

Raman Analysis of Lithium-Ion Battery Components – Part III: Electrolytes

Robert Heintz, Ph.D., Thermo Fisher Scientific, Madison, WI, USA

Key Words

DXR Microscope, Electrolytes, Lithium-Ion Battery, Raman Spectroscopy, Solid Polymer Electrolytes (SPE)

Today's society is very mobile and with this comes 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 charge 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 LiPF_6 . The main issue with LiPF_6 is that it must be kept scrupulously dry to avoid hydrolysis to generate corrosive HF .² Other electrolytes such as LiAsF_6 are toxic.² Some lithium salts have low ionic conductivity (example: LiSO_3CF_3) and some form higher resistivity barriers at the electrode surfaces (example: LiBF_4).² None of the electrolyte choices is a perfect choice so this is why 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 complimentary 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 have provided examples of how Raman spectroscopy can be used for the analysis of cathode and anode materials.^{3,4} Here that coverage is expanded to include examples of the analysis of electrolytes. The examples presented here 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™ DXR™ Raman microscope is an example of this new class of Raman instruments that are easy to operate but provide high performance results. The DXR 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 DXR microscope eliminates time consuming manual realignment and calibration and provides 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.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 being 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 (example: 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-2,5,27-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™ AtLµs™ 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 a lower concentration. Representative spectra from each of the areas are displayed as well. The spectra are very similar but there are some differences.

Raman spectroscopy can also be used to determine the degree of association of electrolyte ions in solution. This is a very interesting application of Raman spectroscopy 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.

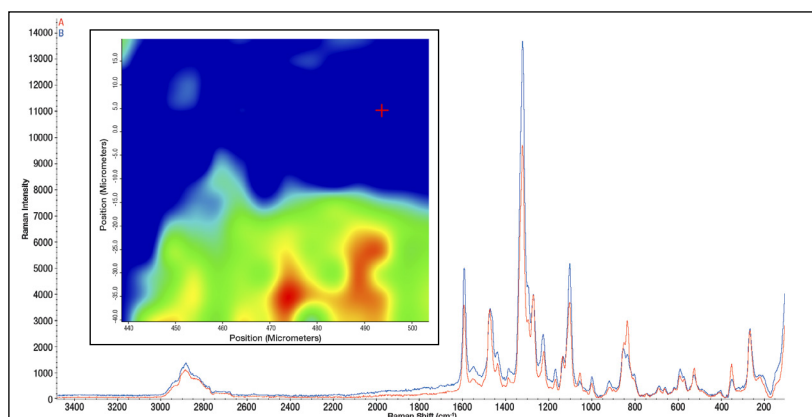


Figure 1: Spatial distribution of Cx2 in a PEO Membrane. Raman image based on the ratio of the 1600 cm^{-1} peak of Cx2 to the 840 cm^{-1} peak of PEO. Red indicates a higher concentration and blue represents a lower concentration of Cx2. The spectrum in blue comes from point B and the spectrum in red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

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 (example: 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.

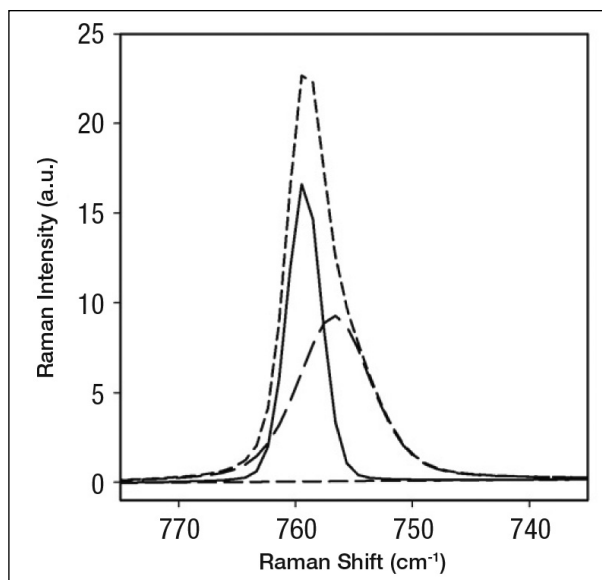


Figure 2: Deconvolution of the δ_{SCF_3} band in Raman spectrum of amorphous domains of a PEO- LiCF_3SO_3 membrane. The peak at 756 cm^{-1} is attributed to free ions (42%) and the peak at 759 cm^{-1} is attributed to ionic pairs (58%). Adapted with permission from M. Pawlowska, G.Z. Zukowska, M. Kalita, A. Solgala, P. Parzuchowski, M. Siekierski, *J. Power Sources*, **173**, 2007, 755–764. Copyright 2007 Elsevier Publishing

These are some of examples of how Raman spectroscopy is being used for the analysis of electrolytes for lithium-ion batteries. There are certainly many more examples available in the literature. These examples demonstrate that Raman spectroscopy can provide additional information beyond just identifying and characterizing materials. Raman spectroscopy can be used to probe subtle molecular interactions such as ionic association. The breadth of applications and the wealth of information that it provides makes Raman spectroscopy an important addition to any laboratory doing materials research and it is particularly suited for the study of battery components. The availability of high performance but easy to use Raman instruments such as the DXR Raman microscope provides a simple and straightforward way to add the power of routine Raman analysis to any laboratory.

References

- Xialong Zhang, Fangyi Cheng, Kai Zhang, Yanliang Liang, Siqi Yang, Jing Liang, Jun Chen, *RSC Advances*, **2**, 2012, 5669–5675.
- L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wieczorek, M. Armand, *J. Power Sources*, **196**, 2011, 1368–1391.
- Raman Analysis of Lithium Ion Battery Components – Part I: Cathodes, Thermo Scientific Application Note
- Raman Analysis of Lithium Ion Battery Components – Part II: Anodes, Thermo Scientific Application Note
- Jaroslav S. Syzdek, Michel B. Armand, Pawel Falkowski, Magdalena Gizowska, Maciej Karłowicz, Lukasz Lukaszuk, Marek L. Marcinek, Aldona Zalewska, Mikolaj Szafran, Christian Masquelier, Jean M. Tarascon, Wladyslaw G. Wieczorek, Zofia G. Zukowska, *Chem.Mater.*, **23**, 2011, 1785–1797
- Helselman, M. Kalita, A. Plewa-Marzewska, G.Z. Zukowska, E. Sasim, W. Wieczorek, M. Siekierski, *Electrochim. Acta*, **55**, 2010, 1298–1307.
- Jaroslav Syzdek, Michel Armand, Marek Marcinek, Aldona Zalewska, Grazyna Zukowska, Wladyslaw Wieczorek, *Electrochim. Acta*, **55**, 2010, 1314–1322.
- M. Pawlowska, G.Z. Zukowska, M. Kalita, A. Solgala, P. Parzuchowski, M. Siekierski, *J. Power Sources*, **173**, 2007, 755–764.
- The Raman mapping data was supplied by Dr. Grazyna Zukowska, Warsaw University of Technology, Faculty of Chemistry.
- L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Armand, M. Bukowska, M. Marcinek, P. Szczecizki, W. Wieczorek, *J. Power Sources*, **192**, 2009, 612–617.
- L. Niedzicki, G.Z. Zukowska, M. Bukowska, P. Szczecizki, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marcinek, W. Wieczorek, *Electrochim. Acta*, **55**, 2010, 1450–1454.

www.thermoscientific.com

©2013 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

Africa +27 11 822 4120	Denmark +45 70 23 62 60	India +91 22 6742 9434	New Zealand +64 9 980 6700
Australia +61 3 9757 4300	Europe-Other +43 1 333 50 34 0	Italy +39 02 950 591	Russia/CIS +43 1 333 50 34 0
Austria +43 1 333 50 34 0	Finland/Norway/Sweden	Japan +81 45 453 9100	Spain +34 914 845 965
Belgium +32 53 73 42 41	+46 8 556 468 00	Latin America +1 561 688 8700	Switzerland +41 61 716 77 00
Canada +1 800 530 8447	France +33 1 60 92 48 00	Middle East +43 1 333 50 34 0	UK +44 1442 233555
China +86 10 8419 3588	Germany +49 6103 408 1014	Netherlands +31 76 579 55 55	USA +1 800 532 4752