Keysight Technologies
CSM and DCM-Express Nanoindentation Mapping on Lithium/Polymer Battery Composites
Application Note

Introduction

The main purpose of this work is to investigate the mechanical properties of a lithium rechargeable battery cathode[1–3] by using both the classic XP CSM and the new DCM Express Test method. Scanning Electron Microscopy (SEM) analysis is used as a support to understand the obtained results and gain information on the differences between the two adopted nanoindentation methods.

In particular, the attention is focused on the analysis of the mechanical and elastic properties of new generation lithium/polymer electrodes, with the final aim of correlating the life cycle and the number of charge and discharge cycles with the mechanical properties of the electrodes.

Using the an improved grid nanoindentation method[4–6], it was possible to perform a statistical deconvolution of the mechanical properties and to understand which and how many heterogeneous material phases are there and how they interact between themselves. A last aspect of interest, related to the lithium/polymer batteries, is to investigate the mutual mechanical interaction among the different components, in order to gain information on the correlation between chemical and mechanical properties.
A lithium/polymer battery[1–3] is made of lithium-polymer conductive composite materials, obtained by embedding lithium salt solutions in opportune polymeric matrix. The polymeric cells have a flexible sheet structure, so external pressure is not needed since the electrode sheets and the separator (dielectric) are laminated one on top of the other. This kind of batteries has the significant advantage to be realized in any form or dimension and, since the lack of usefulness of any metal container, they could be lighter and shaped to fill the space reserved to it. An example of a cathode's microstructure is reported in Figure 1a.

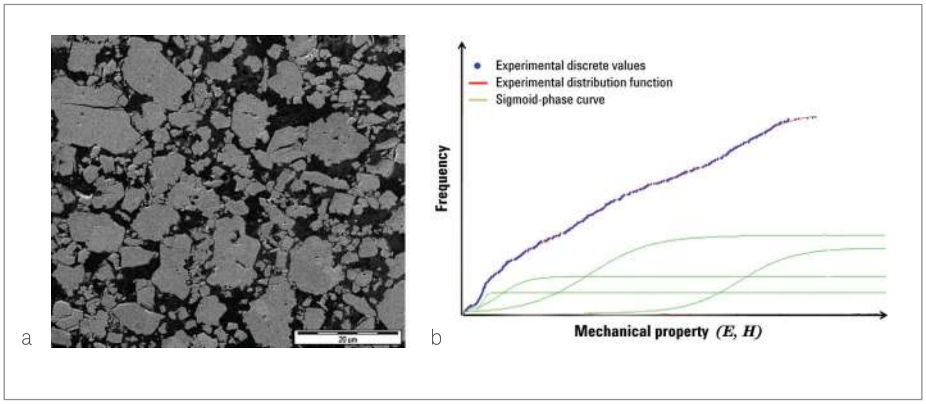

Figure 1. (a) Example of a microstructure of a lithium/polymer battery cathode. (b) Principle of property deconvolution using the Cumulative Distribution Function (CDF).

However, the main critical issue related to the functional behavior of such devices is intrinsically related to the strong difference, in terms of mechanical properties, between the two main components of the composite material.

In view of this, evaluating the mechanical properties of such materials, by using proper nano-mechanical testing, is extremely important.

In this work, mechanical properties have been investigated by the use of an improved statistical nanoindentation method, which is described in the next chapter. The developed procedures allows for the accurate determination of the elastic and plastic properties of each single phase, together with a careful analysis of the gradients of the same properties within single particles, an aspect which becomes more important when analysing the mechanical property loss after several charge/discharge cycles.

Statistical Nanoindentation Method

The statistical (or grid) nanoindentation method was originally proposed for cement-based materials[4]. The method consists of the realization of grids of hundreds of indentation tests, coupled with a statistical analysis (deconvolution) of either the elastic modulus or hardness data for the identification of the different mechanical phases and their distribution over the sampled area.

The deconvolution process is applied to the Cumulative Distribution Function (CDF) of obtained data, and used to get the weighted sum of hoarded curves that best fit the empirical cumulative probability distribution.

A generic cumulative distribution function (CDF) is given by:

$$F(x)=\sum_{J=1}^{n} f_J D_J(x); \qquad j=1,n$$

where $D_j(x)$ is the hoarded probability distribution of the j phase :

$$D_j(X)=\frac{i}{N}-\frac{1}{2N} \quad \text{with } i \in [1,N]$$

being: $\sum_{J=1}^{n} f_J = 1$

There are 3n-1 unknowns which are calculated imposing that the theoretical function has a minimal square deviation compared with the empirical cumulative probability curve showed from the indentation tests :

$$(\mu_J, s_J, f_J) \text{ from min } \sum_{i=1}^{m}\frac{(F_i-F(x_i))^2}{m}; \quad i=1,m$$

where Fi are the empirical values of the cumulative probability corresponding to the i-class.

The principle of the method is reported in Figure 1b.

Using the cumulative function is extremely useful when the number of phases in the material under investigation is mostly unknown; in fact, when the cumulative experimental function is built, it is possible to find the polynomial that best fits the cumulative curve (see Fig.1). The number of the phases can be correlated to the polynomial order of the CDF function which best fit the experimental cumulative curve. In particular, if ***n*** is the polynomial order of the CDF, the number of real phases will be equal to ***n-2*** (i.e. the number of flexes).

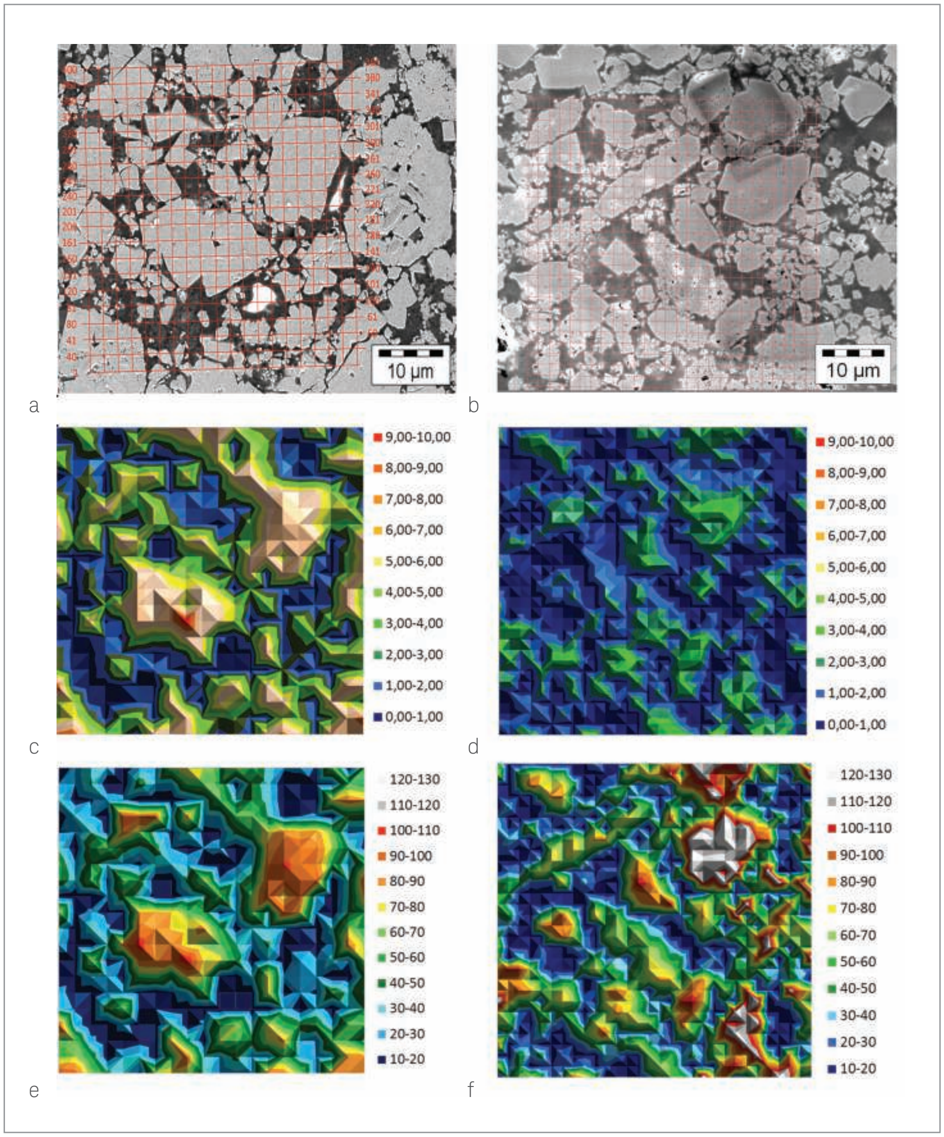

Figure 2. (a) XP-CSM Nanoindentation Grid. (b) DCM Express Nanoindentation Grid. (c) XP CSM Standard – Hardness [GPa], calculated at depth 100 nm. (d) DCM Express – Hardness [GPa]. (e) XP CSM Standard – Modulus [GPa], calculated at depth 100 nm. (f) DCM Express – Modulus [GPa].

Experimental Details

A Lithium-ion battery cathode, composed by a mixture of active particles ($LiMn_2O_4$) and carbon black in a polymeric matrix of Polyvinylidene fluoride (PVDF), was embedded in epoxy and mirror polished before mechanical testing. The cathode thickness is about 150 µm. Lithium particles, exhibit significant variance in their size and internal porosity, as shown in Fig.2; this leads to a different response in terms of mechanical properties.

The methodology that was developed in this work is mostly based on the combined and synergic application of several experimental techniques, i.e.:

- Scanning Electron Microscopy (SEM) morphological analysis before and after nanoindentation testing
- Nanoindentation tests with standard XP CSM mode and DCM Express Test mode
- Improved Statistical analysis, consisting of:
  - 2D mapping of mechanical properties (Elastic Modulus E, Hardness H)
  - Deconvolution of the cumulative distribution functions (CDF) for the analysis of single-phase mechanical properties

The deconvolution process is performed using a Matlab-based routine.

XP CSM tests were performed using a

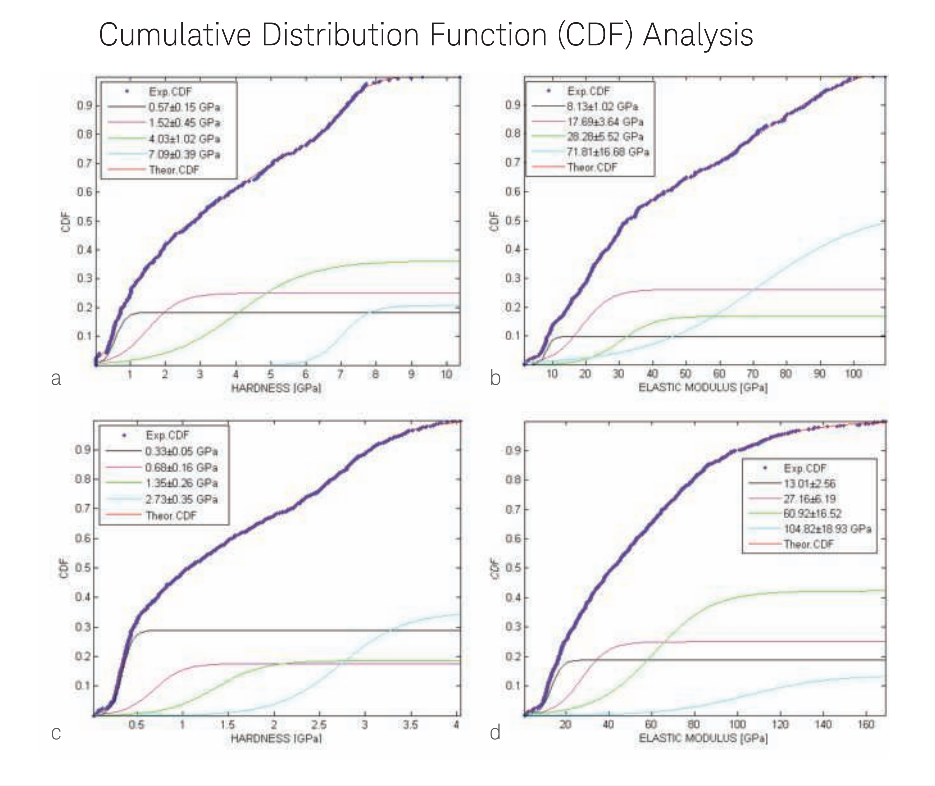
Cumulative Distribution Function (CDF) Analysis

Figure 3. (a) CDF analysis (for the hardness) on 400 indents obtained by the conventional CSM method at 100 nm depth. (b) CDF analysis (for the elastic modulus) on 400 indents obtained by the conventional CSM method at 100 nm depth. (c) CDF analysis (for the hardness) on 900 indents obtained by the DCM Express method at 80 nm depth. (d) CDF analysis (for the elastic modulus) on 900 indents obtained by the DCM Express method at 80 nm depth.

Berkovich tip, with a frequency of 45 Hz, amplitude of oscillation 2 nm, constant strain rate of 0.05 s-1, maximum penetration depth 150 nm (which roughly corresponds to 1.0 µm of lateral dimension of indents). In this way, the results allows for the statistical analysis of obtained data at different penetration depths.

A grid of 20x20 indentations was realized, being the spacing between indents is fixed at 10 µm. In this way, any mutual interaction among contiguous indentation marks can be assumed to be negligible. Shallower indentations would be required in case of a finer mesh. A full week-end session was required to complete one single matrix (400 indents).

DCM ultrafast tests were performed by using the Keysight Express Test method and a Berkovich tip, by fixing a maximum depth of 80 nm and a spacing of 1.5 µm and an area of analysis of 50x50 µm^2. Six different matrices were performed in a single session (roughly two hours to realize more than 5000 indents). The instrument was completely re-calibrated (area function and frame stiffness) before and after testing, by performing a series of indentations on a certified amorphous fused silica reference sample.

Detailed microstructural and compositional observation of the same areas of the tests were finally performed by SEM analysis.

Results and Discussions

The obtained mechanical maps (Fig.2c–f) show a good representation of the actual microstructure and phase distribution, in comparison with the SEM images (Fig. 2a–b). After a careful analysis of both the load-displacement curves and the SEM images, all the out-of-range tests were clearly correlated to the presence of micro-cracks or porosity in correspondence of the indentations.

The CSM approach mode used in the tests with the XP head is useful to highlight that the mechanical maps at the three different depths (50, 100, 150 nm) show, with qualitative agreement, different values of hardness and elastic modulus. This is due to the effects of the surrounding compliant matrix on the stiffer particles

Modulus and hardness values increase (in average) with decreasing indentation depth when looking at the CSM data.

The gradients of hardness and modulus over a single particle are reduced with decreasing penetration depth. This is a direct consequence of the relevance of the edge effects, which obviously are reduced as the penetration depth is reduced.

Using the XP CSM method it is possible to choose, for the calculation of the average value of Hardness and Elastic Modulus, the range of displacement into the surface. In this work the ranges selected are 45–55, 95–105 and 145–155. This method permit to discriminate the artifacts of the roughness effects, that affect the lower displacement, or the substrate influence, that affect the higher displacement. This second effect is particularly significant in the evaluation of the Elastic Modulus that is a massive property.

However, using the CSM data resulted to be not sufficient in order to get reliable deconvolution of the actual mechanical properties, due to the limited number of valid tests that can be obtained in a reasonable time.

The use of the Express Test method was then required in order to gain more reliable information on the single-phase hardness and modulus.

With this in mind, the optimization of the CDF results in the identification of 4 most representative phases (see Figure 3):

- A phase representing the lithium particles (the higher values of hardness and the lower values of elastic modulus)
- A phase representing the matrix (the lower values of hardness and the higher values of elastic modulus)

These first two peaks are characterized by a relatively small standard deviation, as a direct suggestion that they really represent the properties of the two main constituents

- Two phases representing the matrix influence for the smaller particles, the edge effect, the defects in the particles (the intermediate values) and roughness effects.

These last two peaks are characterized by a relatively higher standard deviation, as a direct suggestion that they represent the properties of various artefacts.
It is interesting to note how the Elastic modulus value achieved with the DCM Express Test is higher than the values obtained with the XP CSM, due to the higher strain rate applied during indentation and the viscoelastic properties of the polymer matrix.

Conclusion

The use of Express Test nanoindentation testing is extremely useful to identify the single-phase mechanical properties and their spatial distribution in lithium/polymer battery composites.

Careful mapping of elastic modulus and hardness, together with robust statistical analysis allows for a reliable analysis of the microstructural/mechanical features of such materials.

The effects of applied strain rate and the selection of the optimal penetration depth for lithium/polymer heterogeneous materials is possible by the comparison between XP CSM and DCM Express nanoindentation mapping results.

References

1. P. Kurzwell, K. Brandt, Secondary batteries – Lithium rechargeable systems, (2007).
2. J. Zhu and K. Zeng, Electrochimica Acta, 15:52–59, 2012.
3. J. Vetter, P. Novak, M.R Wagner, C. Veit, K.-C. Muller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche – Ageing mechanisms in lithium-ion batteries. J Power Sources, 147:269–281, 2005.
4. G. Constantinides, F.J. Ulm, J. Mech. Phys Solids 55 (2007) 64–90.
5. M. Vandamme, F.J. Ulm, P. Fonollosa, Cement Concr. Res. 40 (2010) 14–26.
6. M. Vandamme, F.J. Ulm, Cement and Concrete Research 52 (2013) 38–52.

Nanomeasurement Systems from Keysight Technologies

Keysight Technologies, Inc., the premier measurement company, offers high-precision, modular nanomeasurement solutions for research, industry, and education. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Keysight's leading-edge R&D laboratories ensure the continued, timely introduction and optimization of innovative, easy-to-use nanomeasure system technologies.

www.keysight.com/find/nano

For more information on Keysight Technologies' products, applications or services, please contact your local Keysight office. The complete list is available at:
www.keysight.com/find/contactus

Americas

Canada	(877) 894 4414
Brazil	55 11 3351 7010
Mexico	001 800 254 2440
United States	(800) 829 4444

Asia Pacific

Australia	1 800 629 485
China	800 810 0189
Hong Kong	800 938 693
India	1 800 112 929
Japan	0120 (421) 345
Korea	080 769 0800
Malaysia	1 800 888 848
Singapore	1 800 375 8100
Taiwan	0800 047 866
Other AP Countries	(65) 6375 8100

Europe & Middle East

Austria	0800 001122
Belgium	0800 58580
Finland	0800 523252
France	0805 980333
Germany	0800 6270999
Ireland	1800 832700
Israel	1 809 343051
Italy	800 599100
Luxembourg	+32 800 58580
Netherlands	0800 0233200
Russia	8800 5009286
Spain	0800 000154
Sweden	0200 882255
Switzerland	0800 805353 Opt. 1 (DE) Opt. 2 (FR) Opt. 3 (IT)
United Kingdom	0800 0260637

For other unlisted countries:
www.keysight.com/find/contactus
(BP-07-10-14)

Published in USA, August 3, 2014
5991-3519EN
www.keysight.com