



# Electrochemical Impedance Spectroscopy response study of a commercial graphite-based negative electrode for Li-ion batteries as function of the cell state of charge and ageing



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## ABSTRACT

The successful development of electrified vehicles is a key factor in the transition to a more environmentally friendly transportation sector. Li-ion batteries, which are today's choice to power electrified vehicles, have to fulfill more stringent requirements in terms of ageing and need advanced tools to study the interfaces evolution upon cycling. This work is thus focused on understanding the impedance behavior of a commercial graphite-based negative electrode, which is used in a Li-ion battery designed for such vehicles. 3-electrode pouch cells were assembled with such negative electrode, a LMO-layered oxide-based positive electrode, a Celgard<sup>®</sup> type separator soaked with a carbonate solvents-LiPF<sub>6</sub> mixture electrolyte and a LTO-based electrode as reference. Electrochemical Impedance Spectroscopy measurements were performed at different cell states of charge and ageing times. The impedance of the graphite-based anode is analyzed for first time with *de Levie's* equation for porous electrodes. The analysis is supported by designed SEI layer formation experiments with vinylene carbonate and vinylene ethyl carbonate additives. The high frequency domain of the interfacial kinetic loop reflects porosity effects and the graphite particles-composite matrix electric transfer. The SEI layer and charge transfer phenomena are reflected in the medium and medium to low frequency domains respectively, and their impedance contributions depend on the Li content of the graphite particles. Upon ageing, the interfacial impedance of the graphite-based electrode should increase due to SEI layer growing. However, from 100% to 80% of battery capacity retention, the impedance decreases. Our analysis backed by post-mortem characterizations allows to assign this unexpected behavior to porosity rise and slight Mn-contamination of the SEI layer.

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## 1. Introduction

Li-ion batteries are today's choice for powering the Battery-Electric and Hybrid-Electric Vehicles (BEV and HEV respectively) that are progressively entering into the transportation market. In order to fulfill the long lifetimes required for such applications, the industrial and the scientific sectors have oriented their efforts towards understanding the electrochemical behavior and ageing

mechanisms of these batteries. Electrochemical Impedance Spectroscopy (EIS) is commonly applied, since it brings substantial information regarding the electrochemical processes that take place inside the battery, at different time scales. The non-destructive character of EIS renders this technique promising for *in-situ* diagnosis of State of Charge (SOC) and State of Health (SOH) [1,2]. However, interpreting the EIS response of a Li-ion battery is not straightforward due to the complexity of conduction phenomena in the battery, which include namely electronic, ionic and interfacial conduction [3]. In addition to that, the presence of two electrodes with different chemistries increases the impedance response complexity. This renders necessary the study of each

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electrode behavior separately by implementing 3-electrode cells or devising electrical equivalent circuit models.

Graphite-based composites are the most common negative electrodes in today's commercial Li-ion batteries. Their EIS responses have been extensively reported [4–13], and it is well established that their interfacial impedances reflect the following phenomena: Li<sup>+</sup> transport through the solid electrolyte interphase (SEI) layer, charge transfer accompanied by double layer phenomenon on the particle surfaces [5–8,10–12,14,15], effects deriving from the electrode architecture as porosity [6,16], and electronic conductivity [17]. However, there are ambiguities in relation to the impedance dependence on the Li content in the graphite particles, since impedance increase, decrease and constant impedance are found in the literature as a function of this factor [4–6,16–21]. These discrepancies derive from the different cell set-ups used for the measurements (half-cells, 3-electrode cells and single particle set-ups), the composite electrode properties (porosity, active material loading, binder, etc.), the type of graphite particles (beads or flakes-like), the electrolyte or additives used and whether the measurements are performed during or after the SEI layer formation [4–6,16–21].

In a first part of this study, we focus on analyzing the EIS response variations with SOC of a “fresh” graphite-based negative electrode that is implemented in a commercial high-energy density Li-ion cell for BEV applications. For this sake, 8 mAh three-electrode pouch cells [22] were assembled with negative and positive electrodes recovered from the high-energy density cell. The interfacial impedance of the negative electrode is analyzed by combining *de Levie's* model for porous electrodes [23–25] and Equivalent Electric Circuits (EEC). In the literature, *de Levie's* model is applied for analyzing the impedance related to corrosion phenomena [23–25]. Herein, we show that this model can also be implemented to account for porosity effects in the case of graphite-based electrodes designed for Li-ion systems. The utilization of EEC could bring controversies and broad interpretations to the impedance analyses [26]; to avoid this issue, the physical interpretations associated with the EEC are supported by designed experiments to modify the SEI layer.

In a second part of this study, the electrode impedance variations with ageing are also explored by assembling the three-electrode pouch cells with electrodes recovered from aged commercial cells. Impedance result interpretations are supported by post-mortem analyses.

## 2. Experimental procedure

### 2.1. Characteristics of the high-energy density cells

The commercial Li-ion cell from which the electrodes were recovered was a 5.7 Ah pouch cell operating between 3.0 and 4.15 V. The double-face negative electrode was a ~59 μm thick graphite-based composite on a ~10 μm thick Cu current collector. The graphite particles were bead-shaped with a D<sub>50</sub> value of ~14 μm. The positive electrode was a double-face “LiMn<sub>2</sub>O<sub>4</sub> – layered oxide” blend composite (layered oxide content between 25 and 50 in wt. %, proprietary composition), with a side thickness below 60 μm on a ~20 μm thick Al current collector. The electrolyte was a 1 M LiPF<sub>6</sub> salt dissolved in carbonate solvents mixture. The separator was a 25 μm Celgard<sup>®</sup> type.

The “fresh” cell followed the industrial SEI formation step carried out by the battery provider and then a few capacity check-up tests. The graphite-based electrode samples recovered from this cell present a just formed SEI layer.

The aged cells followed a fast-charge (~20 min) ageing protocol at 25 °C, which included a nominal capacity check-up every 100

cycles. Aged cells were selected for impedance analyses, when the nominal capacities dropped below 90%, 80% and 70%.

### 2.2. Characteristics of the 8 mAh 3-electrode pouch cells

The above described high-energy density Li-ion cells were fully discharged to 3.0 V and opened in an Ar-filled glove box. The electrode samples were recovered and prepared gently by wiping off one side of the composite from the current collector with dried 1-methyl 3-pyrrolidinone solvent as described elsewhere [27–29]. The negative and positive electrode samples were dimensioned to assemble 8 mAh 3-electrode pouch cells [22]. These cells have a Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-based Bellcore<sup>®</sup> reference-electrode (called Ref) [15,30]. The design of these cells is carefully chosen to avoid the so-called “impedance distortions” [31,32] that are mainly due to geometrical effects when introducing a reference in a 2-electrode system.

### 2.3. EIS measurement conditions in the 8 mAh pouch cells

Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) measurements were carried out at different SOC, using a multi-potentiostat (VMP Biologic, Claix – France), with potential perturbation (ΔV) of 10 mV<sub>rms</sub> and in the frequency range between 100 k and 10 mHz. Galvanostatic charge at 0.1C was applied to reach the desired SOC for PEIS measurements. Once the SOC was reached, prior to the PEIS test, an Open Circuit Voltage (OCV) period of 2 h was imposed to allow cell relaxation.

### 2.4. Designed SEI layer forming experiments

These experiments were performed to identify how the interfacial impedance is affected when the SEI layer properties are modified. In this case, the 8 mAh 3-electrode pouch cells were assembled with pristine negative and positive electrodes. The term pristine is used to point out that these electrodes have never been formed or cycled before. Four different electrolytes mixtures were tested: EC/DEC<sup>1</sup> (3:7 v/v) + 1 M LiPF<sub>6</sub>+VC<sup>2</sup> (2 wt.%) named electrolyte LRC02, EC/DEC (3:7 v/v) + 1 M LiPF<sub>6</sub>+VEC<sup>3</sup> (2 wt.%) named electrolyte LRC03, EC/DEC (3:7 v/v) + 1 M LiPF<sub>6</sub> called blank electrolyte and EC/DEC (3:7 v/v) + 1 M LiPF<sub>6</sub> + Mn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> (2 wt.%) called ME electrolyte.

Soon after assembling, the 3-electrode pouch cells were formed at room temperature (RT) by imposing a 0.1C galvanostatic charge from the OCV to 4.15 V (100% SOC). After 2 h of OCV, impedance measurements were carried out.

### 2.5. Post-mortem analyses

To support the interpretation of the impedance changes of aged electrodes, post-mortem characterizations were performed. The cell opening and electrode preparation procedures were carried out in an Ar-filled glove box.

#### 2.5.1. Electron Microscopy Techniques

Transmission Electron Microscopy (TEM) analyses on post-mortem samples were performed using a Tecnai F20 S-Twin microscope, operating at 200 keV and coupled with an energy dispersive X-ray analyses (EDX). High Resolution (HRTEM) images were collected for the surface study. The electrode samples were immersed in acetonitrile (CH<sub>3</sub>CN) to dissolve non-volatile electrolyte residues (EC and LiPF<sub>6</sub>) and to disperse some active material

<sup>1</sup> Ethylene carbonate/Diethyl carbonate.

<sup>2</sup> Vinylene carbonate.

<sup>3</sup> Vinylene ethyl carbonate.

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