

# Improving Lithium Ion Batteries

Application note series on analyzing  
cathodes, anodes and electrodes with  
Raman spectroscopy

Li-ion BAT



## Raman analysis of lithium-ion battery components Part I: Cathodes

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### Keywords

DXR3 Microscope, cathodes, lithium-ion battery, Raman

In recent years the increasing demand for powering portable electronic devices from laptops to smart phones has driven the need for improved battery performance, but the emergence of electric and hybrid vehicles is creating additional interest in new battery technologies.

The expanding use of portable energy storage introduces additional factors beyond just improving battery capacity. Cost, safety, and environmental impact are important considerations as the use of battery technology evolves. Lithium-ion batteries offer the highest energy density and output voltage among commercial rechargeable battery systems.<sup>1</sup> Even though lithium-ion batteries are now an established technology there is still considerable interest in improving the current technology and the development of new battery components.

Evaluation of batteries and battery components requires a variety of analytical methods, not only for the development of new materials but also for gaining a greater understanding of the mechanisms involved in charge/discharge cycles. Bulk analysis of components is important but it is also important to understand surface interactions and interfaces. Electrochemical evaluation of cells includes conductivity measurements, electrochemical stability of components, cell capacity, ion mobility, discharge rates, and cycling behavior. Materials characterization of the various cell components can include many different analytical techniques (e.g., XRD, SEM, TEM, TGA, DSC, EDS) but one technique that is rapidly growing in popularity for the analysis of materials is Raman spectroscopy. Raman spectroscopy has many advantages but the most important ones for battery applications are those that involve subtle changes in molecular structure or local chemical environments. The spectral results can usually be correlated with the electrochemical performance.

There have been significant improvements in commercial Raman instrumentation over the last several years. Important advances in both hardware and software have made modern Raman instruments much more user friendly and removed many of the obstacles that in the past made routine use of Raman spectroscopy arduous for users with limited expertise.

Advances in instrumentation also include integration of light microscopes with Raman instrumentation allowing spectroscopic analysis of samples at the microscopic level. Modern Raman instruments, like the Thermo Scientific™ DXR™ 3 Raman Microscope, are fully integrated, high performance research grade instruments that have incorporated extensive automation to simplify the collection of Raman spectra. For example, automated on-demand alignment and calibration present on the DXR3 Raman Microscope are designed to eliminate the need for manual realignment and calibration, resulting in an instrument that is easy to use and maintain at its highest level of performance. This ease of use means it is much quicker to get started and more straightforward to get accurate results. This opens up the use of Raman spectroscopy for all types of users.

Raman spectroscopy has been used for the analysis of many different types of battery components. This includes analysis of cathode materials, anode materials, and electrolytes.<sup>2,3</sup> Part one of this series will focus on some examples of how Raman spectroscopy has been utilized for the analysis of cathode materials. This article is in no way meant as a complete review of the literature, which is beyond the scope of this application note. Included here are some interesting examples from published papers that illustrate how Raman spectroscopy has been used for the analysis of cathode materials.

Developing new cathode materials for lithium-ion batteries has been a very active area of research. Lithium cobalt ( $\text{LiCoO}_2$ ) is the classical cathode material, but there are issues with the cost, safety, and toxicity of this material. The manganese spinel,  $\text{LiMn}_2\text{O}_4$ , is a low-cost alternative that is safer and is more environmentally friendly. This cathode material is used in some commercial lithium-ion cells. The issue with the use of this material is that the cathodes suffer from capacity fade over time. One main contribution to this capacity fading appears to result from manganese (Mn) dissolution via a disproportionation reaction of MnIII at high potentials. This dissolution can be suppressed by doping the material with other transition metals. An example of this can be seen in some interesting work on mixed metal spinels ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5-x}\text{Mn}_{1.5-y}\text{M}_{x+y}\text{O}_4$  M = Cr, Al, Zr).<sup>4</sup> Raman spectroscopy was used to analyze the molecular structures of these spinels.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can be obtained in two different phases depending on the synthesis conditions. The Raman spectra from the two different phases of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are shown in Figure 1.<sup>1</sup> These Raman spectra were collected using a DXR Raman Microscope configured with a 532 nm laser. The peaks in the spectrum of the  $\text{P4}_3\text{32}$  material are sharper and stronger and the peak near 580–600  $\text{cm}^{-1}$  (the  $T_{2g}$  peak of the spinel) is split into two compared to the single peak in the spectra of the Fd3m material.<sup>4</sup> The structures of the two phases have space groups corresponding to Fd3m (normal spinel) and  $\text{P4}_3\text{32}$  (ordered spinel). These phases show poor contrast in the XRD but were distinguishable using Raman spectroscopy.<sup>1</sup>

Figure 2 illustrates how different reaction conditions can lead to different phases.<sup>4</sup> Doping the material with aluminum (Al) or zirconium (Zr) favors the formation of the ordered spinel structure whereas doping with chromium (Cr) favors the normal spinel structure (see Figure 3).<sup>4</sup> Utilizing the differences in the Raman spectra, it is also possible to evaluate the spatial distribution of phases in a sample by mapping the sample. Figure 4 shows an example where there are only a couple of small particles of the  $\text{P4}_3\text{32}$  phase present in a larger field of the Fd3m material.<sup>1</sup> The mapping data was collected using a DXR Raman Microscope with a motorized stage and a 532 nm laser. Thermo Scientific™ AtIµs™ software allows for easy collection and analysis of Raman maps and is part of the Thermo Scientific™ OMNIC™ software used with the DXR3 Raman Microscope. The material with the ordered spinel structure ( $\text{P4}_3\text{32}$ ) displays lower electrical conductivity compared to the materials with the normal spinel structure (Fd3m), so it is important to have an easy way to distinguish between these phases.<sup>4</sup> This illustrates how the DXR3 Raman Microscope could be used for fast easy evaluation of molecular structure.

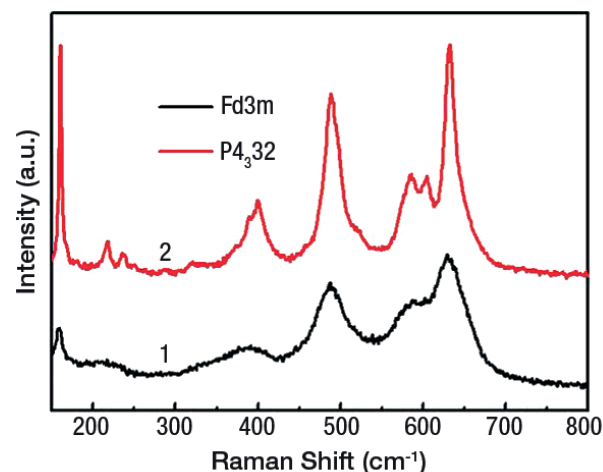


Figure 1. Raman spectra of the two phases of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . Spectra were collected using a DXR Raman Microscope and a 532 nm laser. Adapted with permission from Zhang X, Cheng F, Zhang K et al. (2012) *RSC Advances* 2: 5669–5675.

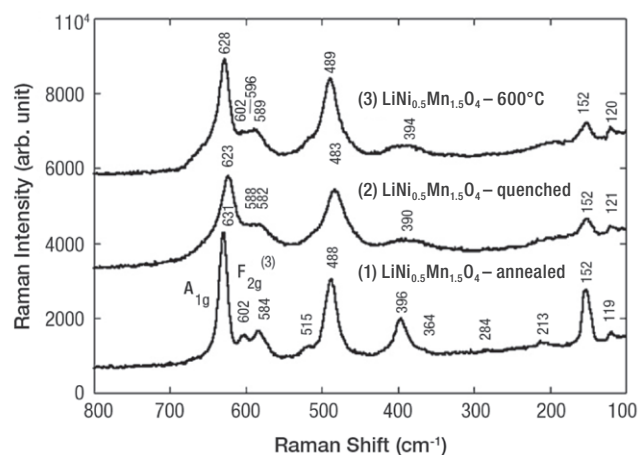


Figure 2. Raman spectra of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  synthesized under various conditions. (1) Annealed at high temperature, (2) quenched, and (3) calcined at lower temperature. Spectra were collected using a Thermo Scientific™ Nicolet™ Almega™ XR dispersive Raman spectrometer equipped with a 633 nm laser. Adapted with permission from Oh SH, Chung KY, Jeon SH et al. (2009) *Alloys Compd* 409: 244–250.

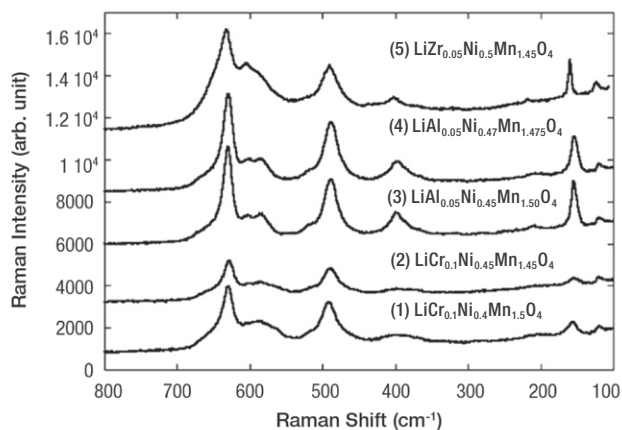


Figure 3. Raman spectra of Zr, Al, and Cr doped  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . (1) and (2) Cr doped (Fd3m structure); (3) and (4) Al doped ( $\text{P4}_3\text{32}$  structure); (5) Zr doped ( $\text{P4}_3\text{32}$  structure). Spectra were collected using a Nicolet Almega XR dispersive Raman spectrometer configured with a 633 nm laser. Adapted with permission from Oh SH, Chung KY, Jeon SH et al. (2009) *Alloys Compd* 409: 244–250.

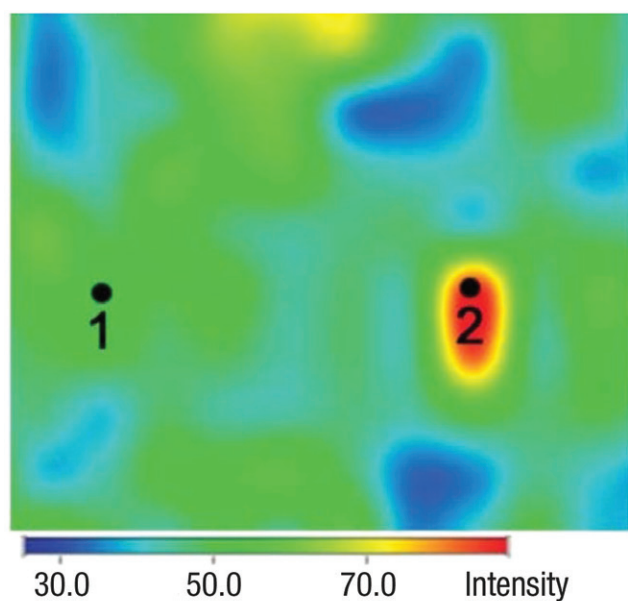


Figure 4. A Raman map showing the distribution of the two different spinel phases in a sample. The red-yellow locations (such as location 2) indicate areas of the  $\text{P4}_3\text{32}$  phase whereas the blue-green areas (such as location 1) represent areas of the Fd3m phase. Mapping data collected using a DXR Raman Microscope with a motorized stage and AtJus software. Adapted with permission from Zhang X, Cheng F, Zhang K et al. (2012) *RSC Advances* 2: 5669–5675.

An alternative approach to doping with other transition metals is to synthesize materials with different morphologies. The approach is typically to target nanoscale materials because the smaller particles and higher surface areas tend to improve the electrochemical properties of the materials. An example of this is the report that porous nanorods of  $\text{LiMn}_2\text{O}_4$  gave enhanced cyclability and high-rate capacity compared to regular  $\text{LiMn}_2\text{O}_4$  cathodes.<sup>5</sup> The enhanced capacity and cycling behavior was attributed to the morphology providing short ionic diffusion distances and a structure that could more readily accommodate the lattice expansion and contraction associated with repeated lithium-ion intercalation and deintercalation. A DXR Raman Microscope was used to confirm the spinel structure (Fd3m) of the material and was also used to monitor the stability of the material after multiple charge/discharge cycles.<sup>5</sup>

Doping  $\text{LiCoO}_2$  with other transition metals has been investigated as a way of improving cathode materials (e.g., cost, safety, performance, and environmental impact). An example of this is the class of materials with the following general formula,  $\text{Li}[\text{Mn}_{1-x-y}\text{Co}_x\text{Ni}_y]\text{O}_2$ . Raman spectroscopy can also be used to monitor the structure of these types of materials as well. It has been reported in a paper that the Raman spectra of the material changed when the lithium content increased from  $\text{Li}[\text{Mn}_{0.45}\text{Co}_{0.40}\text{Ni}_{0.15}]\text{O}_2$  to  $\text{Li}_{1.15}[\text{Mn}_{0.45}\text{Co}_{0.40}\text{Ni}_{0.15}]\text{O}_2$ .<sup>6</sup> Figure 5 shows the Raman spectra of these cathode materials.<sup>6</sup> Increasing the lithium content decreased the electrostatic repulsion between adjacent layers in the structure and resulted in an increase in the Raman intensity and a shift to higher wavenumbers. The change in the Raman spectrum with lithium content illustrates the utility of Raman spectroscopy for monitoring lithium content in these types of materials.

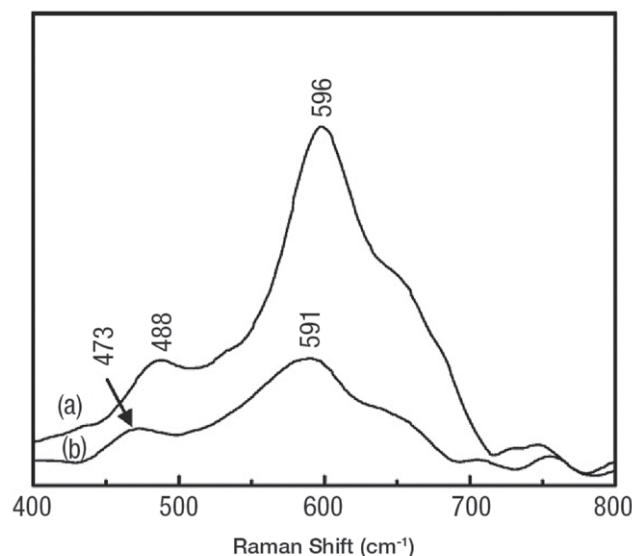


Figure 5. The Raman spectra of (a)  $\text{Li}_{1.15}[\text{Mn}_{0.45}\text{Co}_{0.40}\text{Ni}_{0.15}]\text{O}_2$  and (b)  $\text{Li}[\text{Mn}_{0.45}\text{Co}_{0.40}\text{Ni}_{0.15}]\text{O}_2$ . Peak shift and intensity change with change in lithium content. Spectra collected using a Nicolet Almega XR dispersive Raman spectrometer configured with a 532 nm laser. Adapted with permission from Wang T, Liu Z-H, Fan L et al. (2008) *Powder Technol* 187: 124–129.

There are different ways to try improving the properties of cathode materials. In addition to doping and morphology changes an alternative approach is to coat the cathode with a more conductive material to form a hybrid material. This can change the solid electrolyte interface (SEI) and can improve the performance of the cathode.  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Mn}_{0.13})\text{O}_2$  is a member of a class of layered materials with the general form of  $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$  ( $\text{M} = \text{Mn, Ni, Co}$ ). These materials have attracted attention because of high theoretical capacities up to 250 mAh/g.<sup>7</sup> Unfortunately, they have poor rate capacities and cycling behavior.

Constructing hybrid composite materials with graphene improves the cycling stability and gives enhanced high rate capacity. A DXR Raman Microscope fitted with a 532 nm laser was used to monitor the structure of the  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Mn}_{0.13})\text{O}_2$  material and provided evidence for the incorporation of graphene in the hybrid material. Peaks for both the inorganic oxide material and the graphene-derived coating were observed in the Raman spectra. Figure 6 shows the Raman spectra of the cathode material before and after the reaction with graphene.<sup>7</sup> The significant D band indicates substantial defects from the idealized graphene structure. There are many possible contributions to this defect peak including small domains sizes and vacancies in the graphene sheets. The existence of defects is not unexpected and in some applications can be advantageous. For instance, increased disorder in graphene anodes has been correlated with increased lithium-ion capacity.<sup>8</sup>

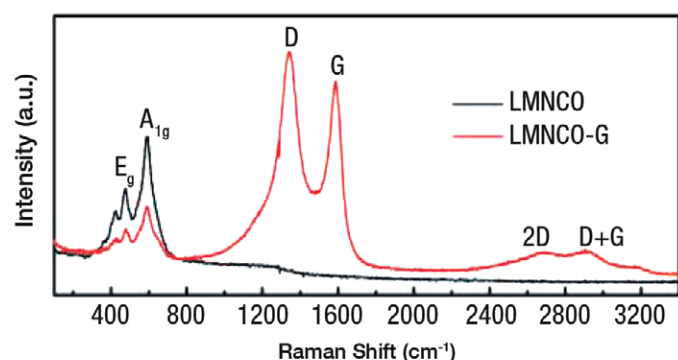


Figure 6. The Raman spectra of  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Mn}_{0.13})\text{O}_2$  (LMNCO) and the graphene wrapped hybrid material (LMNCO-G). Spectra were collected using a DXR Raman Microscope and a 532 nm laser. Adapted with permission from Jiang K-C, Wu X-L, Yin Y-X et al. (2012) *ACS Appl Mater Interfaces* 4(9): 4858–4863.

These are just a few examples to illustrate how Raman spectroscopy can be used for the study of cathode materials. This was not meant as a comprehensive review of the literature. There are certainly other applications in the literature beyond those included here. The intent was to encourage and inspire the use of Raman spectroscopy for the analysis of battery components. Raman provides a fast and efficient way to identify materials and confirm molecular structure. It can be used on a wide variety of materials and can be used for both bulk analysis and the study of surfaces and interfaces. It has proven itself as an important analytical method for the analysis of battery components. The DXR3 Raman Microscope is a high-performance Raman microscope in an easy-to-use package that puts Raman spectroscopy in the reach of any user.

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

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### Keywords

DXR3 Microscope, anodes, carbon, graphene, lithium-ion battery, Raman

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.

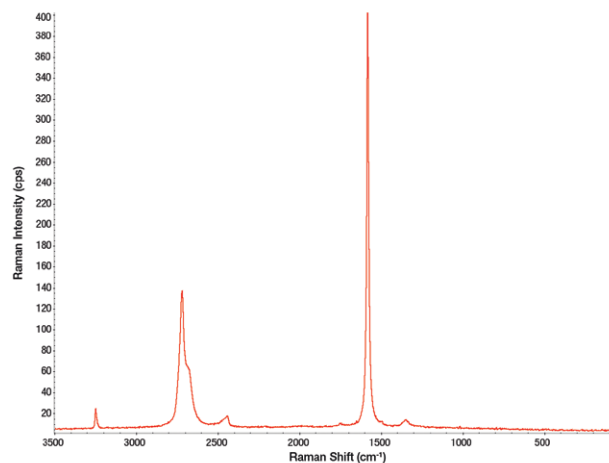
The analysis of battery components is important not only for the development of new materials but also for the study of charge/discharge mechanisms and even for confirming the quality of materials used in battery production. The complex nature of batteries requires a multifaceted combination of electrochemical 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.<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. 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.

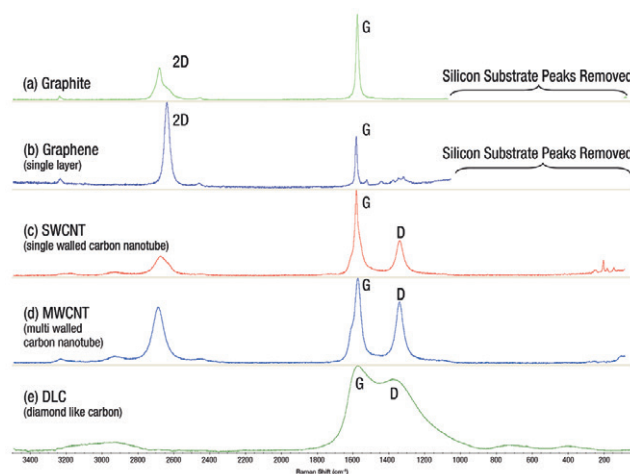
One of the classical anode materials for lithium-ion batteries is graphite. The Raman spectrum obtained from a graphite anode using a DXR3 Raman Microscope with a 532 nm laser is shown in Figure 1. Recently, other allotropes of carbon besides graphite have been investigated for anode materials due to their novel physical and chemical properties. Raman spectroscopy is an excellent choice for the analysis of the different allotropes of carbon (see Figure 2).<sup>3</sup> 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.<sup>4</sup> 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.<sup>4,5</sup>

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.<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.



**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.<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 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).<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 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.<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<sup>2</sup> or sp<sup>3</sup> hybridized carbon.

The I<sub>D</sub>/I<sub>G</sub> 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<sub>D</sub>/I<sub>G</sub> 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<sub>2</sub>) and tin disulfide (SnS<sub>2</sub>) 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<sub>2</sub> were combined with graphene, and, in another, SnS<sub>2</sub> 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<sub>2</sub>/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 SnO<sub>2</sub> nanorods and the graphite-type structures of the graphene sheets (see Figure 3).<sup>13</sup>

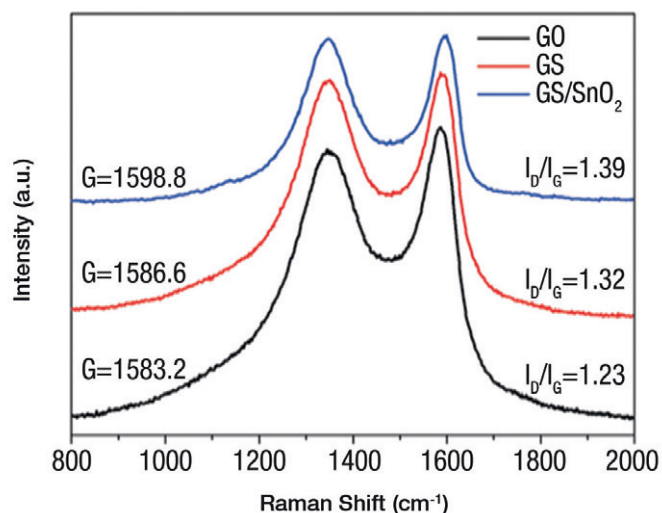


Figure 3. Hybrid anode material SnO<sub>2</sub> and graphene sheet (GS). Comparison of the peak location of the G band between graphene sheet (GS), graphene oxide (GO), and the hybrid anode material (GS/SnO<sub>2</sub>). Raman spectra collected using a DXR Raman Microscope with a 532 nm laser. Adapted 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 SnS<sub>2</sub>/multi-walled carbon nanotube composite anode material displayed peaks associated with nanosheets of SnS<sub>2</sub> (131 (w) 212 (w), 309 peak (s), 450–650 (b) cm<sup>-1</sup>) 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 nanosheet/MWCNT composites exhibited significantly better discharge capacities and cyclability compared to the SnS<sub>2</sub> nanosheets alone.

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>16</sup>



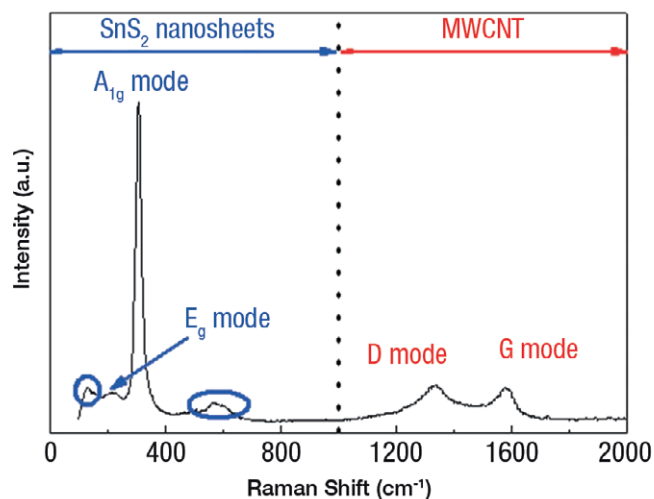


Figure 4. Raman spectrum of the SnS<sub>2</sub>/MWCNT composite material. Peaks associated with both the SnS<sub>2</sub> nanosheets and the multi-walled carbon nanotubes are observed. Raman spectra collected using a Nicolet Almega Dispersive Raman Spectrometer. Adapted with permission from Jin-Gu Kang, 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.

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.

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.

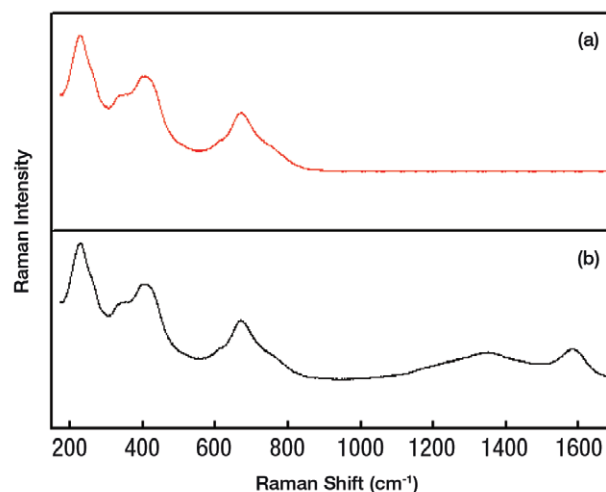


Figure 5. (a) Raman spectrum of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and (b) Raman spectrum of carbon-coated Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. Raman spectra were obtained using a Nicolet Almega XR Dispersive Raman Spectrometer configured with a 633 nm laser. Adapted with permission from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

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## Raman analysis of lithium-ion battery components Part III: Electrolytes

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### Keywords

DXR3 Microscope, electrolytes, lithium-ion battery, Raman Spectroscopy, Solid Polymer Electrolytes (SPE)

Today's society is very mobile and this mobility comes with an increasing need for portable energy sources.

The demand for better battery technology continues to grow. Some applications use very small batteries and others, such as hybrid vehicles, use much larger batteries. The individual requirements (potential, capacity, discharge rate, etc.) vary with the intended use. Battery performance along with cost continue to be very important aspects of any new battery technology, but factors such as safety and environmental impact are becoming increasingly important.

Electrolytes are responsible for the transport of charges in batteries. If this transport is hindered then the performance of the battery is adversely affected. Electrolytes need to be able to transport the charge efficiently, but they also need to be stable under charging and discharging conditions. Side reactions of electrolytes within the battery not only reduce battery performance but shorten battery life. Improving electrolyte functionality involves not only understanding the electrolytes themselves and how they function, but also how they interact with other battery components.

Lithium-ion batteries are a particularly popular battery technology that offers some of the highest energy densities and output voltages among commercial rechargeable battery systems.<sup>1</sup> Various lithium salts have been investigated as electrolytes. A common example of an electrolyte used in lithium-ion batteries is lithium hexafluorophosphate ( $\text{LiPF}_6$ ). The main issue with  $\text{LiPF}_6$  is that it must be kept scrupulously dry to avoid hydrolysis to generate corrosive hydrogen fluoride ( $\text{HF}$ ).<sup>2</sup> Other electrolytes such as lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ) are toxic.<sup>2</sup> Some lithium salts have low ionic conductivity (e.g.,  $\text{LiSO}_3\text{CF}_3$ ) and some form higher resistivity barriers at the electrode surfaces (e.g.,  $\text{LiBF}_4$ ).<sup>2</sup> None of the electrolyte choices is perfect, so the development of new electrolytes is an opportunity for improving the performance, cost, environmental impact, and safety of lithium-ion batteries.

Batteries are complex devices with a variety of different components. Because of this, the analysis of batteries requires a wide variety of analytical tools. The evaluation of battery components usually involves both electrochemical analysis and materials characterization methods. The various analytical techniques are often used together to provide a complementary and comprehensive understanding of the battery components and mechanisms. Raman spectroscopy has already been established as one of the most useful and versatile analytical techniques for the analysis of a variety of different types of materials. Previous application notes provided examples of how Raman spectroscopy can be used for the analysis of cathode and anode materials.<sup>3,4</sup> That coverage is expanded here to include examples of the analysis of electrolytes. These examples are not meant to be an exhaustive review of the literature, but are intended to illustrate some of the ways that Raman spectroscopy can be used and the type of information it can provide.

Commercially available Raman spectrometers have evolved into routine laboratory instruments. The Thermo Scientific™ DXR3 Raman Microscope is an example of this new class of Raman instruments that are easy to operate but provide high performance results. The DXR3 Raman Microscope is a fully integrated, high performance, research grade instrument that incorporates extensive automation that simplifies the collection of Raman data. For example, automated on-demand alignment and calibration present on the DXR3 Raman Microscope eliminates time-consuming manual realignment and calibration, providing an easy way to optimize instrument performance with a minimal amount of effort. This ease of use means it is much quicker to get started and provides confidence that you will get high performance and accurate results. This opens up the use of Raman spectroscopy for all types of users.

Raman spectroscopy probes molecular structure and local chemical environments. It is useful not only for the characterization of new electrolyte materials but it can also be used for studying more subtle changes in materials.

For example, Raman spectroscopy can be used to study the degree of association of electrolyte ions in solutions and in polymer materials. The association of ions has a direct effect on the ion mobility and ion conductivity and thus affects battery performance.

Solid polymer electrolytes (SPE) offer some distinct advantages over electrolytes dissolved in organic solvents. In these composite materials the polymer matrix assumes the role of the solvent and lithium salts dispersed in the polymer are the electrolytes. With typical organic solvents there is a greater risk of leakage and organic-based solvents can be volatile and flammable. The combination of flammable solvents and highly reactive and energetic battery components represents a potentially dangerous combination if something were to happen to the battery. Overcharging or overheating of batteries can have a disastrous effect especially with volatile solvents. The use of solid polymer electrolytes reduces the risk of leakage and thus mitigates some what the danger of toxic, corrosive, or flammable electrolytes and solvents.<sup>5</sup>

The drawback of these solid polymer electrolytic systems is that they often display low ionic conductivity and poor transport of lithium-ions.<sup>6</sup> Poly ethylene oxide (PEO) is an example of a polymer that is used in solid polymer electrolytes. The low ionic conductivity of these polymer electrolytes is attributed to a crystalline phase in the polymer matrix. The low percentage of charge transfer by lithium-ions is hindered because of high anion mobility. A considerable amount of research has focused on circumventing these issues.<sup>6</sup>

One approach to solving the issue of low ionic conductivity has been the use of additives to suppress the crystallinity of the polymer matrix and to improve the mechanical and electrochemical properties of the resulting composite polymer electrolytes. There are reports in the literature where ceramic materials, such as alumina and titania, have been used as fillers. For example, a Thermo Scientific Nicolet™ Almega™ dispersive Raman spectrometer was used to verify the phases of these materials as well as the surface modifications of the fillers (e.g., sulfate –  $\text{SO}_4^{2-}$ ).<sup>7</sup>

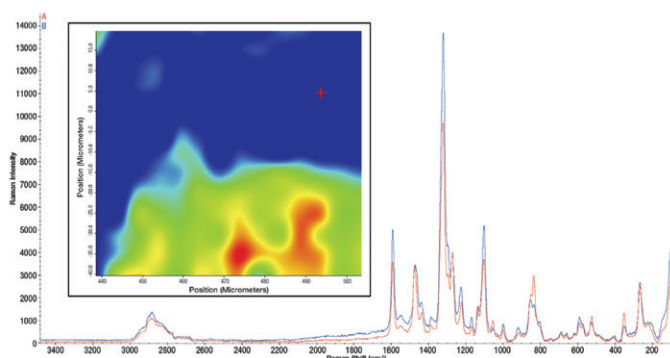


Figure 1. Spatial distribution of Cx2 in a PEO Membrane. Raman image based on the ratio of the 1600  $\text{cm}^{-1}$  peak of Cx2 to the 840  $\text{cm}^{-1}$  peak of PEO. Red indicates a higher concentration and blue represents a lower concentration of Cx2. The spectrum in blue comes from point B and the spectrum in red comes from point A. Mapping data was collected using a Nicolet Almega dispersive Raman spectrometer configured with a motorized stage and using a 780 nm laser. This figure was generated from data sent by the author.

Interesting work has been done studying additives designed to partially immobilize the anions in the polymer composite electrolytes and thus improve cation charge transfer. Raman spectroscopy was not only used to characterize the additives and the electrolytes in the polymer membranes but was also used to study the distribution of the components in the membranes. Raman mapping of the polymeric materials using a Nicolet Almega dispersive Raman spectrometer with a motorized stage and a 780 nm laser, provided images based on the Raman spectra that showed the spatial distribution of the additives and electrolytes in the polymer membranes.<sup>6,8</sup> Figure 1 shows the spatial distribution of the supramolecular additive, 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-bis(((*N*-*p*nitrophenylureido) butyl) oxy)-26,28-dipropoxycalix[4]arene (Cx2), in a poly(ethylene oxide) matrix. The image is based on the ratio of a peak from the supramolecular additive (1598  $\text{cm}^{-1}$ ) to a peak associated with the PEO (840  $\text{cm}^{-1}$ ).<sup>9</sup>

The Thermo Scientific™ Atlys option in the Thermo Scientific OMNIC™ software facilitated the collection and analysis of mapping data. The red color indicates a higher concentration of additive and the blue indicates a lower concentration. Representative spectra from each of the areas are displayed as well. The spectra are very similar but there are some differences.

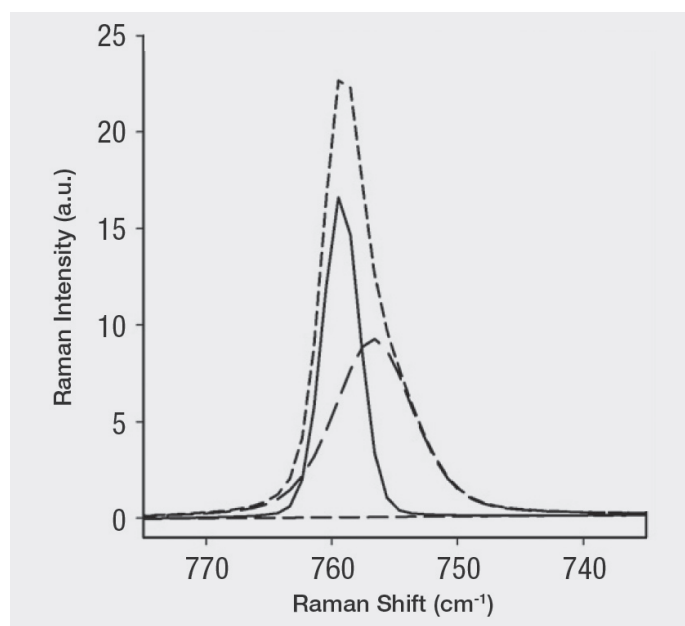


Figure 2. Deconvolution of the  $\delta\text{sCF}_3$  band in Raman spectrum of amorphous domains of a PEO- $\text{LiCF}_3\text{SO}_3$  membrane. The peak at 756  $\text{cm}^{-1}$  is attributed to free ions (42%) and the peak at 759  $\text{cm}^{-1}$  is attributed to ionic pairs (58%). Adapted with permission from Pawloska M, Zukowska GZ, Kalita M et al. (2007) *J Power Sources* 173: 755–764. Copyright 2007 Elsevier Publishing.

Raman spectroscopy can also be used to determine the degree of association of electrolyte ions in solution. This is a very interesting application that is based on the fact that the degree of association of the anions (free ion, ion pairs, and triplets) has a subtle effect on the shift of the anion peaks in the Raman spectra. This is a result of slight difference in the chemical environment due to interaction with other ions.

This type of analysis was reported as part of a paper on the development of potential electrolytes for lithium-ion batteries based on lithium salts of imidazole derived materials (e.g., lithium 4,5-dicyano-2-(pentafluoroethyl)imidazole).<sup>10,11</sup> The peaks associated with CN stretching in the Raman spectra were used to evaluate the relative percentages of the various ionic associations. This was achieved by careful deconvolution and peak fitting of the composite peak. This method can be used either independently or as a compliment to methods such as the Fuoss-Kraus procedure.<sup>10</sup> The ionic associations are of interest because the ionic conductivity is affected by the degree of association of the ions. Electrolytes with weaker associations (higher percentage of free ions) will generally display greater conductivity.

The same type of analysis can be used with other electrolytes as well. The percentages of free ions and ion pairs for lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) in a PEO- $\text{LiCF}_3\text{SO}_3$  solid polymer electrolyte have also been determined by deconvolution and peak fitting of the  $\text{CF}_3$  peak in the Raman spectrum of the composite material.<sup>8</sup> Figure 2 shows the deconvolution of the  $\text{CF}_3$  band of the Raman spectra into bands for the free ions and ion pairs of lithium triflate in PEO- $\text{LiCF}_3\text{SO}_3$ .<sup>8</sup> The Peak Resolve option in the OMNIC software can be used for this type of analysis.

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