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A Physically-Based Equivalent Circuit Model for the Impedance of a LiFePO4/Graphite 26650 Cylindrical Cell

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In this work an Equivalent Circuit Model (ECM) is developed and used to model impedance spectra measured on a commercial 26650 LiFePO4/Graphite cylindrical cell. The ECM is based on measurements and modeling of impedance spectra recorded separately on cathode (LiFePO4) and anode (Graphite) samples, harvested from the commercial cell. Modeling of the single-electrode impedance spectra provided information about the electronic and ionic resistance in the porous composite electrodes, as well as the solid state diffusion. Focused Ion Beam (FIB)/Scanning Electron Microscopy (SEM) of anode and cathode samples was used to make 3-D maps of the electrode microstructures and to obtain microstructural data for the ECM. The complementary analysis was crucial for the resolution of the single electrode impedance parameters and the proposal and validation of a new equivalent circuit used to model the full commercial battery impedance.

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The cylindrical cell continues to be one of the most widely used packaging styles for primary and secondary batteries. The advantages are ease of manufacture and good mechanical stability. The tubular cylinder can withstand high internal pressures without deforming.1 Even though cylindrical cells leave air cavities when placed side-by-side, they can have a higher energy density than prismatic/pouch Li-ion cells.1 The higher energy density of the cylindrical cell compensates for its poor packing abilities and the empty space can be used for cooling to improve thermal management.

Electrochemical Impedance Spectroscopy (EIS) is one of the most powerful tools for the study of electrochemical systems2–4 and is especially suited for extraction of kinetic and transport properties of the electrode materials and for studies of ageing mechanisms.5–9 In the past few years several papers on impedance modelling of porous battery electrode have been published,10–12 and various equivalent circuit models (ECMs) have been developed and proposed in literature to describe the impedance response of single LiFePO4,13,14 and Graphite electrodes.15–17 Most of these have been obtained by isolating the polarization processes that occur at the single electrode from symmetrical cell configurations13,14,20 or three-electrode configurations.18,21

In order to study electrode ageing mechanisms, Transmission Line Models (TLMs; a subset of ECMs) have previously been used to model the impedance response of porous electrodes infiltrated by a liquid electrolyte.15,20,22,23 One important ability of these TLMs is the calculation of ionic resistance in the infiltrated pores R\text{infiltr}. The electronic resistance R\text{e} through the composite electrode is usually considered negligible compared to the ionic resistance. In this case applies a simplified TLM without R\text{e}. LiFePO4 is a poor ionic and electronic conductor,24 and is therefore coated and mixed with carbon additives to improve the electronic conductivity of the electrode.25 Despite this, the electronic resistance of such composite electrode is not always negligible, and it can change considerably during degradation.21

Solid state diffusion inside electrode particles also plays an important role for the electrode performance and is usually modeled by a Warburg element.20 The two TLMs presented in this work models respectively the impedance of the anode and cathode, and incorporate an equivalent circuit element γ which describes the surface reaction at the electrode/electrolyte interface, as well as the solid state diffusion. The difference between the two TLMs reflects the different properties of the two composite electrodes. The two TLMs are subsequently combined in series and inserted in the final ECM that is used to model the impedance response of the full cell. The ECM incorporates elements describing the dominating loss mechanisms and is used to determine both kinetic and transport parameters of the electrode materials in the investigated cylindrical cell.

Methods and Materials

Cell testing and disassembling.—A fresh LiFePO4/Graphite 26650 cylindrical cell with a nominal capacity of 2.5 Ah, denoted "26650CC", was cycled five times at a constant C-rate of 0.1 (250 mA) and characterized by Electrochemical Impedance Spectroscopy (EIS) in a two-electrode setup using a Biologic VMP3 with Pstat/Gstat boards (test conditions shown in Table I).

In order to electrochemically test the cathode and anode in a three-electrode configuration and resolve impedance contributions from each of the two electrodes, the 26650CC battery was dis-assembled in a glove box in the discharged state and the cathode and anode were unrolled. The cylindrical cell (Fig. 1a) consists of a 1.5 m LiFePO4/carbonaceous additive (LFP/CB) positive electrode cast on either sides of an Aluminum foil, a 1.5 m Graphite (Gr) negative electrode cast on either sides of a Copper foil and 2 polymeric separators soaked with liquid electrolyte, schematically presented in Fig. 1b. The carbonaceous additive in the positive electrode is unknown, so we refer to it as Carbon Black (CB), in order to distinguish it from the graphite in the negative electrode (Gr). The total area of each of the battery electrodes and separators was 1950 cm². The two electrode foils were rinsed with diethyl carbonate and vacuum dried at 120 °C in order to remove the liquid electrolyte. Subsequently four circular electrodes with a diameter of 18 mm (area = 2.55 cm²) were punched out (two from the LFP/CB foil and two from the Gr foil) to be used for three-electrode testing and characterization by FIB/SEM.

Two out of the four circular electrodes (one LFP/CB and one Gr) were scratched with a spatula to remove the electrode layer on one side and then tested in two EL-CELL ECC-Combi 3-electrode setups. Lithium metal was used as counter and reference electrodes. The cells were assembled inside the glove box using glass fiber separator (Whatman GF/A) soaked with 200 μL standard 1M LiPF6 in 1:1 v/v EC/DMC electrolyte solution from Sigma-Aldrich. Both cells were cycled at a constant C-rate, calculated as 0.1 C, for a few cycles to stabilize the electrode (see Table I for test conditions and sample names).

FIB/SEM tomography.—The electrodes LFP/CB2 and Gr2 (Table I) were prepared for FIB tomography by rinsing with diethyl carbonate.

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FIB tomography and SEM imaging of the two electrode samples were carried out on a Zeiss 1540XB Crossbeam microscope, using a lateral E-T (Everhart-Thornley) detector and an In-lens detector. A 3D dataset was collected from each of the two electrodes. Table II shows the volume sizes of the two 3D datasets. A Gallium FIB slicing probe was used to mill the LFP/CB electrode with a slice thickness of 27 nm. The slice thickness was calculated by measuring the progress of the milling front in each image during the stack alignment post processing step. For the Gr electrode the current for the Gallium FIB slicing probe was reduced to 1nA and the thickness of each slice was estimated to be 14 nm. The Gr electrode is softer than the LFP/CB electrode. For this reason the FIB current had to be reduced to enable high-quality imaging for the Gr electrode dataset.

The LFP particles in the positive electrode are much smaller than the Gr particles in the negative one. Thus, in order to perform an accurate image segmentation of LFP particles – to be used for 3D reconstruction and particle size distribution (PSD) analysis – it was necessary to collect high-resolution images. The serial sectioning reconstruction and particle size distribution (PSD) analysis – it was accurate image segmentation of LFP particles – to be used for 3D the Gr particles in the negative one. Thus, in order to perform an

### Table I. Test conditions for the examined samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current (mA)</th>
<th>Approx. C-rate</th>
<th>Total cycle number</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>26650CC</td>
<td>250</td>
<td>0.1</td>
<td>5</td>
<td>Cylindrical Cell, 2-electrode setup</td>
</tr>
<tr>
<td>LFP/CB1</td>
<td>0.33</td>
<td>0.1</td>
<td>5</td>
<td>Cathode, 3-electrode setup</td>
</tr>
<tr>
<td>LFP/CB2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Cathode, used for FIB/SEM analysis</td>
</tr>
<tr>
<td>Gr1</td>
<td>0.33</td>
<td>0.1</td>
<td>5</td>
<td>Anode, 3-electrode setup</td>
</tr>
<tr>
<td>Gr2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Anode, used for FIB/SEM analysis</td>
</tr>
</tbody>
</table>

**Figure 1.** Schematic representation of a) 26650CC battery packaging design and b) LiFePO4/Graphite sandwich.

Electrochemical impedance spectroscopy.—EIS measurements were performed at room temperature in two-electrode configuration for the 26650CC cylindrical cell and in three-electrode setup for the LFP/CB1 and Gr1 electrodes, using a Biologic VMP3 with Pstat/Gstat boards. Two-electrode EIS measurements of the cylindrical cell were obtained in a frequency range from 10 kHz to 1 mHz (10 points per decade) at different SOC (state-of-charge) from 0% to 100% SOC in the voltage range 2.8–3.6 V. All spectra were measured at OCV after the cell had reached steady state defined by a change $< 5$ mV/h.

Three-electrode measurements for the LFP/CB1 and Gr1 electrodes were performed in a EL-CELL ECC-Combi, using lithium metal as counter and reference electrodes. The spectra were measured in the frequency range from 100 kHz to 1 mHz (10 points per decade), however for the LFP/CB1 electrode the impedance data recorded above 1 kHz presented an artifact (a “false” semicircle), hard to remove because of the difficulty to scratch LFP from the Al current collector. Therefore the Sauvola algorithm was used to perform local thresholding of the data. The Sauvola algorithm works by dividing the input image into square windows (n x n pixel) and setting thresholds for each of them based on the mean and standard deviation of the pixel intensities. Visualizations of the 3D reconstructions of the analyzed data were performed with the program Avizo (FEI).

The particle size distributions (PSD) of LFP/CB2 and Gr2 electrodes were analyzed based on the method introduced by Münch et al.

The tortuosity factor of the pore network was calculated using TauFactor. The program calculates $\tau$ by finite element modeling of steady state diffusive flow (electrical current/heat transfer/mass transport interchangeably) in a segmented network using normalized potential boundary conditions of 0 and 1 at opposing volume faces. This flow is then related to the flow through a fully open volume.

### Table II. Volumes of collected datasets.

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Volume (voxels) $X \times Y \times Z$</th>
<th>Volume ($\mu m^3$) $X \times Y \times Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP/CB2</td>
<td>80 $\times$ 850 $\times$ 400</td>
<td>2.2 $\times$ 12.5 $\times$ 5.9</td>
</tr>
<tr>
<td>Gr2</td>
<td>328 $\times$ 750 $\times$ 150</td>
<td>4.4 $\times$ 36.6 $\times$ 7.3</td>
</tr>
</tbody>
</table>

The tortuosity factor of the pore network was calculated using TauFactor.
Cathode equivalent circuit model.—The impedance results obtained from the LFP/CB electrode were modeled using the ECM shown in Fig. 2.

$L_d$ is an inductor. The modelled inductance is primarily related to the current leads of the test setup. $R_e$ is a resistor modelling the ionic resistance of the electrolyte. $Q_{el}$ is a constant phase element and $R_{ct}$ is a resistor. $(R_{ct},Q_{el})$, where the brackets indicate a parallel connection between $R_{ct}$ and $Q_{el}$, models the high-frequency part of the electrode impedance spectra associated with the electrode/electrolyte interfacial polarization which is known to be independent on the SOC. The low-frequency part of the electrode impedance spectra is modeled with a generalized TLM for a porous electrode (Fig. 2b). The model assumes cylindrical pores with length $L$ filled with the electrolytic solution and oriented perpendicular to the current collector. $R_{ion,L}$ is the resistance associated with Lithium ions traveling in the pores.

The pores in the electrode are surrounded by carbon coated LFP particles mixed with carbon black particles. $R_{ct}$ is the resistance associated with electrons traveling in the surface coating and CB particles. The equivalent circuit element $Q_{el}$ models the impedance of the electrode/electrolyte interface and includes the diffusion of lithium ions inside a LFP particle with radius $r$. $Q_{el}$ consists of a charge transfer resistance $R_{ct}$ in parallel with a constant phase element $Q$ modeling the apparent double layer capacitance of the insertion particles. Additionally $R_{ct}$ is in series with a General Finite Space Warburg element $W_{GFS,ID}$ which models the impedance associated with lithium ion diffusion in the solid particles. More specifically $W_{GFS,ID}$ models a diffusion process along a one-dimensional diffusion path terminated by an impermeable boundary and is chosen for olivine-structure electrode materials LiMPO$_4$ (with $M = \text{Fe, Co, Mn}$), since they display a diffusion process along one-dimensional diffusion paths in the crystal lattice.

The single-particle lithiation in an LFP electrode occurs through the LiFePO$_4$/FePO$_4$ interface moving perpendicular to the [010] direction, according to an anisotropic two-phase model which appears energetically and kinetically favorable, on the contrary of the isotropic “core-shell” mechanism. Furthermore Allen et al determined that the LiFePO$_4$ phase transformation mechanism in a bulk electrode follows a 1D growth mechanisms in 60–70 nm LiFePO$_4$ particles.

As previously mentioned the electronic resistance is often assumed to be much lower than the ionic resistance of the solution ($R_{ct} < R_{ion,L}$) resulting in a simplified TLM where $R_{ct}$ is omitted. The generalized TLM was used in this study as it reveal non-negligible $R_{ct}$ values. This is further detailed in the Results and Discussion sections.

The impedance of the generalized TLM model is:

$$Z_{TLM} = \frac{R_{ct} * R_{ion,L}}{R_{ct} + R_{ion,L}} \left( L + \frac{2 \lambda_{TLM}}{\sinh (L/\lambda_{TLM})} \right)$$

$$+ \frac{\lambda_{TLM} R_{el}^2 + R_{ion,L}^2}{R_{el} + R_{ion,L}} \coth (L/\lambda_{TLM})$$

[1]

With:

$$\lambda_{TLM} = \frac{Q_{el}}{R_{ct} + R_{ion,L}}$$

[2]

As mentioned above the electrode/electrolyte interface (Fig. 2c) is modeled with the Randles circuit $Q_{el}$ which includes the charge transfer resistance $R_{ct}$, a constant phase element (CPE) $Q$ and the general finite space Warburg element $W_{GFS,ID}$. $W_{GFS,ID}$ has the impedance:

$$Z_{WGFS,ID} = R_w \frac{\coth (j \omega \tau_w)^n}{(j \omega \tau_w)^n}$$

[3]

with the time constant:

$$\tau_w = \frac{r^2}{D}$$

[4]

$R_w$ is polarization resistance, $r$ is the particle radius, $n_w$ is an exponent (0 < $n_w$ < 0.5) reflecting the degree of non-uniform diffusion, and $D$ is the diffusion coefficient of Lithium ion within LiFePO$_4$.

The effective double layer capacitance $C_{dl}$ is calculated using the expression:

$$C_{dl} = Q^{1/n} \left( R_{ct}^{-1} + R_{ion,L}^{-1} \right)^{(n-1)/n}$$

[5]

where $Q$ is the CPE, $n$ the exponent of the CPE, $R_{ct}$ is the ohmic resistance and $R_{ion}$ the generic resistance associated with the CPE.

The units of $R_{ct}$ and $C_{dl}$ in the TLM model are respectively $\Omega \text{cm}^2$ and $\text{F cm}^{-3}$. $R_{ct}$ and $C_{dl}$ values obtained from the modeling can be related to the geometrical electrode area (with the units $\text{cm}^2$ and $\text{F cm}^{-3}$).
Anode equivalent circuit model.—The impedance spectra measured on the Gr1 electrode were modeled using an ECM almost similar to the circuit used to model the LFP/CB1 electrode impedance (Fig. 3a). The $R_\text{f}(Q_1)$ elements model the high frequency part of the impedance spectra. $R_\text{f}$ models the ionic resistance of the electrolyte, while the $Q_1$ element representing the combined copper current collector/electrode polarization.35 Similar to the model for the cathode, the mid- and low-frequency part of the anode spectra are modeled with a TLM for a porous electrode, however here the simplified version is used29,32,33 (Fig. 3b), as the condition $R_\text{el} < R_{\text{ion,L}}$ for the graphite electrode.44-46

For a simplified TLM with negligible $R_\text{ct}$, Equation 1 reduces to:

$$Z_{\text{TLM}} = \lambda_{\text{TLM}} R_{\text{ion,L}} \coth (L / \lambda_{\text{TLM}})$$

with:

$$\lambda_{\text{TLM}} = \sqrt{\sigma_{\text{ion}} / R_{\text{ion,L}}}$$

$\lambda_{\text{TLM}}$ is different from $\lambda_{\text{ion}}$. It is constituted by a resistor $R$ in series with a Randles circuit and in parallel with a constant phase element $Q$ (Fig. 3c).6 The element $\lambda_{\text{TLM}}$ is equivalent to the ECM proposed by Meyers et al. (Case 2)6 which describes the impedance response of a porous electrode, covered by a film (in this case the SEI layer illustrated in Fig. 3a). The parallel connection of $Q_{\text{SEI}}$ and $Q_{\text{film}}$ models the SEI layer resistance, while the film capacitance $C_{\text{film}}$ associated with it is calculated from $Q_{\text{SEI}}$ according to Eq. (3). The Randles circuit includes the charge transfer resistance $R_\text{ct}$, a constant phase element $Q_{\text{ion}}$, and the general finite space Warburg element with a two-dimensional diffusion path, $W_{\text{WGFS,2D}}$, with the impedance:

$$Z_{\text{WGFS,2D}} = \frac{L_0}{(j\omega \tau_{\text{cat}})^{m_0}} \frac{L_1}{(j\omega \tau_{\text{cat}})^{m_1}}$$

where $L_0$ and $L_1$ are modified zero- and first-order Bessel functions of the first kind.

Here a 2D Warburg finite space element with cylindrical geometry is used.15,47 This geometry describes a diffusion along the axial radius, usually associated with layered-structure electrodes, such as graphite, which allow two-dimensional lithium insertion.48

Simulations of the impedance of the full cell electrode/individual circuit elements, and complex nonlinear least squares fitting of the equivalent circuit models to the data was performed using software programmed in Python49 which relies on the scientific Python stack,50-52 and for the 1D/2D elements the library mpmath was used to provide higher precision complex floating-point arithmetic.53

Tortuosity estimation from TLMs.—The ionic resistivity in the infiltrated pore with length $L$, $R_{\text{ion,L}}$ [2cm] calculated from the TLMs is correlated to the effective electrode pore tortuosity $\tau_{\text{el}}$ through the equation:

$$\tau_{\text{el}} = \sigma_{\text{ion}} R_{\text{ion,L}} \varepsilon_{\text{el}}$$

where $\sigma_{\text{ion}}$ is the bulk ionic conductivity with the unit [Scm$^{-1}$], and $\varepsilon_{\text{el}}$ is the electrode porosity.15 In our modeling work we used $\sigma_{\text{ion}} = 1.18 \times 10^{-2}$ Scm$^{-1}$, which is an average of the values reported for 1 M LiPF$_6$ in 1:1 EC/DMC (the electrolyte used for the single electrode tests) by Lombardo et al.,45 and Porion et al.46

Results

FIB/SEM tomography.—Figures 4 and 5 show respectively cross-section lateral E-T images after FIB milling of the LFP/CB2 and the Gr2 electrode. In the top region of the images it is possible to observe a very bright region, which is the sample surface after polishing. Looking inside the milled samples, current collector/electrode and electrode/electrolyte interfaces can be distinguished for both samples. Guidelines are shown in Fig. 4a to indicate how the interfaces extend into the sample. From Fig. 4a, the cathode thickness is estimated to 65 ± 5 μm. Fig. 5b show a higher resolution image of the electrode/electrolyte interface. Inside the electrode, three different phases are distinguished: light gray LiFePO$_4$ particles, dark gray pores (infiltrated with silicon resin) and black CB particles. On the right side of the SEM image (Fig. 4a), where the electrolyte is supposed to be, there is a dark gray bulk of silicon resin with some LFP and CB particles, which probably detached during sample preparation.

Inside the Gr2 electrode (Fig. 5), only two phases can be distinguished: dark graphite particles and gray pores infiltrated with silicon.
Li$_{1-x}$FePO$_4$ and Li$_x$C$_6$ is respectively 76 nm and 1096 nm. These values are implemented in the TLMs used to model the impedance spectra measured on the cylindrical cell and the electrode samples. Volume fraction values for all the phases are shown in Table III.

Fig. 9 shows the normalized 3D potential maps used in the pore tortuosity factor calculations. The calculated cathode pore tortuosity factor is 5.9, while the anode pore tortuosity factor is 24.8. From Fig. 9b it is evident that the volume analyzed for the anode is too small to be representative due to the big graphite particles and the single narrow pathway that connects the two sides of the volume. Thus the accuracy of the calculated anode tortuosity factor is very low. The tortuosity factor for a larger representative part of the electrode is expected to be significantly smaller.

**Galvanostatic cycling with potentiostatic limitation (GCPL).**—The 26650CC cell was cycled between 2.8 – 3.6 V as suggested from the commercial supplier, at a nominal C-rate of 0.1 C. The charge/discharge curve for 26650CC is shown in Fig. 10a (black line).

Figs. 10b and 10c show respectively the charge/discharge curves for the LFP/CB1 and Gr1 electrodes. The LFP/CB1 electrode is cycled between 3.0 – 3.7 V with a constant current of 330 μA, corresponding to a C-rate of 0.1. The charge/discharge curve shows a typical flat plateau of a Li$_{1-x}$FePO$_4$ electrode at around 3.45 V (with 0 ≤ x ≤ 1).

Note that the normalized charge/discharge capacity of LFP/CB1 is 10% higher than the normalized capacity of 26650CC. This matches with the typical 10% lithium loss for SEI layer formation on the graphite surfaces in the anode during the first charge/discharge cycle of the 26650CC. The Gr1 electrode was cycled between 0.01 V and 0.5 V, also at 330 μA (Fig. 10c) showing typical Li$^+$ ion intercalation steps (with 0 ≤ x ≤ 1). Note that the normalized charge/discharge curve of 26650CC resembles well the voltage difference between the LFP/CB1 and Gr1 normalized charge/discharge curves, as shown by the green curve in Fig. 10a. This voltage difference does not match exactly the 0% and 100% SOC voltage cutoff for the 26650CC charge/discharge curves. This may again be explained by either the 10% capacity difference of the LFP/CB1 electrode.

To simplify the nomenclature, “LiFePO$_4$” refers to the Li$_{1-x}$FePO$_4$ electrode at 0% SOC, and “FePO$_4$” denotes the Li$_{1-x}$FePO$_4$ electrode at 100% SOC.

**EIS modelling of Li$_{1-x}$FePO$_4$ electrode (three-electrode configuration).**—Fig. 11 shows the area-normalized EIS spectra measured for the LFP/CB1 electrode in the discharged (Figs. 11a, 11b, 11c, 11d) and charged state (Figs. 11e, 11f, 11g, 11h). Figs. 11a, 11c show respectively a Nyquist and a Bode plot of the EIS spectrum.
Figure 6. 3D reconstructions of a) LFP/CB2 electrode/electrolyte (transparent blue) interface and b) Gr2 electrode/Cu current collector (orange) interface. The scale bar units are [μm].

Figure 7. 3D reconstruction of a) LFP, b) CB and c) pore networks in the LFP/CB2 electrode. 3D reconstruction of d) Graphite and e) pore networks in the Gr2 electrode.

Figure 8. Particle size distributions for a) LFP/CB2 and b) Gr2 electrodes.
Table III. Volume fraction and average size for the different phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Volume Fraction [%]</th>
<th>Avg. size [nm]</th>
<th>Volume Fraction [%]</th>
<th>Avg. size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP/CB2</td>
<td></td>
<td></td>
<td>Gr2</td>
<td></td>
</tr>
<tr>
<td>Active Material</td>
<td>58</td>
<td>76</td>
<td>70</td>
<td>1096</td>
</tr>
<tr>
<td>CB Additive</td>
<td>17</td>
<td>49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pores</td>
<td>25</td>
<td>39</td>
<td>30</td>
<td>159</td>
</tr>
</tbody>
</table>

Figure 9. 3D surface renderings of the normalized potential maps used in the tortuosity factor calculations by TauFactor. a) LFP/CB2 electrode b) Gr2 electrode.

Figure 10. Charge/Discharge curves measured on the a) 26650CC cell, b) LFP/CB1 cathode and c) Gr1 anode.

Discussion

Cathode impedance modelling: three-electrode configuration.—The Nyquist plots of LiFePO4 and FePO4 (Figs. 11b, 11g) consist of a small semicircle in the high frequency region between 192.38.67.116 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Figure 11. a) Nyquist plot, b) Zoomed view, and c) Bode plot of the Li$_{1-x}$FePO$_4$ electrode at 0% SOC ($x$ = 0). e) Nyquist, f) Zoomed view, and g) Bode plot of the Li$_{1-x}$FePO$_4$ electrode at 100% SOC ($x$ = 1). d) and h) show relative residuals between model fit and measured data. Inset in c) and g) shows rescaled Bode plots to highlight the high-frequency part of the spectra.

1 kHz – 100 Hz and a low frequency branch characterized by an almost vertical tail in the charged state, and a less vertical tail in the discharged state.

$R_{Al}$ models the contact resistance between the Aluminum foil and the Li$_{1-x}$FePO$_4$/CB network. From Table IV it is seen that the $R_{Al}$ values change very little for the two different SOCs, in agreement with literature.14

The high frequency side of the semicircle intersects with the x-axis at 12.0 $\Omega$cm$^2$ and 8.0 $\Omega$cm$^2$ for LiFePO$_4$ and FePO$_4$ respectively. However, because of the inductance and in particular due to the non-negligible electronic resistance ($R_e$), the electrolyte resistance ($R_E$) values are somewhat smaller: 11.2 $\Omega$cm$^2$ and 7.4 $\Omega$cm$^2$, respectively as presented in Table S1. When $R_e$ is non-negligible relative to $R_{ion,L}$ the generalized TLM$_{cat}$ features a small ohmic contribution which shifts the starting point of the red semi-circle to the left in the Nyquist plot, Figs. 11b, 11f. If this ohmic contribution was placed on the left side of the red semi-circle it would be easier to see how the semi-circle contributes to the total spectrum, however the semi-circle is deliberately plotted with the TLM$_{cat}$ shifted to the right side to highlight the small ohmic contribution from the TLM$_{cat}$, as this contribution also affects the value of $R_E$. The value of $R_E$ is not expected to change with SOC and the change is possibly related to measurement uncertainties; the impedance measured above 1 kHz, as described before, presented an artifact and was therefore removed before the impedance was modeled. A “false” semicircle was observed and related to some effect of the non-complete scratching of active materials from the Al current collector. It was not observed on the graphite electrode where the active material was much softer and easier to scratch off.

<table>
<thead>
<tr>
<th>Generalized transmission line</th>
<th>LiFePO$_4$</th>
<th>FePO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Al}$ ($\Omega$cm$^2$)</td>
<td>2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>$C_{Al}$ (mFcm$^{-2}$)</td>
<td>0.16</td>
<td>0.24</td>
</tr>
<tr>
<td>$R_{ct}$ ($\Omega$cm$^2$)</td>
<td>34.9</td>
<td>8.2</td>
</tr>
<tr>
<td>$C_{dl}$ (Fcm$^{-2}$)</td>
<td>0.51</td>
<td>0.48</td>
</tr>
<tr>
<td>$D$ (cm$^2$s$^{-1}$)</td>
<td>$4.4 \cdot 10^{-13}$</td>
<td>$1.8 \cdot 10^{-12}$</td>
</tr>
<tr>
<td>$R_{ion,L}$ ($\Omega$cm)</td>
<td>1596</td>
<td>395</td>
</tr>
<tr>
<td>$R_e$ ($\Omega$cm)</td>
<td>109</td>
<td>54</td>
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Table IV. Results from EIS fitting of Li$_{1-x}$FePO$_4$ electrode.
The values used in the TLM_{cat} for the electrode thickness \( L \) and the particle radius \( r \) are 65 \( \mu \)m and 38 nm, respectively. These values were obtained from the presented FIB/SEM analysis and PSD calculation.

Diffusion of \( Li^+ \) ions through the liquid electrolyte in the electrode pores results in a 45° slope in the beginning of the TLM_{cat} curve. The length of the part of the TLM_{cat} curve resembling a line with a 45° slope is determined by \( R_{\text{ion,L}} \) and the thickness of the electrode. Once a \( Li^+ \) ion has traveled through a pore and reached a coated LFP particle, it will adsorb (insert) and diffuse (together with an electron, forming a polaron) into the bulk of the LFP particle. This is modelled by \( \kappa_{\text{cat}} \) and results in a semicircle followed by a 45° curve terminating in a capacitive-like response as seen in Figs. 11a, 11b, 11e, and 11f. The semicircle is the result of charge transfer resistance, \( R_{ct} \), of \( Li^+ \) at the particle/electrolyte interface and double layer capacitance \( C_{dl} \), in parallel, calculated from the CPE used to model it. The 45° line followed by a capacitive-like curve corresponds to the finite space Warburg element \( W_{GES,1D} \) which represents diffusion of \( Li^+ \) ions in the electrode network, until all the active material is lithiated/delithiated.

The fitted values from the TLM_{cat} show that \( R_{ct} \) is not negligible compared to \( R_{\text{ion,L}} \). Both resistances in the pore and the electrode are observed to decrease when the electrode is charged and mainly consists of FePO_4. Li_{1-x}FePO_4 particles are known to be subjected to expansion/contraction with cycling. When the electrode is completely delithiated, FePO_4 particles have a small volume and consequently the pore volume have increased, resulting in a lower \( R_{\text{ion,L}} \). \( R_{ct} \) depends on the CB network tortuosity which changes due to particle movements during lithiation/delithiation process. \( R_{ct} \) is observed to be significantly lower at 100% SOC, in agreement with literature.

<table>
<thead>
<tr>
<th>Simplified transmission line</th>
<th>Meyers element</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1Q_1 ) element</td>
<td>( R_{SEI}(\Omega \text{cm}^2) ) ( C_{SEI}(\mu \text{Fcm}^{-2}) ) ( R_{ct}(\Omega \text{cm}^2) ) ( C_{dl}(\mu \text{Fcm}^{-2}) ) ( D(\text{cm}^2 \text{s}^{-1}) ) ( R_{\text{ion,L}}(\Omega \text{cm}) )</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>16.0</td>
<td>0.43</td>
</tr>
<tr>
<td>LiC_6</td>
<td>8.3</td>
<td>0.39</td>
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</tbody>
</table>

Table V. Results from EIS fitting of \( Li_xC_6 \) electrode.
**Anode impedance modelling: three-electrode configuration.**—

The Nyquist plot of the impedance spectra for Gr1 (Figs. 12a, 12b, and 12e) consists of a small semicircle in the high frequency region, between 100 kHz – 10 kHz, a second bigger semicircle in the mid-frequency range (100 Hz – 10 Hz) and – similar to the LFP/CB1 electrode – a low frequency branch (at frequencies lower than 1 Hz) characterized by an almost vertical tail, in the charged state, and a diffusive tail in the discharged state. Parameter values obtained from the modelling are given in Table V.

The high frequency side of the impedance curve does not intersect with the x-axis, so the electrolyte resistance ($R_\text{el}$) is obtained from the modeling and was 12.9 Ω cm$^2$ and 12.5 Ω cm$^2$ for C and LiC$_6$ respectively, see Table S2. The first semicircle ($R_\text{f1}$,$Q_1$) observed at high frequencies (higher than 10 kHz) can be assigned to the interface between the copper current collector and/or the porous graphite anode or the graphite particle/particle contact resistance, with $R_\text{f1}$ and $Q_1$ representing contact resistance and the double layer capacitance at these interfaces, respectfully. The value obtained for $R_\text{f1}$ is observed to be significantly lower at 100% SOC than at 0% SOC. The double layer capacitance at this interface ($C_1$) is around three orders of magnitude smaller than $C_\text{el}$ at the cathode (Table IV). This is probably due to the smaller specific surface area in the anode: the average graphite particle diameter is around 1.1 μm, while CB grains in the positive electrode are equal to 49 nm.

The second semicircle at 100 Hz – 10 Hz is related to the SEI layer formed around each graphite particle and is modelled by the elements $R_{\text{SEI}}$ and $Q_{\text{SEI}}$ (placed in parallel) which are part of $\zeta_{\text{an}}$ inside the Simplified Transmission Line Model (TLM$_{\text{an}}$) for a porous electrode. 8,30,24,25,33 The low frequency branch (<1 Hz) is associated with the Randles element of $\zeta_{\text{an}}$, inside TLM$_{\text{an}}$. The values used for L and r are respectively 35 μm and 548 nm, obtained from the FIB/SEM analysis and PSD calculation. The fitting values for $R_{\text{SEI}}$ and $R_\text{an}$ are highest for C in the delithiated form. Similarly $D$ is highest for C in the delithiated form which could indicate that Li$^+$ ions travel faster through the graphene planes when they are delithiated. The lithium diffusivity in the anode is observed to be around 2 orders of magnitude larger than the lithium diffusivity in the cathode.

$R_\text{f1}$ is extremely low and could be neglected, enabling the use of a Simplified Transmission Line Model15,24 for the graphite electrode. This is because the entire anode is made of C which is highly conductive. On the contrary the cathode is a mixed LiFePO$_4$/CB electrode with a significant electronic resistance.

The values obtained for $R_{\text{ion,L}}$ for the Gr1 and LFP/CB1 electrode are comparable, which is consistent with expectations since the electrode pore volumes are comparable, see Fig. 8 and Table III. Besides the pore diameter, indicated by the analysis presented in Fig. 8, the electrode pore tortuosity $\tau_{\text{p}}$ and pore volume/ solid phase volume ratio are important factors in determining $R_{\text{ion,L}}$. $\tau_{\text{p}}$ has been calculated as 4.7 and 1.8 for the LFP/CB1 and Gr1 electrodes respectively, using Eq. 9. The calculated tortuosity $\tau_{\text{f1}}$ for the positive electrode is close to the value obtained by TauFactor on the LFP/CB2 3D reconstruction after FIB/SEM analysis (5.9). The presence of both large particles and narrow pore necks in the microstructure of the graphite anode makes accurate estimation of the tortuosity factor infeasible using the applied FIB/SEM methodology. Ilig et al.15 found for a commercial graphite electrode comparable to Gr2, a tortuosity factor of the pore phase equal to 2.72, determined by X-ray tomography from a several orders of magnitude larger volume. This value is in a similar range as the tortuosity we obtained with the EIS modelling.

For both the anode and cathode $R_{\text{ion,L}}$ is observed to be higher in the lithiated state than in the delithiated state. This is believed to be related to the expansion/contraction of the lithiated/delithiated LFP or C particles. LFP particles are known to shrink by approximately 6.8 vol% with delithiation25,26 and C particles expand 10.3 vol% with lithiation.28 The volume reduction of two adjacent LFP particles could highly influence the pores dimension (since the pore dimension is smaller than the dimension of the LFP particles), resulting in the observed significant drop of $R_{\text{ion,L}}$ after delithiation. On the contrary the expansion decreases the pore volume thereby narrowing the electrolyte diffusion channels inside the electrodes which increases the obtained modeling value for $R_{\text{ion,L}}$. The relative change in the obtained values for $R_{\text{ion,L}}$ in the lithiated and non-lithiated form is smaller for the anode than for the cathode. This is possibly because of a smaller tortuosity in the negative electrode, which results in the combined effect of a smaller relative $R_{\text{ion,L}}$ change.

Note that the selection of a TLM w/o $R_\text{el}$ (due to the assumption $R_\text{el} << R_{\text{f1}}$) implies that there is no gap on the x-axis in Figs. 12a and 12d between the blue TLM$_{\text{an}}$ impedance and the green ($R_\text{f1}$,$Q_1$) semi-circle.

**26650CC impedance modelling: two-electrode configuration.—**

**Equivalent circuit description.—**A new ECM is proposed to model the 26650CC spectra and shown in Fig. 14. It is a combination of the two single electrode equivalent circuits (Figs. 2 and 3). The number of variables in the model for the LFP/CB1 and Gr1 spectra is...
Figure 14. Schematic representation of the Equivalent circuit (ECM) used to model the 26650CC impedance spectra. It includes two TLMs used to model the two porous electrodes.

13 and 15, respectively, and putting them in series results in a model with 23 variables. The analysis of the single electrode impedance spectra plays a crucial role for the successful modeling of the full battery since it enables us to determine the parameters that are used as guesses in the final ECM. This allows an accurate modeling of the measured 26650CC spectra. It should be noted that the single electrode models only provided input for the 0% and 100% SOC spectra. Values obtained at intermediate SOCs are obtained from the full model.

The $R_{Al}$ elements model the high-frequency region. $R_{Al}$ models the ionic resistance of the electrolyte, while $(R_{Al}Q_{Al})$ represents the aluminum/cathode polarization observed in the LFP/CB electrode in the frequency range 1 kHz – 100 Hz. The $R_{C}$ element, previously used to model the particle/particle contact in the Gr1 electrode, is not included in the total circuit since this process occurs at relative high frequency ($>10$ kHz), leading to a reduction in the number of model variables. Above $\sim 1$ kHz the 26650CC is dominated by inductance and possibly beginning skin-effects or other processes yielding also an increased real resistance. This contributes to the reduction.

TLM$_{an}$ and TLM$_{cat}$ model the mid- and low-frequency regions of the spectra. More specifically the mid-frequency region (100 Hz – 10 Hz) represents the SEI layer which covers each graphite particle in the anode and is described by the $R_{SEI}$ and $Q_{SEI}$ elements placed in parallel inside $\Sigma_{an}$ (Fig. 3c). The low-frequency branch ($<1$ Hz) is ascribed to the Li insertion or intercalation process at the interface (Li$_{x}$C$_{6}$ or Li$_{1-x}$FePO$_{4}$) and is modelled by the Randles circuits in $\Sigma_{an}$ and $\Sigma_{cat}$ (Figs. 2c and 3c). The results of $R_{SEI}$ and $C_{SEI}$ obtained from TLM$_{an}$ are normalized for both geometrical surface area and internal surface area and reported in Table VI and in the supplementary information.

Table VI and the supplementary information also report normalized values for $R_{d}$ (from TLM$_{an}$) and $R_{ct}$, $C_{dl}$ (calculated from CPE according to Eq. 5), $D$ and $R_{ion,L}$ from both TLMs.

EIS spectra fitting.—The normalized EIS spectra for 26650CC measured at OCV after relaxation at 0, 50 and 100% SOC, after removal of the wire inductance, are shown in Fig. 15. Figs. 15a, 15b, 15c show Nyquist plots of the different EIS spectra, including best-fits to the data using the model described in Equivalent Circuit Description section, and the zoomed views of the high frequency regions in the insets. Figs. 15d, 15e, 15f show zoomed view of the correspondant Bode plots, including best-fits of the model to the data. Relevant values obtained by EIS modelling at the different SOCs are reported in Table VI and values for selected resistors are plotted in Figure 16. All parameter values are reported in Tables S3 and S4 in the supplementary information. The relative residuals and the higher zoomed views of the Nyquist plots are shown in Fig. S2 in the supplementary information.

The red semicircle seen in Fig 15 shows the impedance for the $(R_{Al}Q_{Al})$ element assigned to the interface between the Aluminum current collector and the porous cathode. As reported in Table VI, $R_{Al}$ is slightly dependent of SOC. However, the values obtained for $R_{Al}$ and $C_{Al}$ are comparable to the values obtained for the same variables from the single-electrode Li$_{1-x}$FePO$_{4}$/CB EIS modelling (Table IV).

Figure 15. Nyquist plots of 26650CC impedance spectra measured at a) 0% SOC, b) 50% SOC and c) 100% SOC. Bode plots of 26650CC impedance spectra measured at d) 0% SOC, e) 50% SOC and f) 100% SOC. All the spectra are subtracted of the inductance and include fitted model data (black line) and separate parts of the model data (blue, yellow, red).
The yellow dotted line shows the TLM\textsubscript{in} impedance. From the fitted values, $R_{\text{SEI}}$ decreases upon charging (Fig. 16a) in agreement with the GR1 modeling results. In both cases $R_{\text{SEI}}$ reduces by around 60% when going from the discharged state to the charged state but for the single-electrode EIS spectra the magnitude of $R_{\text{SEI}}$ is observed to be higher. This is probably due to the buildup of a thicker SEI layer with the Gr1 modeling results. In both cases $R_{\text{SEI}}$ decreases upon charging (Fig. 16a) in agreement with previous findings.\textsuperscript{61} However larger values in Table VI, and Figs. 16c, 16d show how $R_{\text{SEI}}$ is observed to slightly raise with SOC and dramatically increase in the fully lithiated graphite, because of particles expansion an pores volume reduction.

The blue dotted line represents the TLM\textsubscript{out} impedance. The fitted values in Table VI, and Figs. 16c, 16d show how $R_{\text{SEI}}$, $R_{\text{LFP\,out}}$, and $R_{\text{LFP}}$ decreases with increasing SOC (or with delithiation of LFP), in agreement with the values obtained from the single-electrode impedance modelling. $D$ is observed to be higher in the fully delithiated state.

From a careful analysis of Fig. 15 is possible to notice that the graphite impedance is characterized in the low frequency region by a capacitive vertical tail, while LFP shows a diffusive tail at 0% SOC (Fig. 15a), and vice versa at 100% (Fig. 15c). This perfectly resembles the behavior observed for the single electrode impedance spectra in Figs. 11 and 12. The values for Li diffusion $D$ obtained from modeling the 26650CC spectrum are found to be around 10\textsuperscript{-12}, 10\textsuperscript{-13} cm\textsuperscript{2}s\textsuperscript{-1} for LFP electrode and about 2–3 orders of magnitude larger in graphite (Fig. 16b), in agreement with previous findings.\textsuperscript{61} However larger particles size in graphite is not negligible and time constant $\tau_w$ is calculated using Eq. 4 for both electrodes. $\tau_w$ is found equal to 24, 61 and 6 s for LFP at 0, 50 and 100% SOC respectively, and equal to 7, 59 and 120 s for graphite at 0, 50 and 100% SOC respectively. From $\tau_w$ comparison is evident how the Li insertion process is diffusion-controlled by LFP when the battery is discharged, by graphite when charged and there is a shared contribution at intermediate SOC.

Conclusions

In this work a commercial 26650 cylindrical LiFePO\textsubscript{4}/Graphite battery was disassembled and the two electrodes were characterized individually by charge/discharge curves and electrochemical impedance spectroscopy (EIS) in a three-electrode setup, and by FIB/SEM tomography. Two different equivalent circuits were used to model the cathode and anode impedance. The circuits included a transmission line model (TLM) for a porous electrode, which, among other parameters, involves pore length and electron resistance $R_{\text{elec}}$ in the pores and lithium diffusivity in the active materials in the electrodes. By comparing the obtained values with the ones obtained from single electrode modeling, it was demonstrated that several of these param-

<p>| Table VI. Results from EIS fitting of 26650CC. a. charging mode, b. discharging mode. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $R_\text{A(QA)}$ element        | $C_\text{A}$    | $R_\text{SEI}$  | $C_{\text{SEI}}$ | $R_\text{ct}$   | $C_{\text{dl}}$ | $D$             |</p>
<table>
<thead>
<tr>
<th>$(\Omega\text{cm}^2)$</th>
<th>(mFcm$^{-1}$)</th>
<th>$(\Omega\text{cm}^2)$</th>
<th>(mFcm$^{-1}$)</th>
<th>$(\Omega\text{cm}^2)$</th>
<th>(mFcm$^{-1}$)</th>
<th>cm$^2$s$^{-1}$</th>
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<tr>
<td>a) 0%</td>
<td>1.83</td>
<td>0.14</td>
<td>8.08</td>
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<tr>
<td>12.5%</td>
<td>2.43</td>
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<td>18.7</td>
<td>0.41</td>
<td>56.4</td>
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<td>27.7</td>
<td>0.41</td>
<td>75.4</td>
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<td>0.41</td>
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<td>87.5%</td>
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<td>39.3</td>
<td>0.41</td>
<td>87.5</td>
<td>0.93</td>
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<tr>
<td>100%</td>
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<td>41.0</td>
<td>0.41</td>
<td>90.8</td>
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</tr>
<tr>
<td>b) 0%</td>
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<td>0.25</td>
<td>3.10</td>
<td>0.28</td>
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<tr>
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<td>0.30</td>
<td>45.1</td>
<td>0.16</td>
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</tbody>
</table>

Figure 16. Fitted values as function of SOC.


6. Y. Zhang et al., “Advances in new cathode material LiFePO4 for lithium-ion batteries,” *Synth. Met.*, 162(13–14), 115 (2012).


