Investigating Li-ion batteries negative electrode swelling processes using electrochemical dilatometer

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Célia Doublet,[a]* Lauréline Lecarme,[a] Sandrine Lyonnard,[b] Claire Villevieille,[a]

[a] Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

[b] Univ. Grenoble Alpes, CEA, CNRS, IRIG-SyMMES, 38000 Grenoble, France

* celia.doublet@grenoble-inp.fr

Li-ion batteries despite being the most commercialised electrochemical energy storage system are still suffering some drawbacks during their cycling. Indeed, several processes are taking place during cycling, i) the electrodes are "breathing" during oxidation and reduction, ii) the electrolyte is reduced and oxidised generating several surface reactions among them the well-known solid electrolyte interphase (SEI). As an example, at the negative electrode, graphite is suffering a volume expansion of up to 10% that is generally reversible but upon long-term cycling can be a caused of fading (ref.1). This induced mechanical stress and its consequence on the electrochemical performance need to be investigated. Nano electrochemical dilatometer can help up addressing the question about the swelling of the electrode as well as the swelling caused by the SEI and other surface reactions. We propose here to investigate the swelling of different graphite grade as a function of the electrolyte by nano electrochemical dilatometer. A scheme of the device is depicted in **Figure 1**. As can be seen, the set-up is made of several part, the most important one being the T-frit that ensures, that the dilatometer is only monitoring one electrode at a time. Indeed, the T-Frit, is a borosilicate separator that is pre-soaked in the dedicated electrolyte and that avoids any influences of the counter electrode. The sensor placed on the top of the cell is thus only measuring the working electrode (WE) displacement during cycling using a three-electrode assembly. Additionally, a thermocouple is linked to the apparatus helping help deconvoluting the influence of the temperature on the sensor displacement.

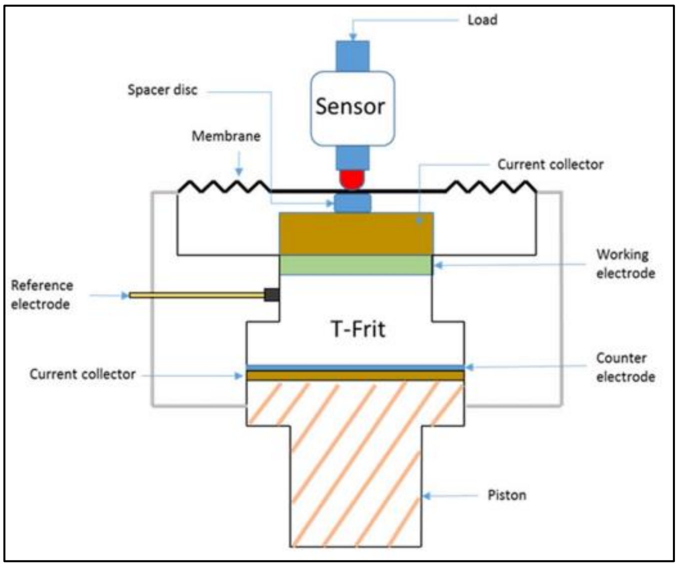

Figure 1 : *Cross section scheme of the nano-dilatometer (ECD-3-Nano, EL-Cell GmbH) device. Only the displacement of the working electrode (WE) is monitored because the glass T-frit is fixed in position. Reprinted from ref. 2.*

Figure 2 is showing the first lithiation of SFG6L graphite coupled to the dilatometer measurement obtained at C/40 rate. The graphite is cycled vs. Li metal, used as both reference electrode and counter electrode, and using LP30 organic-based electrolyte. At first glance the electrochemical signature of graphite is as expected with the SEI formation at 0.8 V vs. Li^{+}/Li followed by the different graphite stages. The monitoring of the displacement (swelling) ot the electrode is to date more difficult to interpreted due to its sensitivity to many parameters such as temperature fluctuation, airtightness and even the device's own drift as reported in the literature (ref.2, 3). In this presentation we will show the influence of the graphite grades onto the dilatometer measurement and presents different mathematical methods to remove artefact from the temperature fluctuation.

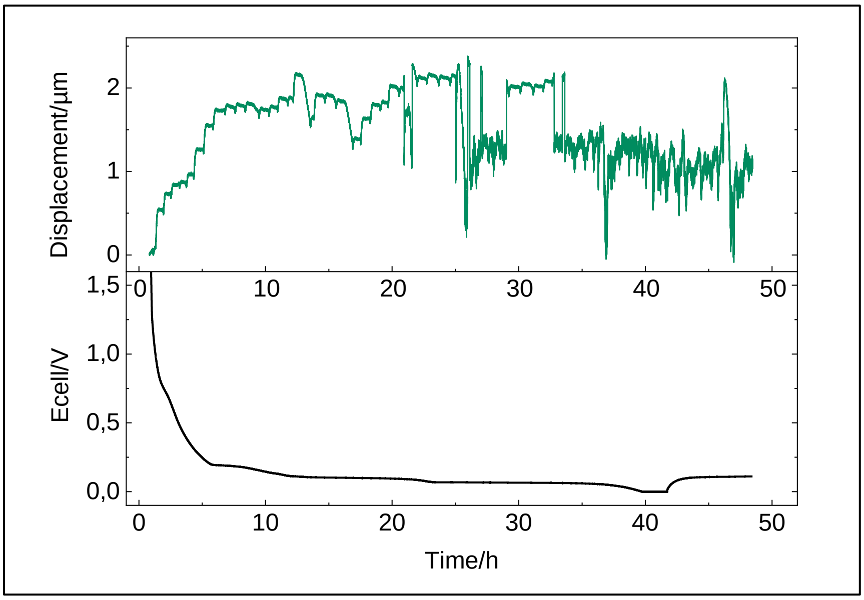

Figure 2: *First lithiation of SFG6 graphite vs. Li metal using LP30 electrolyte at C/40 rate. The second panel is showing the displacement of the dilatometer sensor during the lithiation of graphite.*

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