of paramagnetic sites (not experimentally resolvable), but was observed by Cox and Davis to have a diamagnetic fraction of around 40% [8]. In single-walled nanotubes MacFarlane and co-workers observed a high fraction (about 40%) of vacuum-like muonium [10]. Fullerenes show distinct states corresponding to muons stopping respectively <i>inside</i> and <i>outside</i> the cages.</p>
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## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

Though it is evident that  $\mu$ SR methods distinguish clearly between a variety of different bonding types exhibited by carbonaceous materials, to date there have been no studies in the published literature of muon implantation in nanostructured “activated carbon” materials of catalytic importance.

For this preliminary study the method chosen was low transverse field precession measurement to establish the size of the diamagnetic fraction, together with longitudinal field repolarization measurements to yield an approximate measure of the distribution of hyperfine coupling constants in the material. The nanotube forest materials proved to have a density too low for practicable measurements, so measurements focused on the graphite platelet nanofibers and on the two “Starbon” starch-derived activated carbon materials [12]. An overnight “disk full” issue led to corruption of all of the LF data on the graphite platelet nanofiber material. Calibration of signal asymmetry was accomplished through the use of a holmium target. A substantial fraction of the calibration data set was also corrupted due to the disk problem.

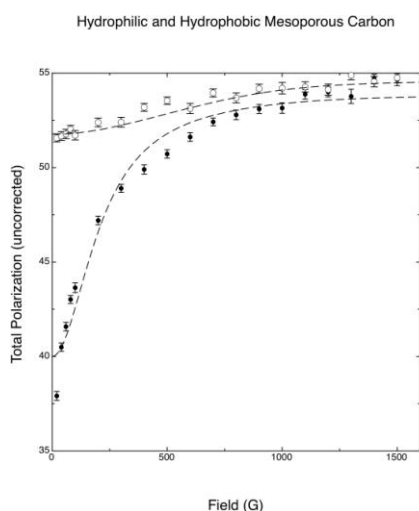


Figure 1. LF scans in hydrophilic (filled circles) and hydrophobic (open circles) “Starbon” catalyst materials.

The “hydrophilic” Starbon material is generated by heat treatment at a lower temperature than the “hydrophobic” material, and might be expected to be less graphitic in character and to retain more of the structural characteristics of the original starch material, modified somewhat by dehydration. This prediction appears to be supported by room temperature LF repolarization data (see Figure 1), which show only a small repolarizing fraction in the hydrophobic sample and a much larger one in the hydrophilic sample, suggesting that the latter retains substantial isolated radical-forming double bond character whereas the former is substantially graphitized. These preliminary results suggest that muon methods can yield insights into the internal bond type distribution and reactivity of these materials.

Attempts to measure the temperature-dependence of the repolarization patterns for the Starbon materials were unsuccessful due to technical issues with the cryostat. (The helium return line had been left open, resulting in the cooling process stalling at 184 K, followed by a slow return to 190 K.)

### References

- [1] Y. Nakayama, S. Akita, *New J. Phys.* 5, (2003), 128; [2] B. Zhao et al., *Appl. Phys. Lett.* 80, (2002), 3144; [3] M. D. Stoller et al., *Nano Lett.* 8, (2008), 3498; [4] MIT LEES laboratory project; see e.g. [http://lees.mit.edu/lees/posters/RU13\\_signorelli.pdf](http://lees.mit.edu/lees/posters/RU13_signorelli.pdf); [5] E. Holzschuh et al., *Phys. Rev. A* 25, (1982), 1272; [6] B. D. Patterson, *Rev. Mod. Phys.* 60, (1988), 69; [7] D. P. Hutchinson et al., *Phys. Rev. Lett.* 7, (1961), 129; J. Chakhalian et al., *Hyperfine Interact.* 106, (1997), 245; S. F. J. Cox et al., *J. Phys.: Condens. Matter* 13, (2001), 2169; [8] E. A. Davis, S. F. J. Cox, 2000 ISIS Annual Report, cited in [11]; [9] E. J. Ansaldo et al., *Nature* 353, (1991), 121; [10] W. A. MacFarlane et al., *Physica B* 289-290, (2000), 589; [11] S. F. J. Cox, *Rep. Prog. Phys.* 72, (2009), 116501; [12] V. Budarin et al., *Angew. Chem. Int. Ed.* 45, (2006), 3782.