

# Raman analysis of lithium-ion battery components

## Part II: Anodes

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### Introduction

From laptops and mobile phones to power tools and hybrid vehicles the use of portable energy storage devices is growing rapidly. As the number and types of applications expand there is a constant demand for expanding battery functionality. Different applications impose their own requirements on the technology (potential, capacity, discharge rates, charging rates, life time, operating conditions, etc.). With wide spread use there also comes greater concern with factors such as safety and environmental impact as well.

The analysis of battery components is important not only for the development of new materials but also for the study of charge/discharge mechanisms and even for confirming the quality of materials used in battery production. The complex nature of batteries requires a multifaceted combination of electrochemical analyses and materials characterization techniques. Raman spectroscopy has emerged as an important analytical technique that can be used for the characterizing of a variety of battery components. Even though a considerable amount of work has been done on the development and commercialization of lithium-ion batteries there is still considerable interest in improving the current technology and the development of new battery components. This application note will focus on examples of the analysis of anode materials for lithium-ion batteries. There are other application notes available that cover examples of the use of Raman spectroscopy for the analysis of cathode and electrolyte materials.<sup>1,2</sup> The examples presented here are not meant to be an exhaustive review of the literature but are intended to illustrate the utility of Raman spectroscopy for the analysis of battery components and in particular anodic materials.



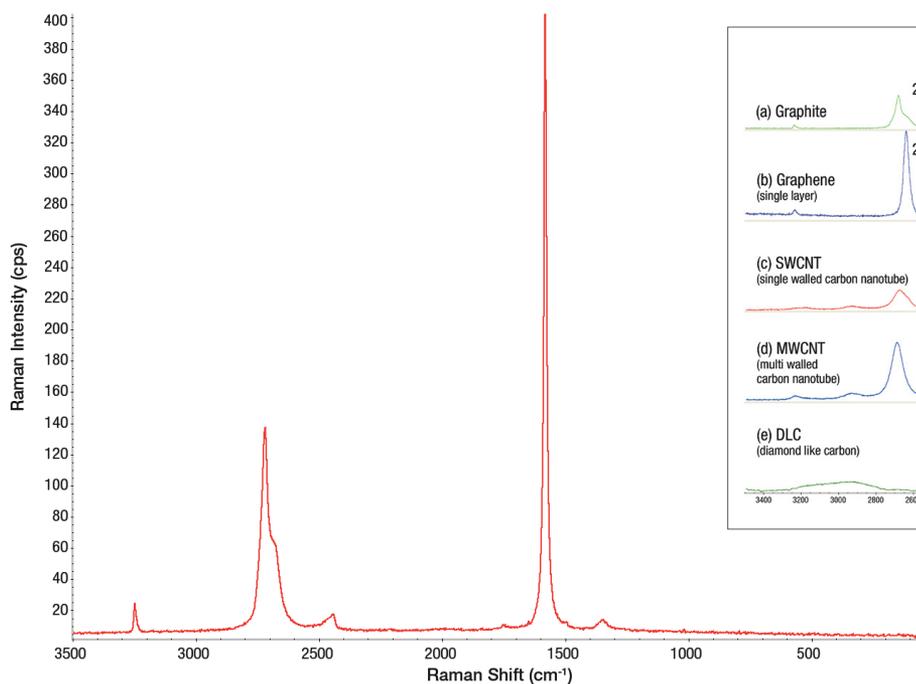
Raman spectroscopy probes molecular structure and local chemical environments and it is very useful for not only characterizing new anode materials but also for studying subtle changes in materials. The changes in the Raman spectra can be correlated with changes in the electrochemical performance of the materials. The development of easy to use but high quality Raman instruments such as the Thermo Scientific™ DXR™ 2 Raman microscope means that Raman spectroscopy can be added as a routine analytical technique to any laboratory. The DXR 2 Raman microscope is a high performance Raman spectrometer integrated with a research quality light microscope to produce a powerful molecular spectroscopy instrument for spectroscopic investigations of samples on a microscopic scale. It also includes many automated features that save time and simplify data collection and analysis without sacrificing performance. Features like SMART backgrounds and auto exposure save the user time when collecting spectra and assist with setting collection parameters. Automated alignment and calibration routines optimize instrument performance with a minimal amount of effort. These are just some of the time saving features found on the DXR 2 Raman microscope that make it easy to use and allow anyone to collect high quality Raman spectra.

One of the classical anode materials for lithium ion batteries is graphite. The Raman spectrum obtained from a graphite anode using a DXR 2 Raman microscope with a 532 nm laser is shown in Figure 1. Recently, other allotropes of Carbon besides graphite have been investigated for anode materials due to their novel physical and chemical properties. Raman spectroscopy is an excellent choice for analyzing the different allotropes of carbon (see Figure 2).<sup>3</sup> Many of these carbon allotrope materials are strong Raman scatters and have diagnostic spectral features. Raman spectra not only can be used to distinguish different allotropes of carbon but also can provide additional information on the molecular structure.<sup>4</sup> For example, Raman spectral data can be used to determine the number of sheets of graphene in a stack, it can provide information on defects and disorder in the structure of graphene, and it can be used to determine diameters of single wall carbon nanotubes.<sup>4,5</sup>

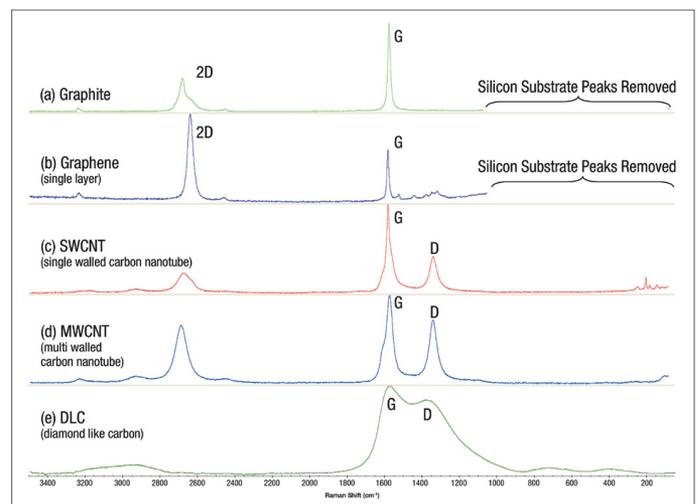
Raman spectroscopy can also be used to monitor changes in anode materials during use. In one published example a DXR 2 Raman microscope was used to study the insertion of lithium into a hard carbon anode.<sup>6</sup> The G band (graphite type structure) of the anode material displayed a slight shift to lower wavenumbers as the lithium insertion increased with the state of charge (SOC) of the battery. This shift has been attributed to a weakening of carbon bonds in the graphite type

structures due to negative charge transfer. This is an example of how Raman spectroscopy can be used to monitor the changes in the anode material with different states of the battery.

An active area of research is the use of carbon coatings to improve the electrochemical properties of other potential anodic materials. These carbon coatings are used to improve properties like low conductivity and cycling stability. Graphene composites have shown improved electrochemical properties. High surface area graphene improves lithium ion intercalation. Also the presence of graphene at the interfaces decreases the mechanical deterioration of anodes caused by large volume changes during cycling. One of the interesting aspects of this is that when many other applications are trending toward the fabrication of defect-free graphene, the presence of defects appears to be advantageous for anode materials. The presence of defects due to edges and vacancies in the graphene actually improves the capacity and cycling stability because it provides additional reversible storage sites for lithium ions.<sup>7</sup> This means that the evaluation of defects in the graphene structures is important because it is directly related to the electrochemical properties. Raman spectroscopy can provide relative defect concentrations and this is typically expressed as the ratio of the defect peak (D band) to the graphite peak (G band) ( $I_D/I_G$ ).



**Figure 1:** Raman spectrum of a graphite anode collected using a DXR 2 Raman microscope equipped with a 532 nm laser

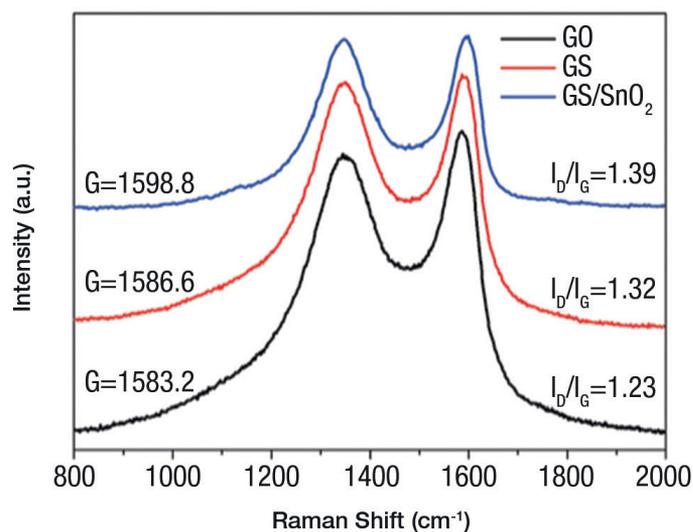


**Figure 2:** Raman spectra of different forms of carbon: (a) Graphite, (b) Single layer of graphene, (c) Single walled carbon nanotube (SWCNT), (d) Multi-walled carbon nanotube (MWCNT), (e) Diamond like carbon (DLC). These spectra were obtained using a DXR 2 Raman microscope and a 532 nm laser.

Silicon has been studied extensively as a promising candidate as an anode material for lithium ion batteries because of its high theoretical capacity (4200 mAh/g).<sup>8</sup> However, silicon electrodes undergo a large volume expansion/contraction during cell cycling and this volume change results in mechanical degradation of the anode and a dramatic fading of capacity. The high potential capacity of the silicon anode has led researchers to try to modify the surface of the silicon anode and thus the solid electrolyte interface (SEI) to improve the cycling behavior. One approach that has been reported is to coat the silicon anode surface with carbon using a fullerene (C60) precursor.<sup>9</sup> Analysis of these thin films using a Thermo Scientific™ Nicolet™ Almega™ dispersive Raman spectrometer configured with a 633 nm laser indicated that the carbon was no longer in the fullerene form but displayed D and G bands typical of other types of carbon coatings. The G band comes from idealized graphite type carbon structures and the D band represents defects edges, vacancies, etc. from the graphite structure and can be either  $sp^2$  or  $sp^3$  hybridized carbon. The  $I_D/I_G$  ratio varied with the plasma power used to create the coating and with boron doping of the fullerene.<sup>10,11</sup> Boron doping lowered the  $I_D/I_G$  ratio with respect to the undoped materials with similar deposition conditions. A similar approach was also carried out using diamond like carbon (DLC) films.<sup>12</sup> In the case of the DLC films the D and G bands overlapped significantly but they were deconvoluted into the two components. Peak fitting software like Peak Resolve in Thermo Scientific™ OMNIC™ software can be used to evaluate the relative contributions from these two types of carbon. Coating the silicon anodes with these carbon films provided more stable cycle performance along with high reversible capacity.

Tin dioxide ( $SnO_2$ ) and tin disulfide ( $SnS_2$ ) are both potentially useful anodic materials for lithium ion batteries. These materials are interesting because they have high theoretical capacities but like silicon they display a very large volume change during cycling and thus suffer from mechanical degradation. To address this issue, nanoscale hybrids of these materials have been investigated. In one report, nanorods of  $SnO_2$  were combined with graphene and in another,  $SnS_2$  nanosheets were combined with multi-walled carbon nanotubes.<sup>13,14</sup> In both of these cases the hybrid materials displayed improved high rate capacities and enhanced cycling behavior.

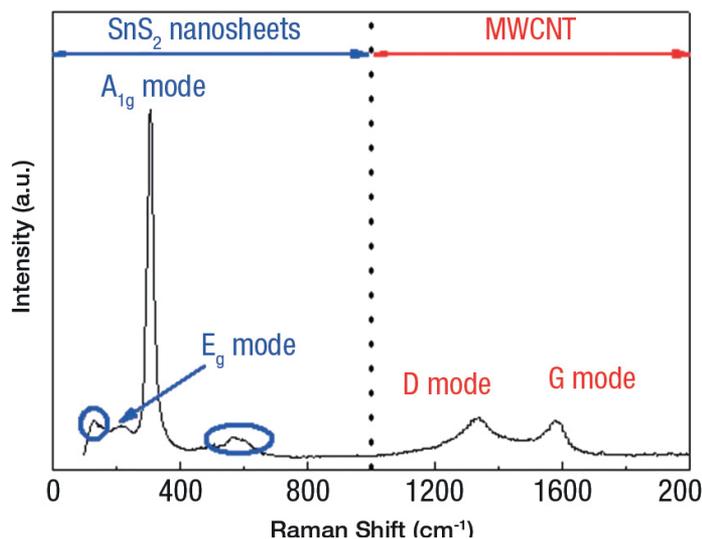
The Raman spectrum of the  $SnO_2$ /graphene composite material collected using a DXR 2 Raman microscope and a 532 nm laser showed both D and G bands typically associate with carbon but the G band was slightly blue shifted compared with the graphene sheet and graphene oxide peaks and this was taken as evidence of electronic interactions between the  $SnO_2$  nanorods and the graphite type structures of the graphene sheets (see Figure 3).<sup>13</sup>



**Figure 3:** Hybrid anode material  $SnO_2$  and graphene sheet (GS). Comparison of the peak location of the G band between graphene sheet (GS), graphene oxide (GO), and the hybrid anode material (GS/ $SnO_2$ ). Raman spectra collected using a DXR 2 Raman microscope with a 532 nm laser. Adapted with permission from Chaohe Xu, Jing Sun, Lian Gao, *J. Mater. Chem.* **22**, 2012, 975-979. Copyright 2012 RSC Publishing

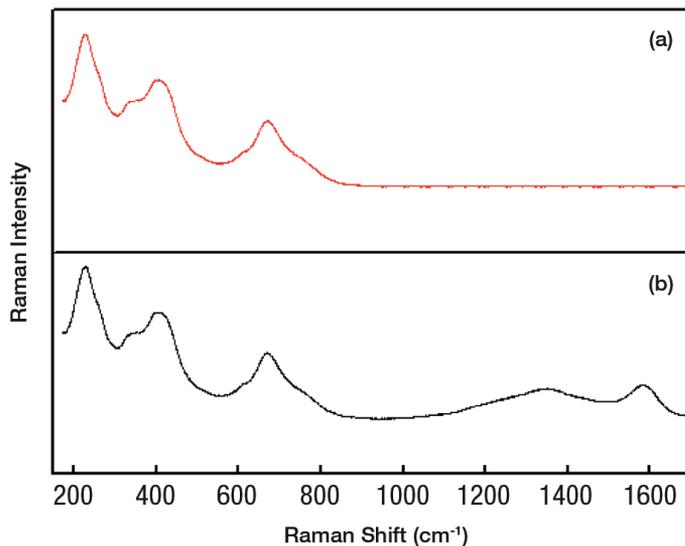
The composite material as well as the starting graphene sheet showed significant D bands indicating substantial disorder from the idealized graphene structure. This is probably not unexpected considering that the materials were prepared hydrothermally and there are many factors that could contribute to the defect concentration (small domains, vacancies, functionality, etc.)

The Raman spectra of the  $SnS_2$ /multi-walled carbon nanotube composite anode material displayed peaks associated with nanosheets of  $SnS_2$  (131 (w) 212 (w), 309 peak (s), 450–650 (b)  $cm^{-1}$ ) as well as peaks associated with the carbon nanotubes (D and G bands) (see Figure 4).<sup>14</sup> No peaks associated with  $SnS$  were observed despite the fact that  $SnS$  powder was used as the precursor. The  $SnS_2$  nanosheet/MWCNT composites exhibited significantly better discharge capacities and cyclability compared to the  $SnS_2$  nanosheets alone.



**Figure 4:** Raman spectrum of the SnS<sub>2</sub>/MWCNT composite material. Peaks associated with both the SnS<sub>2</sub> nanosheets and the multi-walled carbon nanotubes are observed. Raman spectra collected using a Nicolet Almega dispersive Raman spectrometer. Adapted with permission from Jin-Gu Kang, Gwang-Hee Lee, Kyung-Soo Park, Sang-OK Kim, Sungjun Lee, Dong-Wan Kim, Jae-Gwan Park, *J. Mater. Chem.* **22**, 2012, 9330-9337. Copyright 2012 RSC Publishing

Lithium transition metal oxides can be used as anodes for lithium batteries as well as cathodes. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> has the spinel structure and has been used as an anode material for lithium ion batteries. It does not have the high theoretical capacity (175 mAh/g) that materials like silicon have but it is a zero strain insertion material which means it shows only a very small change in volume during charge/discharge cycles.<sup>15</sup> It has excellent cycle characteristics. However, it has a poor rate capacity and low conductivity. Similar approaches (morphology, doping, and coating) have been reported to improve the conductivity of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. One example of this was detailed in a paper on how the conductivity of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was improved by generating a carbon composite material. Raman spectroscopy was used to confirm that the structure of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was retained in the hybrid material and that carbon had been incorporated in the material (see Figure 5).<sup>15</sup> The Raman spectra obtained using a Nicolet Almega XR dispersive Raman spectrometer with a 633 nm laser also showed the D and G bands typically associated with graphitic type carbon and disordered carbon structures were present.



**Figure 5:** (a) Raman spectrum of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and (b) Raman spectrum of carbon coated-Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. Raman spectra were obtained using a Nicolet Almega XR dispersive Raman spectrometer configured with a 633 nm laser. Adapted with permission from Ju Bin Kim, Dong Jin Kim, Kyung Yoon Chung, Dongjin Byun, Byung Won Cho, *Phys. Scr.* **T139**, 2010. Copyright 2010 IOP Publishing

These are few examples illustrating how Raman spectroscopy can be used to analyze anode materials for lithium-ion batteries. Many anode materials involve some form of carbon and Raman spectroscopy has proven itself very useful for the analysis of carbon based materials. Not only can Raman spectroscopy be used to differentiate one form of carbon from another but it also can provide detailed structural information. However, the utility of Raman spectroscopy does not stop with carbon based materials and it can also be used to probe the structure of other materials. Transition metal oxides and tin disulfide examples were included in this application note. The versatility of use with many different types of materials and the extraordinary structural information that it can provide make Raman spectroscopy an ideal choice for the analysis of battery components. The DXR 2 Raman microscope allows for spectroscopic analysis on a microscopic scale. Advances in Raman instruments, such as the DXR 2 Raman microscope, make them easy to use while still providing high quality Raman data. Easy access to high quality Raman data is one reason for the growing number of Raman applications.

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