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Application Note

Energy

Raman Spectroscopy

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Raman Spectroscopy Applied to the Lithium-ion Battery Analysis

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Abstract

The application note explains how the Raman Spectroscopy can be helpful in the analysis of cathodes and anodes in Li-ion batteries.

Key words

Li-ion batteries, materials analysis, Raman spectroscopy, Raman imaging

Introduction

The Lithium-ion batteries (LIB) are of a great interest for many years as they are a rechargeable type of batteries, contrary to Lithium batteries. They are widely used in all kind of portable electronic devices or cordless tools, and they are used in newly developed electrical cars. As the need for power of all this devices is growing with their complexity, the performances of Li-ion batteries become an issue.

These performances will be influenced by the state of the cathode and the anode. During charging and discharging process the lithium ions travel from one electrode to the other (through the electrolyte) which induces the structural changes of both materials. Ideally all observed changes are reversible, but in some cases, the charging/discharging process can provoke irreversible changes in cathode or anode.

Raman spectroscopy gives a direct answer about structural changes occurring in analysed materials. Being contactless and fast, it does not influence the samples and in case of batteries, allows real-time analysis during charge/discharge cycle. Easy-to-use, but still information-rich, Raman spectroscopy is an excellent tool on several analysis levels, from various R&D needs to automatic quality control measurements.

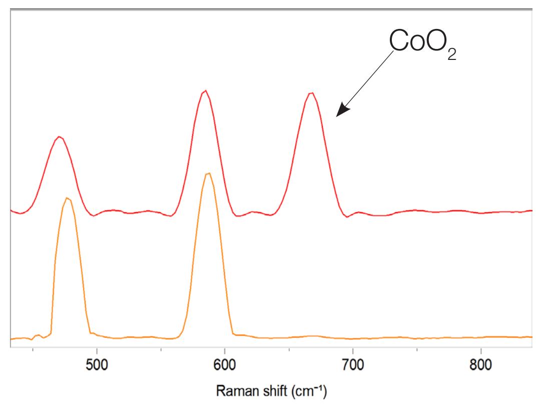

Figure 1: Spectral difference between $LiCoO_2$, and $LiCoO_2$ with a presence of cobal oxide CoO_2.

Cathode analysis

The most often used material for a cathode is a layered lithium cobalt oxide $LiCoO_2$ (LCO). During charge and discharge process the lithium ions are de-intercalated or intercalated into the layered cobalt-oxygen octahedral structure. It is known that the over-discharge will decompose this oxide, most probably in an irreversible way, into lithium oxide (Li_2O) and cobalt oxide (CoO). Over-charge will convert $LiCoO_2$ into cobalt dioxide (CoO_2). All these changes can be observed using Raman spectroscopy (figure 1). The Raman map recorded on the cathode after the charge/discharge process clearly shows the presence of Cobalt dioxide (figure 2).

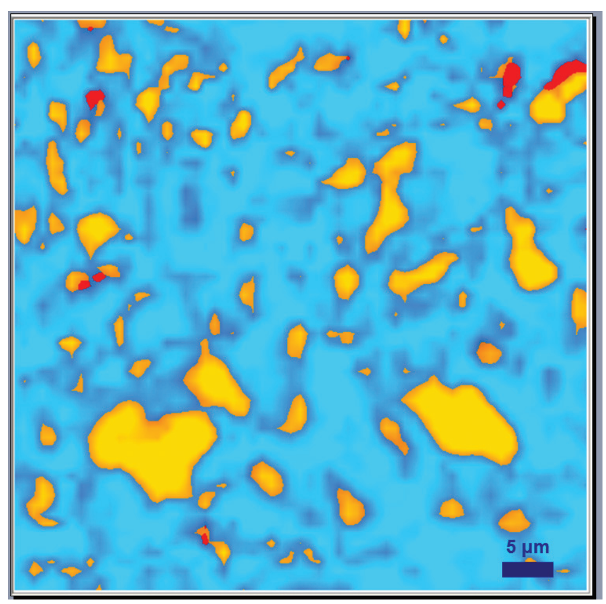

Figure 2: Raman image $LiCoO_2$ cathode after a cycling process, the presence of CoO_2 was detected: blue colour corresponds to the presence of amorphous carbon, orange spots shows the distribution of $LiCoO_2$, and red spots corresponds to different concentrations of CoO_2.

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New materials are investigated as potential cathode materials; these are usually different types of lithium-transition metal(s) mixed oxides $Li(Ni,Mn,Co)O_2$, $LiMn_2O_4$, Li_2TioO_3 compared to $LiCoO_2$.
Raman spectroscopy can bring some new information about the possible structural and chemical changes of these materials (figure 3).

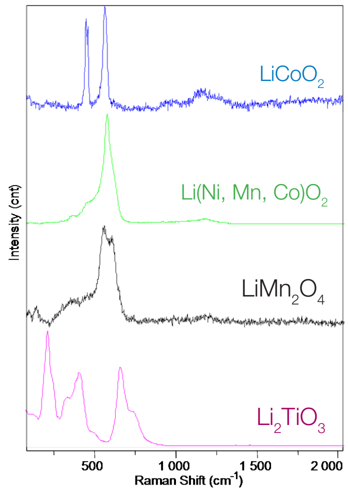

Figure. 3: Raman spectra of cathode materials: $LiCoO_2$, $Li(Ni,Mn,Co)O_2$, $LiMn_2O_4$ and Li_2TiO_3.

Anode analysis

The common material for anode is graphite. As for cathode layered materials, the graphite can be deteriorated after charging/discharging process. The I_D/I_G ratio of bands D and G of Raman spectrum is related to damages in the structure. The increasing intensity of D band with respect to intensity of G band, shows the degradation of graphite. Raman imaging can show clearly the changes occurred in the graphite structure (figure 4.)

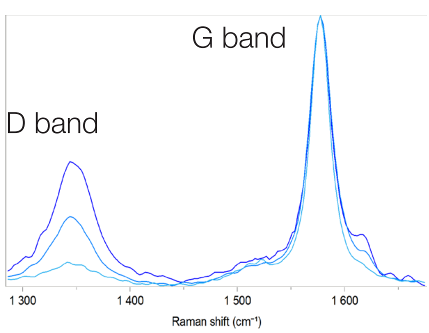

Figure. 4: Raman spectra of graphite with different I_D/I_G ratio.

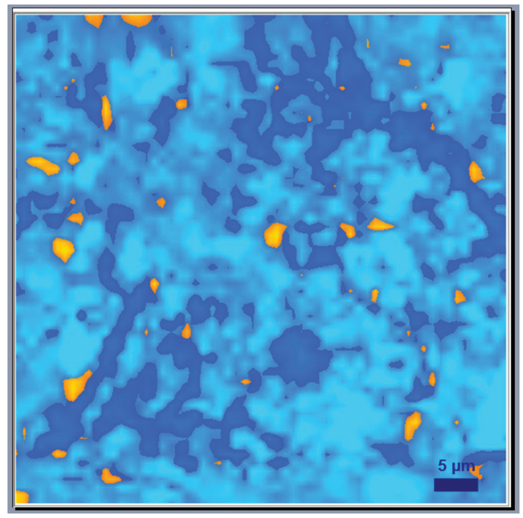

Figure. 5: Raman image graphite anode after a cycling process: blue zones show graphite with a relatively low level of defects; and dark blue show graphite with higher level of defects; and orange zones correspond to presence of a binder (resin).

Conclusions and perspectives

Today's state of art of technology requires more reliable, more efficient and powerful energy sources. Lithium-ion batteries are thus of high interest. Raman spectroscopy adapts to the different stages of life of these batteries, such as the characterisation of new materials for more flexible systems, failure analysis; but also more standard analysis of used material during charge/discharge process, including structural and electronic properties, and even robust, automated QC tests.

Further reading

*R. Baddour-Hadjean and J.-P. Pereira-Ramos, Chem. Rev., 110 (2010) 1278–1319
*V. A. Sethuraman, L. J. Hardwick, V. Srinivasan, R. Kostecki, Journal of Power Sources, 195 (2010) 3655–3660
*R. Kostecki, J. Lei, F. McLarnon, J. Shim, K. Striebel, J. Electrochem. Soc., 153 (2006) A669-A672
*R. Kostecki, X. Zhang, P.N. Ross Jr., F. Kong, S. Sloop, J.B. Kerr, K. Striebel, E. Cairns, F. McLarnon, F., report LBNL-48359, DOI:10.2172/861953
*Paul Scherrer Institute, http://www.psi.ch/lec/electrochemical-energy-storage
*Berkley Energy Storage & Conversion for Transportation and Renewables Program, http://bestar.lbl.gov/