

Integrated SEM and Raman Imaging of Lithium Ion Batteries



Seeing beyond

Integrated SEM and Raman Imaging of Lithium Ion Batteries

Authors: Stefanie Freitag, Dr. Christina Berger
Carl Zeiss Microscopy GmbH, Germany

Christian Weisenberger, Andreas Kopp,
Dr. Timo Bernthaler
Institut für Materialforschung, Hochschule Aalen,
Germany

Dr. Ute Schmidt, Dr. Philippe Ayasse
Witec GmbH, Germany

Date: October 2015

Introduction

Compared to lead-acid batteries, lithium-ion batteries (LIB) have a higher specific energy as well as higher specific power, thus they have become the most popular power source for portable computing and telecommunication equipment [1]. Today, the main driver of battery research projects are the automotive industry, developing portable batteries, and the renewable energy market, discovering new materials for stationary energy storage as well as the electronics industry [2].

The battery commonly consists of two electrodes that are isolated by a separator and soaked in electrolyte to promote the movement of ions (Figure 1). Usually graphite is the main component of the anode. On the side of the cathode mainly lithium transition metal oxides such as $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ (NCM) or LiMn_2O_4 (LMO) are used as active materials. To achieve specific cell properties composite electrodes with two or more different active materials are also widely used.

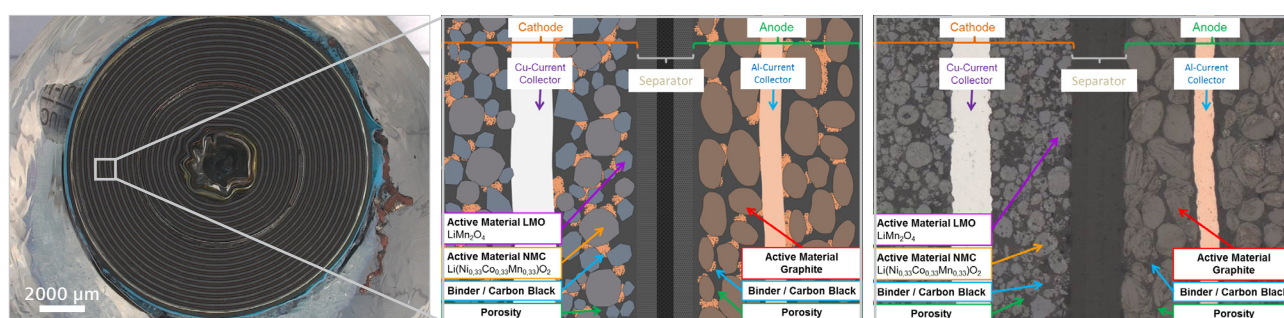


Figure 1 Components in commercial batteries

The active materials are mixed with a conductive agent (carbon black) and a binder (e.g. Polyvinylidene fluoride PVDF) and are then coated onto a metal foil, the current collectors (copper or aluminum). As electrolyte a solution of LiPF_6 in a mixture of e.g. dimethyl carbonate (DMC) and ethylene carbonate (EC) is commonly used. The separator is of special importance. It is polymeric and often comprising of polyethylene as well as polypropylene. The composition of the separator determines the working temperature of the battery and is crucial for the safety of the battery [3].

The main aims of researchers are the increase of travel range and to decrease ageing. Thus life time, cycle time and energy density need improvement. In addition higher capacities and properties independent from the temperature are targeted. To reach this aim for commercial rechargeable batteries, researchers are trying to improve various aspects of the cell design including new active materials for both cathodes and anodes like overlithiated or nickel rich NCM, high voltage spinels (e.g. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) or anode material combined with silicon particles.

The development of new active materials and electrode designs calls for analytical methods which are capable of displaying various morphological and chemical properties within a reasonable amount of time.

The analysis of the cathode, anode and separator within one measurement system is enabled by the in situ integration of a Raman system into a scanning electron microscope, thus delivering complementary information. SEM enables the detailed analysis of the cathode material including EDX measurements which reveal compositional information and Raman imaging is the tool of choice for separator, binder and anode material investigations.

Materials and Methods

Two cylindrical batteries type 18650 (diameter 18 mm, height 65 mm) have been used for the examinations. One cell is shown in its initial condition (new) the other cell was cycled at 25 °C with 8 °C over 480 cycles resulting in a SOH (state of health) of approximately 64 %. The cells were discharged and cut open in a glove box under protective Argon atmosphere. Subsequently the electrode foils were separated, washed in DMC and dried. Small samples were cut from the electrodes and the separator. The samples were mounted in resin. A mechanical preparation by grinding and polishing was used to create the cross sections of the electrodes.

High resolution scanning electron microscope images were performed with ZEISS GeminiSEM 500. Due to its high resolution at low voltages (1.2 nm @ 500 V) GeminiSEM 500 is well suited for battery analysis without observable damage of the single components. For EDX mappings ZEISS Sigma VP 500 and Oxford detector were used. Raman imaging measurements were carried out using WITec RISE Microscopy™ system equipped with a 532 nm excitation laser, a high throughput UHTS 300 spectrometer and a Peltier cooled back illuminated CCD camera optimized for the visible range. The RISE system can be laterally attached at the front of the SEM chamber by means of an extension. For this configuration, changes on the chamber door and an adjustment of the stage length are required in order to be able to move from the SEM to the Raman position and back within one chamber and within the vacuum.

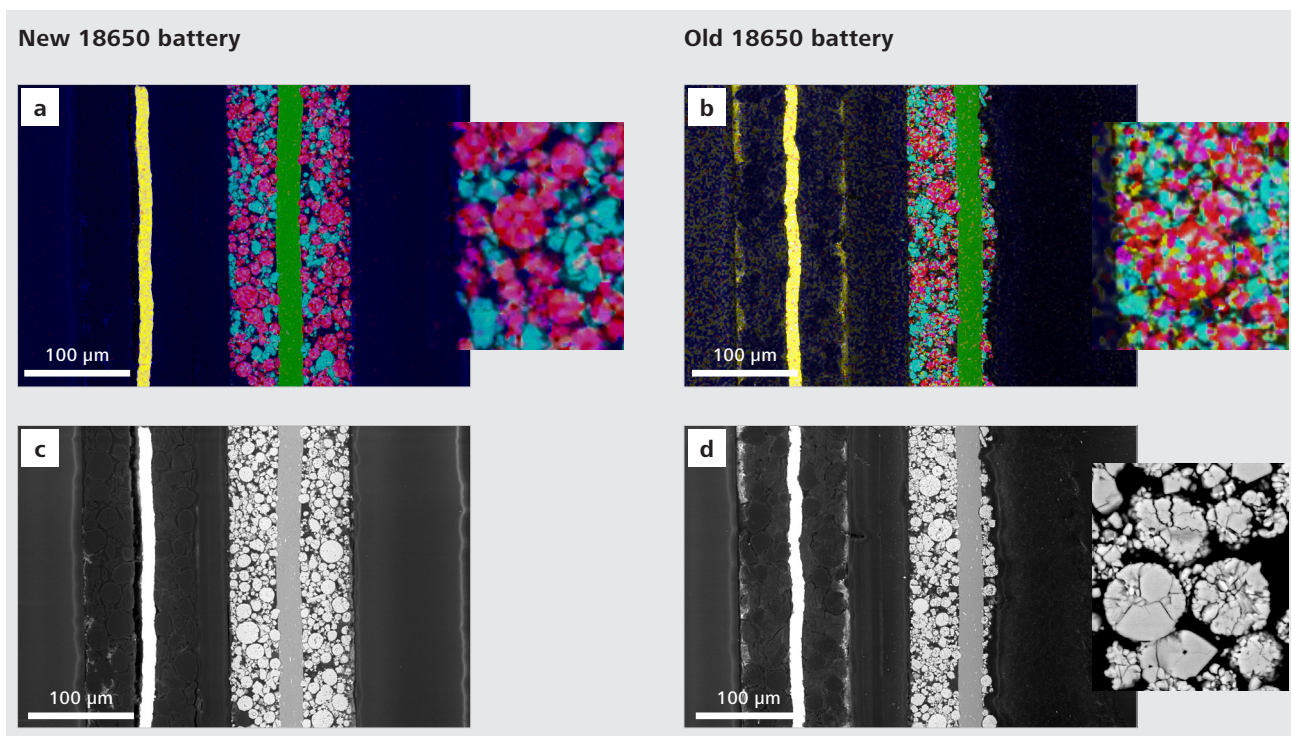


Figure 2 a: EDX mapping and c: SEM image of the new battery. Showing big particles in the cathode material with just a few small cracks. b: EDX mapping and d: SEM image of the cycled battery. Big cracks have developed and a volume expansion of both electrodes is observable.

FE-SEM Results

The current collectors are made of aluminum (green) and copper (yellow) respectively as highlighted in the EDX images in Fig. 2a,b. The cathode shows two different active materials: one Mn-rich phase which can be identified as LiMn_2O_2 and a Co,Ni-rich phase with the approximate stoichiometry of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (NCM111), see Figure 2. Another observation is the formation of cracks within the active material particles of the cycled electrode. Those cracks are presumably due to volume changes occurring during intercalation/deintercalation of lithium and the subsequent evolution of stress and strain inside the cathode material grains. The measured anode thickness difference was approximately 18% and the measured cathode thickness changed by 7%. The crumbling of particles normally leads to contact loss between particles and between particles and current collector [5]. This can be seen electrically by measuring an increased impedance and a power and capacity fading [6]. The thin layer which appears at the surface of the old anode contains heavy elements because it shows a bright signal in the back scattered electron image. Literature mainly reports about the SEI (solid electrolyte interface) layer on anodes which forms primarily during the first charging and discharging cycle and then slowly grows with each cycle, increasing the impedance

due to for example decreasing the accessible surface area at the anode [5]. But the SEI layer consists of light elements and inorganic compounds like LiF , Li_2Co_4 , Li_2O , LiOH and organic compounds like $\text{CH}_2\text{OCO}_2\text{Li}$, $(\text{CH}_2\text{OLi})_2$, $(-\text{CH}_2-\text{CH}_2-\text{O})_n$, thus the observed thin layer must be something different. High surface sensitive methods, for example XPS (X-ray photoelectron spectroscopy) are commonly used to characterize the SEI layer [4, 5]. But also SIMS (Secondary ion mass spectroscopy) which can be attached to a ZEISS SEM [6], determines the composition of SEI layer [4, 5]. The SEM and EDX images show limitations when it comes to polymeric material and light elements like carbon and lithium. Thus the anode material, the separator and the SEI cannot be characterized. While EDX measurements reveal information about the existing elements and metals, Raman spectroscopy is not able to detect metals but adds information about elements below $Z=4$ (Beryllium) and organic as well as inorganic material. Parameters that can be evaluated are for example the actual stoichiometry, the strain and stress, crystal symmetry, orientation, doping and crystallinity [7]. To be able to understand all morphological and compositional changes within a battery, Raman microscopy is the perfect complementary method.

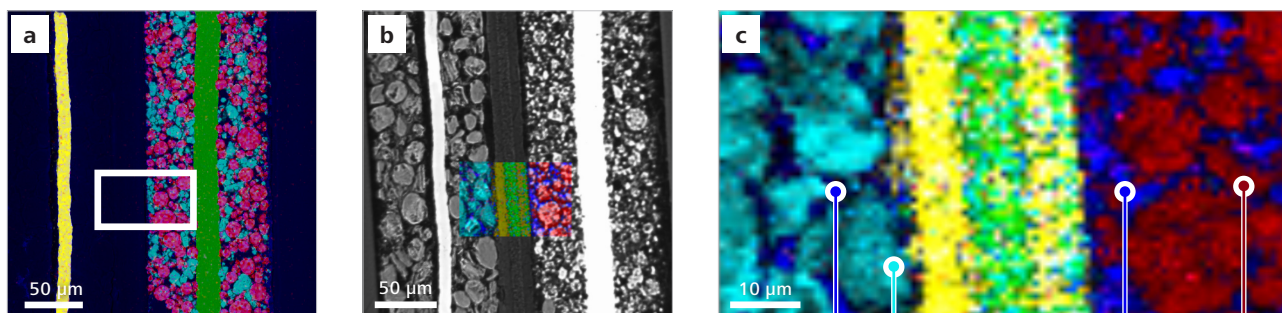


Figure 3 a: SEM image with EDX mapping, b: LM and Raman overlay of exactly the same region c: Raman mapping showing 2 different polymers in the separator

Raman results

The selected region in the white rectangle was analyzed by means of Raman microscopy, see Figure 3a. The anode is as expected graphite material and the amorphous carbon between the grains is the binder material of PVdf ($-(C_2H_2F_2)_n-$). Both parameters, anode composition and homogeneity of the binder, were not detectable in the SEM, however Raman serves with this complementary information. In addition a trilayer separator of polypropylene(PP)/polyethylene(PE)/polypropylene(PP)/ was found [8]. The comparison of the separator in a new and cycled battery element revealed a change of the orientation of the PP chains molecule orientation in the polypropylene, see Figure 4. While the new battery consisted of uniaxial polypropylene, the old battery is of bi-axial polypropylene. The direction of structures is indicated with the black arrows. The molecule orientation changes the properties of polypropylene in various ways, described in many papers [9, 10, 11, 12]. Polymers, by definition, are long chain molecules in which the atoms are bound to one another by means of strong covalent bonds. High strength and stiffness values in the chain direction are expected since the applied load would then be opposed by the covalent bond themselves. Most of the commercial polymers exhibit strength and stiffness values far below their theoretical limits. To improve these mechanical properties for example highlychain extended/oriented polymers are manufactured [11]. Biaxial polypropylene can be stretched at lower temperatures compared to uniaxial polypropylene [8]. And because of the biaxial orientation, good mechanical properties are achieved, for example strong chemical resistance, abrasion resistance, and good wettability with organic solvents. Also

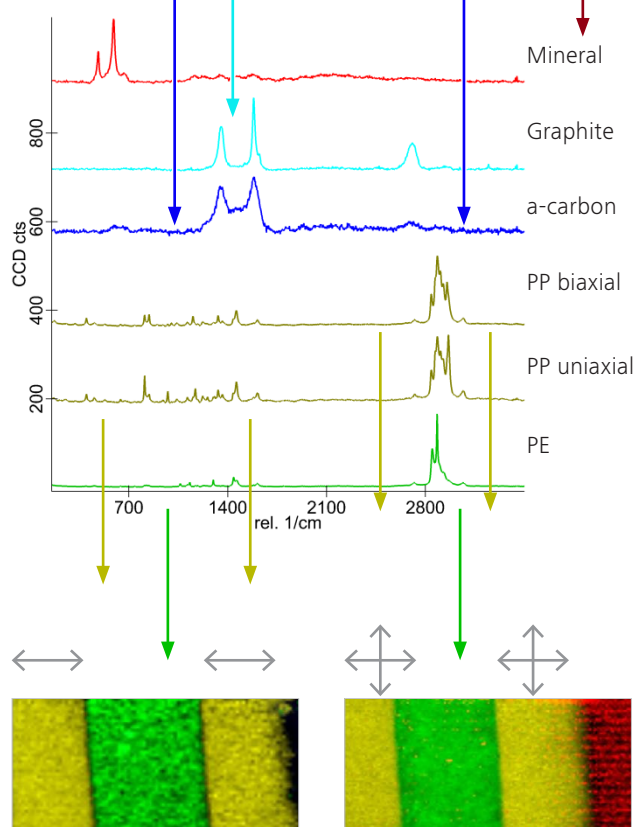


Figure 4 The Raman spectra refer to figure 3c, verifying graphite and binder in the anode and active mineral and binder being in the cathode. The images below show a Raman mapping of the new separator (left) and old separator (right).

the pore and void size, which normally lies between 35 % and 50% changes [12]. Hence the observed new molecule orientation can influence significantly the performance of the Li-ion battery.

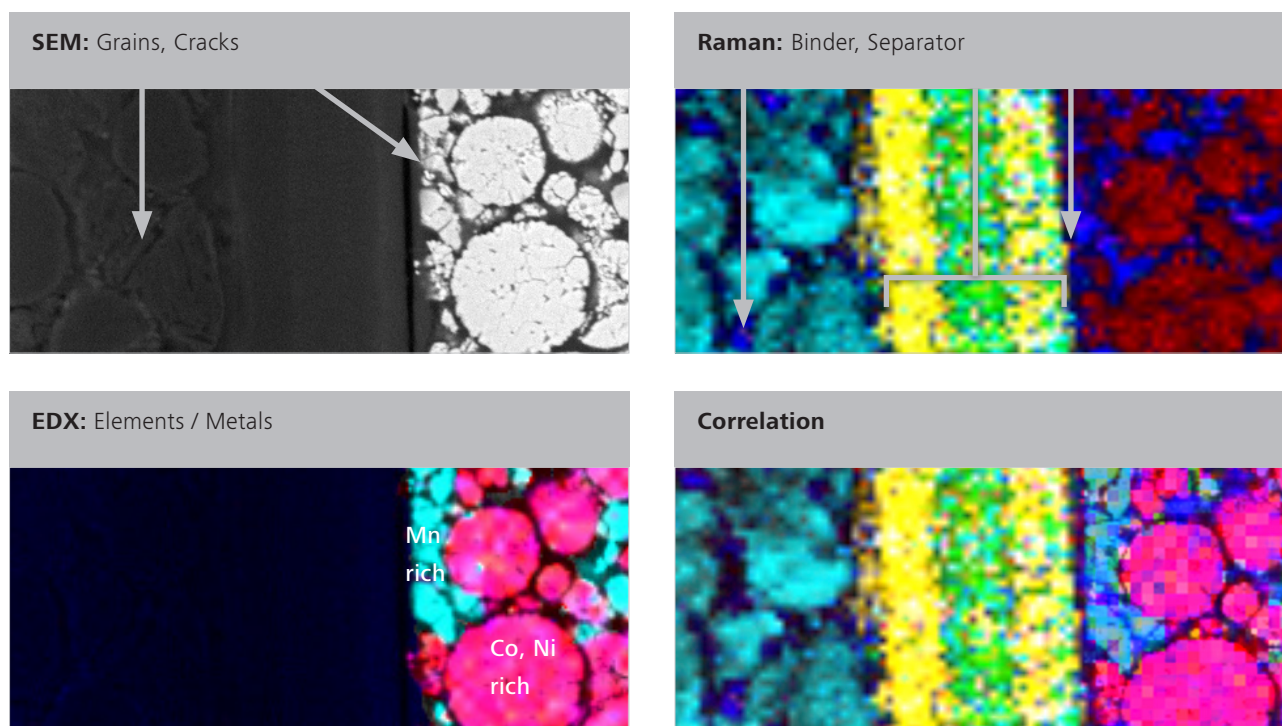


Figure 5 New battery: Overlay of SEM and Raman mapping

Summary

In this study, a multi-modal approach was used to analyze several parts of a commercial 18650 lithium ion battery within one system. High resolution scanning electron microscope images and EDX measurements revealed information about morphological changes like the cracking of particles after cycling and the exact composition of the cathode material. Raman microscopy was in addition used for infor-

mation gathering about the mainly carbon containing anode material as well as the polymeric separator. Also the homogeneity of the binder was made visible. It was possible to either perform a point measurement or a full mapping and then to overlay the complementary information of SEM and Raman imaging, see Figure 5.

References:

- [1] Isidor Buchmann, Batteries in a Portable World, April 2011
- [2] ISI Fraunhofer, Technologie-Roadmap Lithium-Ionen-Batterien 2030, 2010
- [3] C. J. Orendorff, Interface, Summer 2012, p61
- [4] Catarina Pereira-Nabais et. Al Applied Surface Science 266 (2013) 5–16
- [5] J. Vetter et. al Journal of Power Sources 147 (2005) 269–281
- [6] <http://mikroskopiadlaprzemyslu.pl/images/doc/microscope-zeiss-crossbeam-eng.pdf>
- [7] EN_ZEISS SEMs with integrated Raman system.pdf
- [8] A. H. Kuptsov and G.N. Zhizhin, Handbook of Fourier Transform Raman and Infrared Spectra of Polymers, Elsevier 1998
- [9] Stefan Rettenberger, Uni- and biaxial stretching of isotactic polypropylene in the partly-molten state, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), 2004
- [10] C.P. Lafrance and R.E. Prudhomme, "Characterization of the molecular-orientation in highly oriented rolled polypropylene sheets by X-ray-diffraction", Polymer, 35(18), 1994, pp. 3927-3935
- [11] Magill, J.H., et al., Int. Polym. Process. (1987) , 66–76
- [12] <http://entek.com/lithium-ion/>



Carl Zeiss Microscopy GmbH
07745 Jena, Germany
microscopy@zeiss.com
www.zeiss.com/microscopy

Not for therapeutic, treatment or medical diagnostic evidence. Not all products are available in every country. Contact your local ZEISS representative for more information.
EN_42_013_184 | CZ 10-2015 | Design, scope of delivery and technical progress subject to change without notice. | © Carl Zeiss Microscopy GmbH