**Application Note**

**Lithium Polymer Battery Mapping - Express Test**

**Introduction**

The main purpose of this work is to investigate the mechanical properties of a lithium rechargeable battery cathode\(^1\) 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 a grid nanoindentation method,\(^4\) it was possible to perform a statistical deconvolution of the mechanical properties, and to understand the many heterogeneous material phases that exist and the interaction between them. Another aspect of interest, related to the lithium polymer batteries, was also to investigate the mutual mechanical interaction among the different components to gain information on the correlation between their chemical and mechanical properties. A lithium polymer battery\(^1\) 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 battery can be lighter and variable in shape due to the lack of use of a metal container. An example of a cathode’s microstructure is reported in Figure 1(a). The main critical issue related to the functional behavior of such devices is intrinsically related to the difference in mechanical properties between the two composite materials. In view of this, using proper nanomechanical testing to evaluate the mechanical properties of such materials is extremely important.

In this work, mechanical properties have been investigated using an improved statistical nanoindentation method, which is described in the next chapter. This procedure allows for the accurate determination of the elastic and plastic properties of each single phase and the gradients of the same properties within single particles, a factor that becomes more important when analyzing the mechanical property loss after several charge/discharge cycles.

**Statistical Nanoindentation Method**

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

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 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:

\[
F(x) = \sum_{j=1}^{n} f_j D_j (x); \quad j \in [1, N]
\]

being:

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

\[
\sum_{j=1}^{n} f_j = 1
\]
There are 3n-1 unknowns that are calculated requiring that the theoretical function has a minimal square deviation compared with the empirical cumulative probability curve showed from the indentation tests:

\[
(\mu_i, s_i, f_i) \text{ from } \min \sum_{i=1}^{m} \frac{(F_i - F(x_i))^2}{m}; \ i=1,m
\]

where \( F_i \) are the empirical values of the cumulative probability corresponding to the i-class.

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

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 Figure 1). The number of phases can be correlated to the polynomial order of the CDF function which best fits 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).

**Experimental Details**

A lithium-ion battery cathode, composed of a mixture of active particles (LiMn2O4) and carbon black in a polymeric matrix of Polyvinylidene fluoride (PVDF), was embedded in epoxy and mirror polished before mechanical testing. The cathode thickness was about 150μm. Lithium particles exhibit significant variance in their size and internal porosity, as shown in Figure 2. This leads to 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 (CDFs) 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 Berkovich tip with a frequency of 45Hz, an amplitude of oscillation 2nm, a constant strain rate of 0.05s⁻¹ and a maximum penetration depth 150nm (which roughly corresponds to 1.0μm of lateral dimension of indents). In this way, the results allow for the statistical analysis of obtained data at different penetration depths.

A grid of 20 x 20 indentations was realized, with indent spacing fixed at 10μm. In this way, any mutual interaction among contiguous indentation marks can be assumed to be negligible. Shallower indentations would be required in the case of a finer mesh. A full weekend session was required to complete one matrix (400 indents).

DCM ultrafast tests were performed by using the Express Test method and a Berkovich tip by fixing a maximum depth of 80nm, a spacing of 1.5μm and an area of analysis of 50x50μm². 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 (Figure 2(c)–(f)) show a good representation of the actual microstructure and phase distribution in comparison with the SEM images (Figure 2(a)–(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 microcracks or porosity in correspondence with the indentations.

The CSM mode used in the tests with the XP head highlights that the mechanical maps at the three different depths (50nm, 100nm, 150nm) 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 (on 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 edge effects, which diminish as the penetration depth is reduced.

Using the XP CSM method, it is possible to choose the range of displacement into the surface for the calculation of the average value of Hardness and Elastic Modulus. In this work, the ranges selected were 45-55nm, 95-105nm and 145-155nm. This method facilitated the discrimination of artifacts of the roughness effects, which affect the lower displacement, or the substrate influence, which affect the higher displacement. This second effect is particularly significant in the evaluation of the elastic modulus.

However, using the CSM data was insufficient for reliable deconvolution of the actual mechanical properties due to the limited number of valid tests that can be obtained in a reasonable time.

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

With this in mind, optimization of the CDF results in the identification of the four 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 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 high standard deviation, suggesting that they represent the properties of various artifacts. It is interesting to note that 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.

Cumulative Distribution Function (CDF) Analysis

![CDF analysis graphs](image)

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

The Express Test method of 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 through the comparison of XP CSM and DCM Express nanoindentation mapping results.

References