In situ Broadband Dielectric Spectroscopy of electrodes for lithium batteries from low frequencies to microwaves

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The fruitful contribution of Broadband Dielectric Spectroscopy (BDS) to study hierarchical materials applied to batteries electrodes has been previously shown [1-4]. The results demonstrate that the broadband dielectric spectroscopy technique is very sensitive to the different scales of the electrode architecture involved in the electronic transport, from interatomic distances to macroscopic sizes, as well as to the morphology at these scales, coarse or fine distribution of the constituents. When the frequency increases, different kinds of polarizations appear from interatomic distances to macroscopic sizes (Fig. 1) and give rise to dielectric relaxations in the following order [1-4]: (a) space-charge polarization (low-frequency range) due to the interface sample/current collector; (b) polarization of clusters of particles (micronic scale) and (c) polarization of particles due to the existence of resistive junctions between them; d) electron transfers (nanometric or interatomic scale).

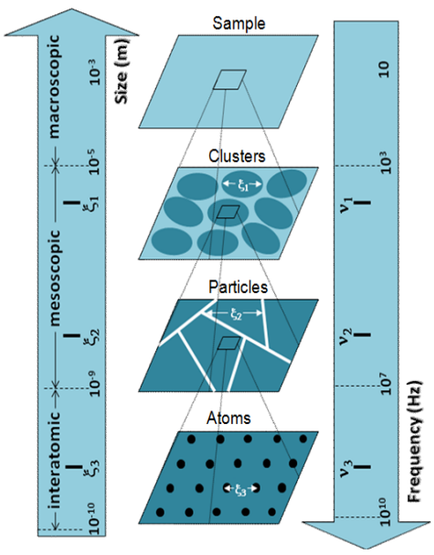

Figure 1. Schematic description of a hierarchical architecture at different scales of a powdered material: different sources of polarizations vs. frequency and size.

The BDS measurement was up to now ex situ measurement, on dry electrode. They provide a fundamental insight into the conduction properties at all scales of the materials before being integrated in a real battery. An innovative device (measurement cell) has been developed to make synchronized BDS measurements and electrochemical cycling. The frequency range is about 10^3 - 10^{10} Hz. In this work, data acquisitions were made on dry electrode ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ / Carbon black / PVdF) (Fig. 2) and then on the same electrode wetted with an electrolyte, after the first charge and the first discharge.

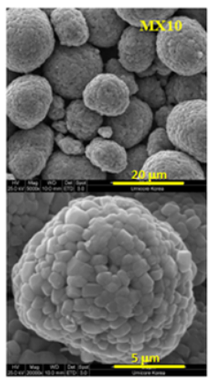

Figure 2. SEM images of the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder: MX10 (mean cluster size = 10 µm)

Since all the polarizations at different scales are additive owing to their vectorial character, their contributions (relaxations) can thus be evidenced by a decomposition procedure of the Nyquist plots (ε" vs. ε'). Data acquisitions as function of temperature were also carried out, in order to determine the activation energies of the conductivity and relaxation frequencies at the different scales of the materials architectures.

The new device opens thus important prospects to determine the evolutions of the multi-scales electrical properties during electrochemical cycling.

References

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