The modified inductance element La

I – INTRODUCTION

It is convenient to use a Constant Phase Element (CPE) instead of a capacitor when for instance the Nyquist diagram of the impedance of a system shows a semi-circle whose center is located below the Real axis, instead of on the Real axis.

The difference between a capacitor C and a CPE Q is that the expression of the impedance of a CPE contains an additional parameter $\alpha$:

$$Z_Q(f) = \frac{1}{Q(j2\pi f)^\alpha}$$  \hspace{1cm} (1)

whereas the expression of the impedance of the capacitor is:

$$Z_C(f) = \frac{1}{C(j2\pi f)}$$  \hspace{1cm} (2)

with C and Q the value of the capacitor in F and of the CPE in F $s^{(\alpha-1)}$ with $0 < \alpha \leq 1$. It is important to note that $Z(f)_Q = Z(f)_C$ for $\alpha = 1$. A CPE is physically interpreted as an effect of the surface roughness of the sample, leading to an heterogeneity of the capacitance.

Analogously, the modified inductance La can be used to represent the presence of an unusual inductance in the Nyquist diagram. The expression of the impedance of an inductance is:

$$Z_L(f) = Lj2\pi f$$  \hspace{1cm} (3)

The expression of the impedance of the modified inductance La is:

$$Z_{La}(f) = La(j2\pi f)^\alpha$$  \hspace{1cm} (4)

with $L$ and $La$ the value of the inductance in H and of the modified inductance in H $s^{(\alpha-1)}$, respectively, with $0 < \alpha \leq 1$. Again, $Z_{La}(f) = Z_L(f)$ for $\alpha = 1$.

This application note introduces a few practical examples for which the modified inductance component can lead to a much better fit of impedance data.

II – HIGH-FREQUENCY INDUCTANCE IN LI-ION BATTERIES

Figure 1 shows the Nyquist impedance diagram of an LiPF$_6$ Li-ion battery with a capacity of 60 Ah and a nominal voltage of 3.2 V. An inductive behaviour can be seen at high frequencies ($f > 22$ Hz), most likely due to the connection cables to the battery. This behaviour is more visible in cells with low apparent resistance such as batteries. As shown by the least square linear fit in Fig. 1, these high frequency data points are on a straight line that is not perpendicular to the x-axis. Consequently, this behaviour cannot be represented by a simple inductance.

Figure 1: Nyquist impedance diagram of an LiPF$_6$ battery for frequencies $\in [0.1, 2000]$ Hz.

Figure 2 shows the equivalent circuit chosen to fit the data shown in Fig. 1.
It is a Randles circuit with an inductance $L_a$ in series. The simple $L$ is a particular example of the inductance $L_a$. As stated above, if $a=1$, $L_a=L$. $R_1$ is associated to the internal resistance of the battery, $C_1$ to the double layer capacitance, $R_2$ to the charge transfer resistance and $W$, the Warburg component, to the semi-infinite diffusion. Figure 3 shows the fitting curve obtained using the equivalent circuit shown in Fig. 2 with a simple inductance. Fig. 4 shows the same results but with a modified inductance $L_a$. A comparison of the results of the two fitting, i.e. the values of the parameters and of $\chi^2$ (an estimation of the goodness of the fit [1]) are given in Table 1.

### Table I : Values of the parameters for the equivalent circuits used in Fig. 3 and Fig. 4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Using L (Fig. 3)</th>
<th>Using $L_a$ (Fig. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1$ /$\mu$H</td>
<td>0.14</td>
<td>0.48</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1</td>
<td>0.84</td>
</tr>
<tr>
<td>$R_1$ /$\Omega$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$C_1$ /F</td>
<td>109</td>
<td>429</td>
</tr>
<tr>
<td>$R_2$ /$\mu$\Omega</td>
<td>14.3</td>
<td>50.3</td>
</tr>
<tr>
<td>$s_1$ /$\Omega$ s$^{-1/2}$</td>
<td>0.17</td>
<td>0.158</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.53x10$^{-6}$</td>
<td>2.67x10$^{-9}$</td>
</tr>
</tbody>
</table>

III – LOW FREQUENCY INDUCTIVE BEHAVIOR OF A FREELY CORRODING METAL

Another example of a system for which the component $L_a$ can be used is a metal corroding in an acidic solution. In this case, the reduction reaction is the proton reduction.
which involves an adsorption step, following the Volmer-Heyrovský mechanism [2, 3]. Fig. 5 shows the impedance graph obtained on a partially painted Zn sample immersed in 0.5 mol L⁻¹ H₂SO₄ and the corresponding fitting curve using the equivalent circuit shown in Fig. 6. In this equivalent circuit, Q1/R1 is associated to the larger semi-circle in Fig. 5 (possibly related to the coated part of the sample), Q2/R2 to the inductive semi-circle (related to an adsorption process at the rough metal surface) and Q3/R3 to the third semi-circle (also possibly related to the bare metal). The solution used in this example was not a perfect ionic conductor but its resistance of around 1 Ω was considered negligible. Another way to interpret the impedance diagram is to consider a Volmer-Heyrovský chemical desorption mechanism.

In the fitting results shown in Table II, the elements Q2/R2 correspond to the inductive loop and have negative values. It might be difficult for the user to handle and interpret negative values. It is then possible to use an equivalent circuit for which the elements have positive values. This can be done by replacing the circuit R1+Q2/R2 in Fig. 6 by R1/(R2+La2) as shown in Fig. 7.

In Fig. 8, the blue curve shows the experimental data, the red curve, the fitting curve obtained using the equivalent circuit in Fig. 7 with a simple inductance (a2 = 1) and the green curve, the fitting curve obtained using the equivalent circuit in Fig. 7 with a modified inductance. As can be seen in Table III, all the elements of the equivalent circuit have now positive values. In terms of choosing the best equivalent circuit, it seems the red curve fit less tightly to the real data than the green curve, which shows that the modified inductance increases the goodness of the fit (see Table II).
inset of Fig. 8). This is confirmed by the values of the $\chi^2$ shown in Table 3.

**IV – CONCLUSION**

The new element La is a modified inductance element. It can be used to fit impedance characteristics related to either an unusual connection inductance at high frequencies, mostly visible in batteries or a heterogeneous adsorption mechanism at low frequencies, mostly visible in corrosion.

**REFERENCES**

1) EC-Lab™ User’s Manual p. 113

**Data files can be found in**:

**Fig. 1 :**
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Battery\AN42_battery

**Fig. 5 :**
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Corrosion\AN42_coating

**APPENDIX**

1) It is noteworthy that if the inductive loop in Fig. 5 could be fitted with an R/C instead of an R/Q (i.e. if $a_2$ was equal to 1) then an R+L would be enough and R+La unnecessary.
2) Furthermore, to widen the perception of what an equivalent circuit is, it is worth noting that $Z_0(f) = Z_{aQ}$ with $a_Q = -a_{La}$ and $Q = 1/La$, $a_Q$ being the $a$ parameter for the element Q and $a_{La}$ for the element La.

If we replace in Eq. 4, $a$ by $-a_Q$:

$$Z_{La}(f) = L_a (j2\pi f)^{-a_Q}$$ (5)

$$Z_{La}(f) = \frac{L_a}{(j2\pi f)^{a_Q}}$$ (6)

$$Z_{La}(f) = \frac{1}{Q(j2\pi f)^{a_Q}}$$ (7)

With $L_a = \frac{1}{Q}$

$$Z_{La}(f) = Z_Q(f)$$ (8)
Finally, the impedances of the C, L, Q and La elements are all particular forms of the general expression:

\[ Z(f) = A(j2\pi f)^m \]  \hspace{1cm} (9)

with A the value of the component and \( m \in [-1,0[ \cup ]0,1] \).

If \( m = 0 \), then the impedance \( Z \) is a simple resistance.

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