

### Nanostructured Tin/Carbon Hybrids as Anodes in Lithium Ion Batteries

Kristopher J. Harris,<sup>1</sup> Dongniu Wang,<sup>2</sup> Xifei Li,<sup>2</sup> Hanshuo Liu,<sup>3</sup> Gianluigi A. Botton,<sup>3</sup> Xueliang Sun,<sup>2</sup> and Gillian R. Goward<sup>1</sup>

<sup>1</sup>Dept. of Chemistry and Brockhouse Institute for Materials Research, McMaster University, 1280 Main St. W. Hamilton, ON, L8S 4M1 Canada

<sup>2</sup>Dept. of Mechanical and Materials Engineering, Western University, London, Ontario, N6A 5B9

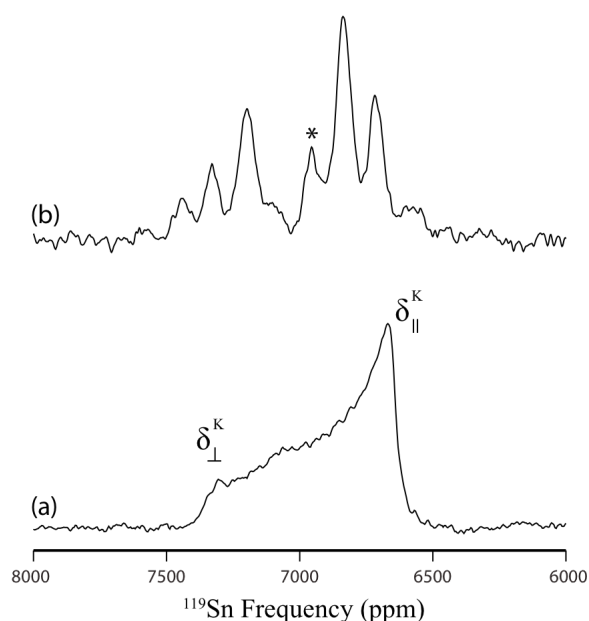
<sup>3</sup>Dept. of Materials Science and Engineering, Brockhouse Institute for Materials Research, and Canadian Centre for Electron Microscopy; McMaster University, 1280 Main St. W. Hamilton, ON, L8S 4L7 Canada

A crucial component of the energy marketplace is the availability of high-capacity, low-loss methods for energy transport that have minimal environmental costs. Lithium ion batteries (LiBs) find use in applications ranging from personal electronics to electric vehicles, and are particularly desirable when light weight, rechargeable storage is required. However, many applications are limited by the capabilities as well as the financial and environmental costs of the current generation of LiBs.<sup>1</sup> Current research into new types of anode materials for LiBs is driven by the need to improve capacity-to-weight ratios, charge/discharge rates, spontaneous flammability ratings, electrolyte compatibility, environmental sustainability, and manufacturing costs.

We present here a study of a recently developed anode material composed of approximately 100 nm tin-core/carbon-shell nanoparticles supported on graphene nanosheets, Sn@C-GNs.<sup>2</sup> Because both tin and graphene are capable of lithium storage as anode materials, this hybrid material would be expected to have two mechanisms for incorporating lithium. Tin containing materials have an extremely high lithium capacity when employed as LiB anodes; however, structural breakdown accompanying the volume changes of Li<sup>+</sup> absorption and discharge cycles leads to premature capacity losses. The nanostructure of Sn@C-GNs has a stabilizing effect,<sup>2</sup> preserving much of the high capacity of the tin component, while greatly extending the lifetime of the anode.

Molecular-level description of changes in promising anode materials which lead to differences in total capacity, irreversible capacity losses, or safety issues is critical for their further development. Since solid-state NMR is an extremely sensitive reporter of local chemical changes, it is clearly an ideal spectroscopic method to study Sn@C-GNs. In particular, further details on the chemical makeup of this complicated heterogeneous material, and changes induced by electrochemical cell cycling are important topics that can be addressed using solid-state NMR. The metallic tin nanoparticles are synthesized via reduction of SnO<sub>2</sub> (supported on GNs) with ethylene gas. Magic-angle spinning (MAS) <sup>119</sup>Sn NMR spectra of Sn@C-GNs demonstrates that this reaction is carried to completion as no trace of SnO<sub>2</sub> remains. Further reduction with ethylene gas creates a carbonaceous shell on each tin nanoparticle. High-speed MAS <sup>1</sup>H NMR spectroscopy provides convincing evidence that the carbonaceous shell is composed of fully unsaturated carbons, and almost no protonated carbons

remain from the input ethylene gas. Stationary sample <sup>119</sup>Sn NMR spectra of Sn@C-GNs (**Figure 1a**) shows clear evidence of metallic Sn. The extremely large Knight shifts seen in the spectra are created by the conduction electron band in the metallic nanoparticles. Orientational averaging of the interactions through MAS allows a higher-resolution measurement of the orientation-independent portion of the Knight shift (\* in **Figure 1b**). NMR studies of the anode at varying lithium charge levels are ongoing. In particular, lithium is expected to be incorporated into the anode as a tin/lithium alloy and/or associated with the high surface-area carbon components. Solids NMR spectroscopy is an ideal method to study the partitioning of Li between these two environments, and how this partitioning evolves with cell cycle number. The <sup>119</sup>Sn MAS spectrum shows that the resolution is sufficient to measure changes in the Sn electronic band structure as alloying occurs. Furthermore, <sup>7</sup>Li is an extremely receptive nucleus for NMR spectroscopy, and provides a definitive measure of metallic versus ionic lithium.<sup>3</sup> Therefore, <sup>7</sup>Li NMR is a second means of measuring the site partitioning of lithium ions in Sn@C-GNs versus cell cycling number. Transmission electron microscopy studies will be carried out to complement the NMR data with structural information so as to elucidate the structure of Sn@C-GNs and the growth mechanisms of these nanostructures.



**Figure 1.** <sup>119</sup>Sn NMR spectra of Sn@C-GNs. (a) Static sample, showing the parallel (6700 ppm) and perpendicular (7400 ppm) components of the Knight shift. (b) Sample undergoing 14 kHz MAS, with the peak corresponding to the isotropic Knight shift (6900 ppm) marked with an asterisk.

#### References:

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