



Raman analysis of lithium-ion battery components Part II: Anodes

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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 widespread use, there also comes greater concern with factors such as safety and environmental impact.

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 characterization 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.^{1,2} 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. It is very useful not only for 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 still high-quality, Raman instruments such as the Thermo Scientific™ DXR3 Raman Microscope means that Raman spectroscopy can be added as a routine analytical technique to any laboratory. The DXR3 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 you 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 DXR3 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 DXR3 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 the analysis of the different allotropes of carbon (see Figure 2).³ Many of these carbon allotrope materials are strong Raman scatterers and have diagnostic spectral features. Raman spectra can be used not only to distinguish different allotropes of carbon but also to provide additional information on the molecular structure.⁴ For example, Raman spectral data can be used to determine the number of sheets of graphene in a stack, provide information on defects and disorder in the structure of graphene, and determine diameters of single-wall carbon nanotubes.^{4,5}

Raman spectroscopy can also be used to monitor changes in anode materials during use. In one published example, a DXR Raman Microscope was used to study the insertion of lithium into a hard carbon anode.⁶ 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.

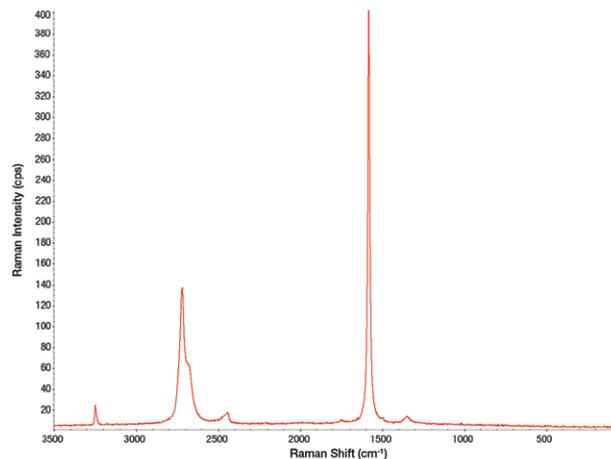


Figure 1. Raman spectrum of a graphite anode collected using a DXR3 Raman Microscope equipped with a 532 nm laser.

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.⁷ 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).

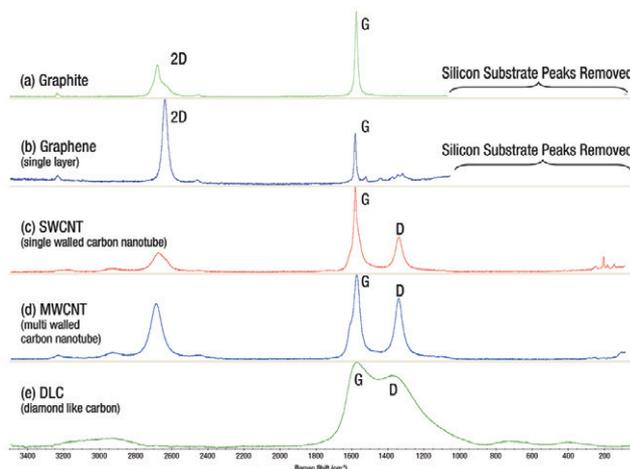


Figure 2. Raman spectra of different forms of carbon: (a) graphite, (b) single layer of graphene, (c) single-walled carbon nanotube (SWCNT), (d) multi-walled carbon nanotube (MWCNT), (e) diamond-like carbon (DLC). These spectra were obtained using a DXR Raman Microscope and a 532 nm laser.

Silicon has been studied extensively as a promising candidate as an anode material for lithium-ion batteries because of its high theoretical capacity (4,200 mAh/g).⁸ 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 lead 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.⁹ 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 sp² or sp³ 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.^{10,11} 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.¹² 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 (SnO₂) and tin disulfide (SnS₂) 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 SnO₂ were combined with graphene, and, in another, SnS₂ nanosheets were combined with multi-walled carbon nanotubes.^{13,14} In both of these cases, the hybrid materials displayed improved high-rate capacities and enhanced cycling behavior.

The Raman spectrum of the SnO₂/graphene composite material collected using a DXR 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. This was taken as evidence of electronic interactions between the SnO₂ nanorods and the graphite-type structures of the graphene sheets (see Figure 3).¹³

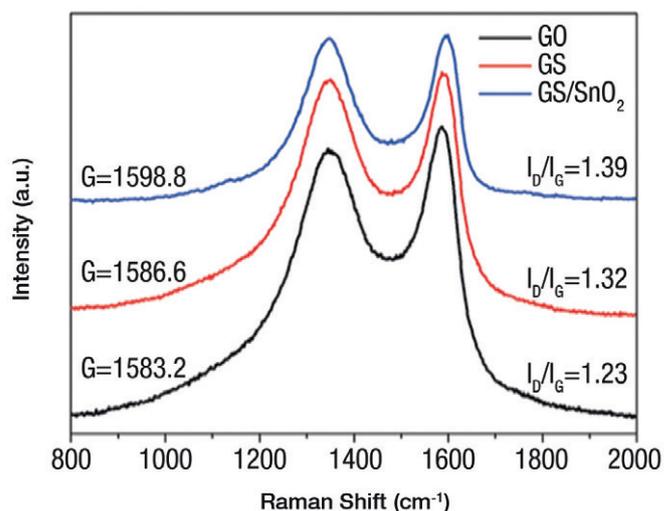


Figure 3. Hybrid anode material SnO₂ and graphene sheet (GS). Comparison of the peak location of the G band between graphene sheet (GS), graphene oxide (GO), and the hybrid anode material (GS/SnO₂). Raman spectra collected using a DXR Raman Microscope with a 532 nm laser. Adapted with permission from 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 SnS₂/multi-walled carbon nanotube composite anode material displayed peaks associated with nanosheets of SnS₂ (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).¹⁴ No peaks associated with SnS were observed despite the fact that SnS powder was used as the precursor. The SnS nanosheet/MWCNT composites exhibited significantly better discharge capacities and cyclability compared to the SnS₂ nanosheets alone.

Lithium transition metal oxides can be used as anodes for lithium batteries as well as cathodes. Li₄Ti₅O₁₂ 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.¹⁵ 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 Li₄Ti₅O₁₂. One example of this was detailed in a paper on how the conductivity of Li₄Ti₅O₁₂ was improved by generating a carbon composite material. Raman spectroscopy was used to confirm that the structure of the Li₄Ti₅O₁₂ was retained in the hybrid material and that carbon had been incorporated in the material (see Figure 5).¹⁶

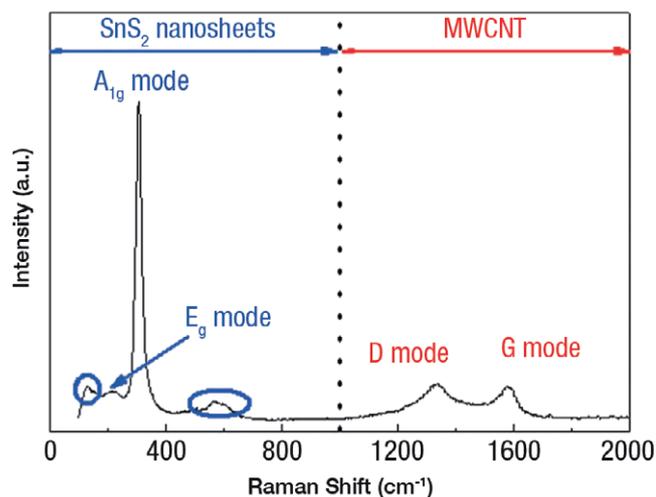


Figure 4. Raman spectrum of the SnS₂/MWCNT composite material. Peaks associated with both the SnS₂ nanosheets and the multi-walled carbon nanotubes are observed. Raman spectra collected using a Nicolet Alpha XR Dispersive Raman Spectrometer. Adapted with permission from Jin-Gu Kang, Gwang-Hee Lee, Kyung-Soo Park, Sang-OK Kim, Sungjun Lee, Dong-Wan Kim, Jae-Gwan Park, *J. Mater. Chem.* 22, 2012, 9330-9337. Copyright 2012 RSC Publishing.

The Raman spectra obtained using a Nicolet Alpha 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.

These are a 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; 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 DXR3 Raman Microscope allows for spectroscopic analysis on a microscopic scale. Advances in Raman instruments, such as the DXR3 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.

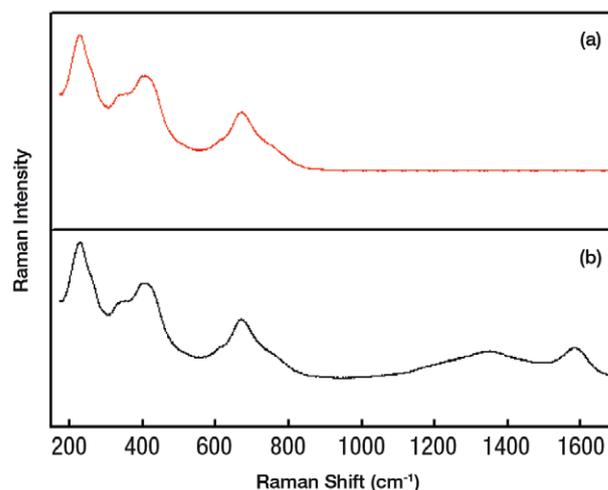


Figure 5. (a) Raman spectrum of Li₄Ti₅O₁₂ and (b) Raman spectrum of carbon-coated Li₄Ti₅O₁₂. Raman spectra were obtained using a Nicolet Alpha XR Dispersive Raman Spectrometer configured with a 633 nm laser. Adapted with permission from Ju Bin Kim, Dong Jin Kim, Kyung Yoon Chung, Dongjin Byun, Byung Won Cho, *Phys. Scr.* T139, 2010. Copyright 2010 IOP Publishing.

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