Explicit Conversion between Different Equivalent Circuit Models for Electrochemical Impedance Analysis of Lithium-Ion Cells

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Despite the accuracy and non-intrusive nature of Electrochemical Impedance Spectroscopy, the impedance spectra of commercial Lithium-ion cells are notoriously hard to interpret. Consequently, the literature is filled with various equivalent circuit models, which differ greatly in their physical significance, but which produce very similar impedance spectra. In this paper, explicit formulas are given to convert between various equivalent circuits made of resistors and capacitors of the sort discussed in the literature. Furthermore, all these formulas have been implemented in a Python program, in the hope that studies done assuming one circuit might be compared to studies done with a different circuit, for instance. This paper considers cases where two different circuits can produce two impedance spectra which are identical. For instance, explicit conversions are given between Ladder circuits, Voight circuits, and Maxwell circuits for various time constants. This gives a conceptual foundation to explore the more difficult case of circuits producing impedance spectra which are similar to each other (e.g. within 5%).

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Impedance spectroscopy1–4 is a powerful method which can be applied to electrochemical cells, for diagnostic purposes, fundamental research, and for the development of future electrochemical storage systems. It is non-intrusive and doesn’t damage cells. The impedance spectrum of a lithium-ion cell may be the best in-situ probe of solid-electrolyte-interphase (SEI) properties which are hard to measure. Spectrum of a lithium-ion cell may be the best in-situ probe of solid-electrolyte-interphase5 (SEI) properties which are hard to measure otherwise. Furthermore, it is repeatable and flexible (short measurements vs long measurements, low temperature vs high temperature, etc.) and can automatically be integrated with long-term cycling.6

However, impedance spectra are notoriously difficult to interpret correctly,2 and the difficulty increases with the complexity of the electrochemical cell. For instance, in commercial lithium-ion cells, the behavior of both electrodes, the contacts with the current collectors, the primary and secondary particles, surface coatings, and the SEI all contribute to the measured spectra.

In this paper, the problem of fitting a large number of impedance spectra to a physical model in an effort to extract some trends is considered. Perhaps the most basic part of this problem is to choose an equivalent circuit model to fit the spectra. However, there are multiple models discussed in the literature with various interpretations. Choosing between these models just based on the spectra themselves is difficult. For instance, it is known2,3 that many of the circuits discussed in the literature, despite having different physical interpretations, are mathematically equivalent or approximately equivalent to each other in the sense that they can produce exactly the same spectra, although not with the same parameters.

However, in order to automate this analysis and gain some insights from the observed trends, it is valuable to know how to explicitly compute the parameters of one model such that the impedance spectrum is the same as the spectrum from another model without needing to fit the original spectrum directly. This paper explains how this is done and provides a simple Python implementation which can readily be integrated into a bigger computer program, and which implements the ideas discussed in this paper.

Circuits made up of resistors and capacitors are analyzed in this paper. This gives a simple tool to understand the more directly applicable problem of circuits with more realistic components (constant phase elements) and to find approximate conversions between two models.

Note, however, that the conversions discussed below are only a tool, and not meant to replace a physical analysis of impedance spectra. Many circuits that will fit a complex spectrum have nothing to do with the underlying physics, and yet the conversions shown in this paper will demonstrate that many circuits can fit the experimental data identically to the physically meaningful circuit. Judgement must be used when using this tool.

In an industrial setting, or a high-throughput setting, when an appropriate circuit is not yet known, the conversions can be used to explore some plausible options, compare trends, and verify the interpretation with some supporting experiments. In such a case, the conversions can be used to see the impact of a certain choice of equivalent circuit more clearly. For instance, by varying the parameters of one model circuit and seeing how the corresponding parameters of a second model circuit change by fitting to the experimental data one can select which circuit is most appropriate to describe the experiment.

When knowledge of the most physically meaningful circuit exists, then that circuit should be used, and each component in the circuit should ideally have a known physical meaning. Even in that case, the conversions reported here might be useful.

It is possible that some literature studies might have reported the results fitted to an inappropriate circuit topology. To understand these results, some conversion to a more appropriate equivalent circuit must be performed and that is where the results of this paper can be used. The conversions described in this paper do not require fitting, and therefore do not suffer from convergence issues.

Furthermore, once software has been written to reliably fit to one circuit topology, the conversions described in this paper can extend the use of the software without having to rewrite the core software.

Finally, to understand the equivalent circuit model, there needs to be some physical meaning given to the various components of the circuit, such as representing the negative electrode SEI by an RC parallel circuit. The same circuit can be interpreted in different ways, for instance when two RC elements are in series, their meaning can be interchanged without changing the topology of the circuit. For this case, the conversions described in this paper are not useful. However, sometimes a reinterpretation can cause a change in topology. This is where the conversions come into play. Since the equations used to perform the conversion do not depend on the interpretation given to the various components, this paper does not discuss the interpretations further.

Methods

The program given in the supplementary information was written in Python and tested with Python 2.7 on Windows 10. It is structured as a single function. The first argument gives the parameters of the original circuit, and the second argument is a string which identifies
Figure 1. Example of one circuit (left, original) that can mimic another’s impedance spectrum (right, converted) by using different values for the parameters. The impedance formulas are shown under the circuits.

Table 1. The conversion of interest. The function returns the parameters of the converted circuit.

| Original | Converted | Formula |
|----------|-----------|---------|
|          |           |         |

The function is followed by a few example calls to illustrate the behavior.

Results and Discussion

It is worth illustrating what is meant by “converting between two circuits.” To accomplish this, the simplest non-trivial example will be investigated.

Figure 1 shows two circuits. They look different, but they can produce exactly the same impedance spectra, when their parameters are chosen appropriately. Below the Figure, the formula for the complex impedance of each circuit is shown. Each circuit contains two resistors and one capacitor. The original circuit on the left has three parameters (R11, R12, C11). If these values are fixed (e.g. R11 = 1 Ω, R12 = 10 Ω, C11 = 1 F), then the impedance spectrum is fully determined. To say that the original circuit can be converted to the “converted” circuit is to say that one can determine the values of the “converted” parameters (R21, R22, C21) so that the impedance of the “converted” circuit will be exactly the same as the impedance of the original circuit at all frequencies. This conversion is given in the third column of Figure 1, and has previously been published.

The notation works as follows. The parameters have two indices. The first index determines whether the parameter belongs to the original circuit (index = 1) or the “converted” circuit (index = 2). The second index serves to differentiate the various resistors and the various capacitors. The formulas for more complicated circuits are often correspondingly more complicated. However, since they are implemented in a Python program (given in the supplementary information), the formulas themselves are only given for reference.

By tracking the impedance of a given electrochemical cell through time, charge-discharge cycle number, cell potential, etc., a dynamic characterization of the cell can be obtained. Yet, different models might produce very different trends. Figure 2 shows an example of this phenomenon based on the conversion in Figure 1. On the left side, the original circuit of Figure 1 has three parameters, and all parameters except one are kept constant. R12 is increased linearly in 1 Ω steps from 1 Ω to 10 Ω. All of the parameters of the two circuits are plotted as a function of R12. On the right side of Figure 2, the “converted” circuit parameters are plotted against the original value of R12.

As Figure 2 shows, the trends in the converted parameters are more complicated. Indeed, all three parameter changes, most trends are non-linear, and even though the capacitance doesn’t vary in the first circuit, it has a very dramatic variation in the second.

Looking at Figures 1 and 2, it is natural to wonder if there are some limits on the conversion formulas. In other words, are there any parameter choices in the original circuit which, after applying the conversion formula, would not yield the same impedance spectrum?

As it turns out, the only case where this happens is if the formulas require a division by zero. In the case of Figure 1, this would correspond to cases where R11 is zero or R11 + R12 is zero. Assuming...
that resistances are positive, this corresponds to cases where $R_{11}$ is zero. For more complicated formulas the story is the same. If the conversion formula requires division by zero, then the circuits most likely cannot give identical spectra. In the exceptional case that the circuits can give identical spectra with the problematic parameters, then a different formula would be required.

Looking at Figure 1, one might get the impression that conversions, either implicit or explicit, only work for simple circuits. However, this is not the case. To illustrate this, Figure 3 shows two complicated circuits which look quite different, and whose topologies are quite different. Despite this, one can explicitly convert from the upper circuit to the lower based on the formulas described in this paper. In order to keep the flexibility to convert to such unusual topologies, a set of elementary conversions was considered such that one can chain one after another to cover various possibilities.

Before going to the explicit conversions, it is helpful to understand which circuit can be converted to which other circuit. Many circuits with multiple time constants have impedance formulas that can be rewritten in a universal form, and therefore potentially can be converted to each other.

Figure 4 shows a circuit with $n$ time constants, represented mathematically as the division of two polynomials in the complex variable $s = i\omega$. The numerator is labelled $U$ and the denominator is labelled $D$. Furthermore, the coefficients of these polynomials are represented as lowercase letters. (e.g. $u_0$ is the constant coefficient of the numerator).

The universal representation shown in Figure 4 is equivalent to many circuits (in the sense that many circuits can be converted from and to it), and was previously discussed in the literature. For example, in the original circuit of Figure 1, $u_0 = R_{11} + R_{12}, u_1 = R_{11}R_{12}C_{11}, d_0 = 1, d_1 = R_{11}C_{11}$. Note that the presence of the series resistor causes the numerator and denominator to have two terms each. Without a series resistor, the numerator would have one less term than the denominator.

Figure 5 shows examples of several topologies which are both common and equivalent to the universal representation (and therefore to each other). Note that, in the literature, the ladder configuration is often drawn similarly to the lower right configuration in Figure 5. However, this configuration and the upper right configuration are topologically the same (no conversion required), and it is more convenient to write a general $n$-time constant ladder in the upper right configuration, so it is used later in the paper.

Figures 6, 7 and 8 give the various elementary conversions. The Python code implements all of them.
Figure 6. Explicit elementary conversions between circuits (Part 1).

In order of appearance, Figure 6 shows in the first two rows, the conversion from an “RC” circuit to the universal representation, then the inverse conversion. In the next two rows, Figure 6 shows the conversion from a partially universalized ladder circuit to a universal circuit, and vice versa. Note that by applying these conversions recursively, one can fully convert back and forth between a ladder circuit and a universal circuit with the same number of time constants (this is how the Python code implements it). In fact, these two conversion steps don’t make assumptions about the universal components. Therefore, it is possible to apply these elementary steps in conjunction with other steps to obtain circuits that do not fall within the families of Figure 5 (for instance, the lower circuit shown in Figure 3).

In the next two rows, Figure 6 allows one to convert from a partially universalized Voight circuit to a universal circuit, and from a universal circuit with two time constants to a Voight configuration. It is possible, with numerical methods, to convert from universal to Voight even when there are 3 or 4 time constants. Alternatively, the impedance spectra may be fitted directly to the Voight configuration to obtain the parameters if the numerical conversion fails.

So far, the elementary conversion steps deal with electrochemical cells where diffusion is ignored. To investigate this important aspect of cell behavior, Figure 8 shows how to introduce a series capacitor in the analysis. Understanding how a series capacitor impacts the conversions is useful in understanding the Warburg element (the traditional way to model diffusion). One way to see this is to notice that, replacing \( s = i\omega \) by \( S = (i\omega)^k \), it is possible to obtain conversion formulas which work for circuits where all capacitors have been replaced by constant phase elements where all the exponents have the same value, and the traditional way to model diffusion is with a constant phase element with an exponent near 0.5.
Critically, whichever convention is used must be consistent across all the conversion formulas. In this paper, circuits equivalent to the Voigt configuration (Figures 6, 7) follow the convention that \( d_0 = 1 \). It is easy to verify that all the transformations in Figures 6, 7, and 8 will preserve this property. For circuits equivalent to the Voigt configuration with a series capacitor, a different convention must be chosen. Namely, these circuits follow the convention that \( d_0 = 0 \) and \( u_0 = 1 \). Again, it is easy to verify that all the transformations in Figures 6, 7, and 8 will preserve this property. Note that without this convention, the second transformation of Figure 8 must be replaced by \( C_{21} = d_{11}/u_{10} \). However, these conventions are enforced by the conversions themselves (for instance, the first conversion of Figure 8). Therefore, the formulas can be used without worrying about them.

The last row of Figure 8 shows how to incorporate a capacitor in series within a universal representation. It turns out that these three simple conversions, together with those given in Figure 6 and 7, are all that are required to convert between many circuits comparable to those shown in the literature (where the constant phase elements were replaced by capacitors).

The transmission line model is an example of a circuit that cannot be converted to and from a universal representation with the formulas given in this paper. However, in the simple case given in Reference 9, the impedance has the universal form, and therefore might be converted to a ladder configuration using the formulas of this paper, as long as no division by zero occurs. The transmission line model is a good example of a circuit model which produces impedance spectra which are approximately equal to some impedance spectra produced by a Randles-type circuit. It should therefore be revisited when discussing approximate conversions between non-ideal circuits.

Despite this exception, there are many examples in the literature which are compatible with the formulas given in this paper, as long as we replace constant phase elements and Warburg elements with capacitors. For instance see Fig. 5 of Reference 11, Figures 1, 2, 3, 8, 11, 13, and 14 of Reference 1, ignoring the inductances and the series resistors, Reference 12, Fig. 7 of Reference 13, Figures 1, 2, and 3 of Reference 14, Figure 6 of Reference 15, as well as many others. So far, many formulas were shown, but in order to demonstrate that they work in a real example, Figure 9 uses the code to convert from a Voight configuration (with a series capacitor) to a ladder configuration (with a capacitor embedded in the inner part of the ladder). Figure 9c shows the two circuits considered. Concretely, Figure 9 shows 3 examples of conversion. For each example, parameter values were chosen for the Voight configuration, and the impedance spectrum was computed and plotted. Next, the circuit was converted to the ladder configuration.

Figure 7. Explicit elementary conversions between circuits (Part 2).

| Original | Converted | Formula |
|----------|-----------|---------|
| \((U_1/D_1)\) | \((U_2/D_2)\) | \(U_2 = (1 + R_{11}C_{11}s)U_1\) \(D_2 = (1 + R_{11}C_{11}s)D_1 + (C_{11}s)U_1\) |
| \(R_{11}\) \(C_{11}\) | \(R_{21} = u_{10}\) \(C_{21} = d_{12}/u_{11}\) \(R_{22} = d_{11}/(d_{12}u_{10} + u_{11})\) \(C_{22} = u_{11}/u_{10}R_{22}\) |

Figure 8. Explicit elementary conversions between circuits (Part 3). Note \( d_{10} = 0 \) and \( u_{10} = 1 \) in the second and third rows.

| Original | Converted | Formula |
|----------|-----------|---------|
| \(C_{11}\) | \((U_2/D_2)\) | \(U_2 = 1\) \(D_2 = 0 + C_{11}s\) |
| \((U_1/D_1)\) | \(C_{21}\) | \(C_{21} = d_{11}\) |
| \(C_{21}\) | \((U_2/D_2)\) | \(D_2 = D_1/sd_{11}\) \(U_2 = U_1 - D_1/sd_{11}\) |

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Figure 9. An example of explicit conversion from a Voight-type circuit configuration to a Ladder-type circuit configuration.

The code implementation of the elementary conversion steps, as well as many common cases is available as supplementary material.

Conclusions

This work introduced and implemented explicit conversion formulas to go from the Voight configuration to the ladder configuration, or the Maxwell configuration, as well as providing the building blocks to explore many more conversions. This allows for the comparison of different assumptions about the underlying physical principles, for instance by looking at trends in the model parameters as a function of cycling time, voltage, temperature, etc. Two different models might show very different trends. Furthermore, it allows for the comparison of the results of different studies with incompatible assumptions about the equivalent circuit topology. Finally, it gives a relatively simple framework to understand the more general case where two circuits produce slightly different spectra, and where the capacitors are replaced by constant phase elements with various exponents.

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