



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

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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.¹ Various lithium salts have been investigated as electrolytes. A common example of an electrolyte used in lithium-ion batteries is lithium hexafluorophosphate (LiPF_6). The main issue with LiPF_6 is that it must be kept scrupulously dry to avoid hydrolysis to generate corrosive hydrogen fluoride (HF).² Other electrolytes such as lithium hexafluoroarsenate (LiAsF_6) are toxic.² Some lithium salts have low ionic conductivity (e.g., LiSO_3CF_3) and some form higher resistivity barriers at the electrode surfaces (e.g., LiBF_4).² 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.^{3,4} 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.

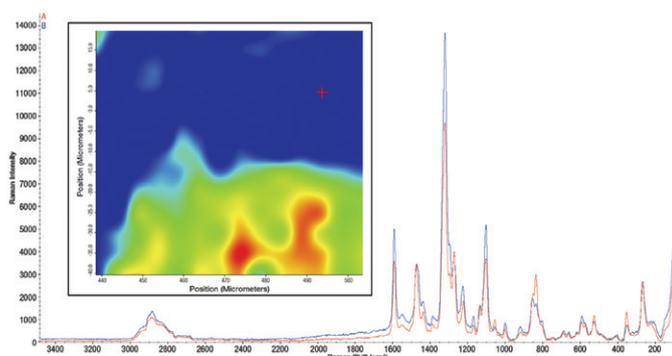


Figure 1. Spatial distribution of Cx2 in a PEO Membrane. Raman image based on the ratio of the 1600 cm^{-1} peak of Cx2 to the 840 cm^{-1} peak of PEO. Red indicates a higher concentration and blue represents a lower concentration of Cx2. The spectrum in blue comes from point B and the spectrum in red 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.

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.⁵

The drawback of these solid polymer electrolytic systems is that they often display low ionic conductivity and poor transport of lithium-ions.⁶ 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.⁶

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 – SO_4^{2-}).⁷

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.^{6,8} 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 cm^{-1}) to a peak associated with the PEO (840 cm^{-1}).⁹

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.

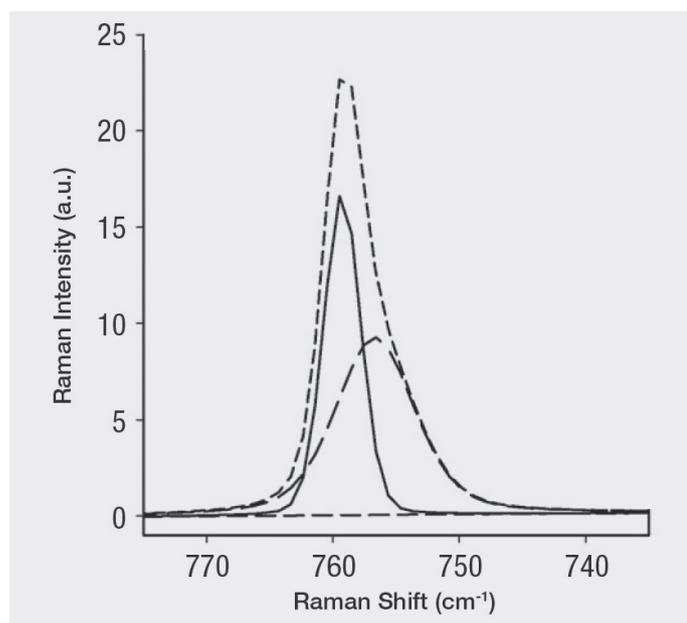


Figure 2. Deconvolution of the δsCF_3 band in Raman spectrum of amorphous domains of a PEO- LiCF_3SO_3 membrane. The peak at 756 cm^{-1} is attributed to free ions (42%) and the peak at 759 cm^{-1} is attributed to ionic pairs (58%). Adapted with permission from Pawloska M, Zukowska GZ, Kalita M et al. (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).^{10,11} 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.¹⁰ 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 (LiCF_3SO_3) in a PEO- LiCF_3SO_3 solid polymer electrolyte have also been determined by deconvolution and peak fitting of the CF_3 peak in the Raman spectrum of the composite material.⁸ Figure 2 shows the deconvolution of the CF_3 band of the Raman spectra into bands for the free ions and ion pairs of lithium triflate in PEO- LiCF_3SO_3 .⁸ The Peak Resolve option in the OMNIC software can be used for this type of analysis.

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