The CIRCUIT DESCRIPTION CODE explained

1. Introduction

The Circuit Description Code (CDC) is the symbolic representation of an equivalent circuit model. Using the CDC it is quite simple to instruct the modelling part of the program how to calculate the impedance or admittance (or any other dispersion representation) given a set of parameter values. The program 'reads' the CDC from left to right and interprets the symbols for what action to take. A clear description of this process, together with the relevant equations, is presented in [1].

Construction of the CDC is straightforward, but certain restrictions must be taken into account. Also one should realise that an equivalent circuit, and hence its 'CDC', is only a model. Reality may be more complex, eluding this simple description method.

2. Definitions and construction procedure

The circuit description code (CDC) is based on the assumption that every element of an equivalent circuit can be regarded as a black box, having two (and only two) terminals and a known transfer function (i.e. impedance or admittance function). Two types of elements are defined here, **simple elements** and **complex elements**:

- A **simple element** is defined as an element with a (complex) transfer function, which cannot be separated further into independent parts, e.g. a resistance, capacitance, etc. Generally a simple element can be related to a single (macroscopic) physical process, for example the resistance of a material (R), the double layer capacitance (C) or a diffusion related process which is represented by a Warburg (W).

- A **complex element** is defined as a two terminal box which internally is build up out of either a series or a parallel circuit containing **simple** and/or **complex** elements of a higher order. These two different types of complex elements are shown schematically in Fig. 1.

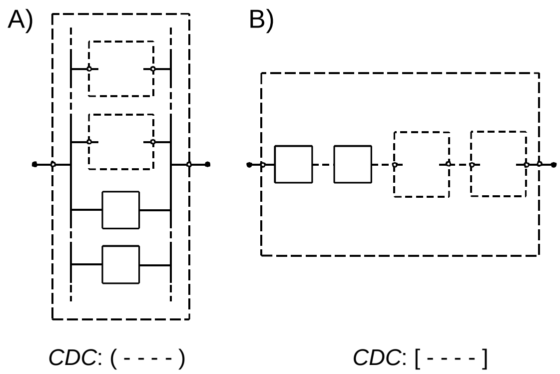

Figure 1. Schematic representation of two types of composite elements. **A)** With a parallel internal sub-circuit (odd level, enclosed by parenthesis). **B**: With a series sub-circuit (even level, enclosed by square brackets). Solid lined boxes represent 'simple elements', broken lined boxes composite elements.

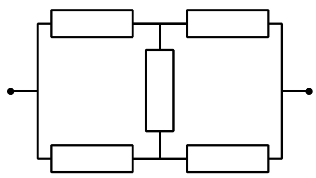

Figure 2 Type of equivalent circuit that cannot be represented by the Circuit Description Code (**CDC**).

From Fig. 1 it is obvious that there are two types of complex elements, i.e. parallel structure versus series structure internally. This is indicated in the *CDC* by the brackets enclosing the complex element. A parallel internal arrangement (Fig. 1A) is enclosed by a set of parenthesis: (RQC), while a series internal arrangement (Fig. 1B) is enclosed by a set of square brackets: e.g. [RQC]. The *CDC*-entry software automatically selects the proper bracket, hence in typing '[' and '(' are equivalent. The same holds for ']' and ')'.

The **order of a complex element** is defined here as the number of boxes in which the complex elements is contained, including its own box.

The essence of these definitions is that only equivalent circuits are considered which can be broken down into two-terminal complex elements of increasing order. Hence the circuit of Fig. 2 cannot be considered as it can not be broken down into complex circuits of increasing order without violating the two-terminal condition. Such a circuit would require a special transfer function. It will be considered in future software developments.

The Circuit Description Code is the translation of an equivalent circuit into a representation that can be interpreted by the program. It has the form of a string of symbols in which each symbol (character) represents a specific type of element, e.g. **R** for resistance, **C** for capacitance, **L** for inductance, etc. A list of currently supported elements and their dispersion relations (transfer functions) is given in Table 1., see page 8.

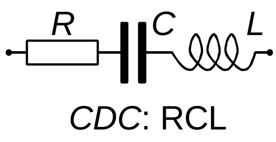

Figure 3: Series circuit of a resistor, ***R***, a capacitor, ***C***, and an inductor, ***L***.

The simplest case is a series circuit of simple elements, e.g. a resistance, capacitance and inductance (Fig. 3). The CDC is simply given by:

R C L (1)

All permutations of description (1) are of course equivalent. The circuit is quite different if the inductance is arranged in parallel to the capacitance (Fig. 4). According to the definitions above, the parallel part of the circuit can be regarded as a complex element (of order 1), as it can be enclosed by a box with two terminals, outlined by the dashed line in Fig.4. This complex element is signified in the CDC by a set of parenthesis: '(' and ')'. In a schematic representation:

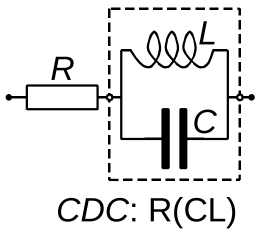

Figure 4: Circuit of a resistor in series with a parallel circuit of a capacitor and an inductor.

R (complex element) (2)

Here **R**, '**(**' and '**)**' are part of the CDC, '**complex element**' has to be replaced by a proper description of its contents: a simple parallel circuit of a capacitance and an inductance: **CL**. The CDC then becomes:

R (C L) (3)

The left parenthesis is a reminder for the program that the response of a complex element has to be calculated first. The right parenthesis signifies that the response of the complex element has been evaluated and that it must be transformed and added to the lower level (sub-) circuit dispersion. Fig. 5 shows an arbitrary equivalent circuit with a more complex structure. Establishing the CDC for this circuit can best be done as follows. First locate the series circuit which is at the zero or ground level. It is formed by R_1 and what ever is enclosed by box-1 (dashed outline) which represents a complex element of order 1. The following step is to examine box-1 using the recursive definition for the complex element. It contains a parallel circuit build up by R_2 and a complex element of order 2 enclosed by box-2.

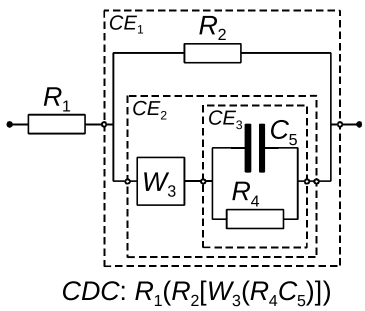

Figure 5: Arbitrary equivalent circuit. The rectangles (presented by the dashed lines) form the complex elements (CE_i) of order i.

The next step is to consider box-2. On its turn it consists of a series circuit formed by the Warburg element W_3 and the complex element of box-3. This complex element of order 3 contains a parallel circuit of two simple elements, R_4 and C_5. Developing the CDC along these steps, one can write down the following sequence:

level-0: $\mathbf{R_1}$ **(** **box-1** **)**

level-1: $\mathbf{R_1}$ **(** $\mathbf{R_2}$ **[** **box-2** **]** **)**

level-2: $\mathbf{R_1}$ **(** $\mathbf{R_2}$ **[** $\mathbf{W_3}$ **(** **box-3** **)** **]** **)**

level-3: $\mathbf{R_1}$ **(** $\mathbf{R_2}$ **[** $\mathbf{W_3}$ **(** $\mathbf{R_4}\,\mathbf{C_5}$ **)** **]** **)** (4)

The indices are only used here for illustrative purpose. The actual Circuit Description Code for the circuit of fig. 5 will be:

R (R [W (R C)]) (5)

From the foregoing it will be clear that a complex element of odd order will have a parallel internal structure (fig. 1a), while a complex element of even order will have series internal structure (fig. 1b). Thus the ground level circuit (zero order) is a series circuit, even if it contains only one complex element (which is of order 1 and thus a parallel circuit). The CDC for the equivalent circuit of fig. 6 must then be written as:

(R C L) (6)

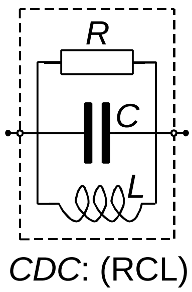

Figure 6: Parallel circuit of a resistor ***R***, a capacitor ***C*** and an inductance ***L***.

In short, the CDC for a complex equivalent circuit can be obtained by locating the complex element(s) of order 1. Subsequently these complex elements are devided into alternating series/parallel arrangements of simple and complex elements of increasing order, until only simple elements remain. For a detailed description of how the CDC is interpreted by the program see [1].

3. Summary of circuit elements and their representations

3.a Standard electrical elements:

Besides the three well known dispersive elements **R**, **C** and **L**, the CDC can accomodate four diffusion related elements. These elements and the representation of their transfer functions will be discussed in some detail below. For most elements the parameters must be passed to the program in the admittance representation (ohm^{-1} or **S**iemens related). The two exceptions are the resistance **R**, which must be given in ohms, and the inductance **L** which must be given in Henri, thus both in the impedance representation.

3.b Warburg element:

A well known diffusional element is the Warburg (CDC symbol: **W**), also known as the semi-infinite transmission line. The dispersion relation follows from Fick's second law for a (one dimensional) semi infinite diffusion problem. The general form is:

$$Y(\omega) = Y_0\sqrt{j\omega} = Y_0[\sqrt{\omega/2} + j\sqrt{\omega/2}] \quad (7)$$

where Y_o is the adjustable parameter containing the diffusion coefficient [2,3] and other parameters which depend on the characteristics of the electrochemical system. ω is the angular frequency: $\omega = 2\pi f$.

3.c Constant Phase Element:

A very general diffusion related element is the Constant Phase Element or **CPE** [4-6], CDC symbol: **Q**. It is encountered frequently in solid state electrochemistry, however no general physical interpretation has been given yet. The CPE behaviour of interfaces has been ascribed to a fractal nature (special geometry of the roughness) of the interface [7-9]. As for bulk effects no direct derivation has been given, but a phenomenological approach by Jonscher [10] and Almond and West [11,12] looks promising. The admittance representation of the CPE is given by:

$$Y(\omega) = Y_0\,(j\omega)^n = Y_0\,\omega^n \cos(n\pi/2) + j\,Y_0\,\omega^n \sin(n\pi/2) \qquad (8)$$

In fact this is a very general dispersion formula. For n=0 it represents a resistance with $R = Y_0^{-1}$, for $n = 1$ a capacitance with $C = Y_0$, for $n = 0.5$ a Warburg and for $n = -1$ an inductance with $L = Y_0^{-1}$.

3.d. Finite length diffusion elements, the FSW:

There are two diffusion-related elements dealing with **finite** length diffusion. The first one describes diffusion through a medium where one boundary is blocking for the diffusing species, e.g. a (thin) mixed conducting electrode [2,3,13]. The result is a dispersion relation with a tangent-hyperbolic function (CDC symbol: **T)**:

$$Y(\omega) = Y_0\sqrt{j\omega}\,\tanh[B\sqrt{j\omega}] \qquad (9)$$

where Y_0 and B contain the diffusion coefficient and other system dependent parameters. Separating this formula into a real and an imaginary component, one obtains:

$$Y(\omega) = Y_0\sqrt{\frac{\omega}{2}}\left[\frac{\sinh z - \sin z}{\cosh z + \cos z} + j\,\frac{\sinh z + \sin z}{\cosh z + \cos z}\right] \qquad (10)$$

where $z = B\sqrt{2\omega}$. For large values of z equations (9) and (10) can be approximated by the Warburg representation (eq. 6). For small values of z equation (10) reduces to the simple dispersion relation of a resistance in series with a capacitance (for clarity in the impedance representation):

$$Z(\omega) = B / 3\,Y_0 - j / Y_0\,B\,\omega \qquad (11)$$

This type of 'finite length diffusion' is often called the '*Finite Space Warburg*' (or *SFW*), signifying the limited space for the intercalating ion.

3.e. Finite length diffusion elements, the FLW:

The second finite length diffusion element deals with the case where one boundary imposes a fixed concentration (or activity) for the diffusing species, thus it is permeable for the diffusing species. This type of dispersion relation is generally found in oxygen conducting electrodes, as well as in corrosion related diffusion [14,15]. The dispersion relation contains in the admittance representation a cotangent-hyperbolic function (CDC-symbol: **O**):

$$Y(\omega) = Y_0\sqrt{j\omega}\,\coth[B\sqrt{j\omega}] \qquad (12)$$

Separating equation (12) in a real and imaginary part yields:

$$Y(\omega) = Y_0 \sqrt{\frac{\omega}{2}} \left[\frac{\sinh z + \sin z}{\cosh z - \cos z} + j \frac{\sinh z - \sin z}{\cosh z - \cos z} \right] \tag{13}$$

which is closely related to equation (10). Again for large z we obtain the Warburg expression. For small values of z a parallel circuit of a capacitance and a resistance is obtained:

$$Y(\omega) = Y_0 / B + j\, Y_0\, B\, \omega / 3 \tag{14}$$

As the diffusion takes place over a 'finite length' this element is also called the '*Finite Length Warburg*', or *FLW*.

3.f. Gerischer Impedance:

The Gerischer impedance combines Faradaic diffusion with a 'non Faradaic' reaction. This reaction takes place along the diffusion path and influences the concentration of at least one of the diffusing species (e.g. by forming electrochemically inactive complexes). The general admittance formula for the Gerischer dispersion is represented by:

$$Y(\omega) = Y_0 \sqrt{K_a + j\omega} \tag{15}$$

where K_a is the net reaction rate. This equation can be split into a real and imaginary part:

$$Y(\omega) = \frac{Y_0}{\sqrt{2}} \left(\sqrt{\sqrt{\omega^2 + K_a^2} + K_a} + j \sqrt{\sqrt{\omega^2 + K_a^2} - K_a} \right) \tag{16}$$

or alternatively:

$$Y(\omega) = Y_0 \sqrt{\frac{\omega}{2}} \cdot \left(\sqrt{\sqrt{1 + g^2} + g} + j \sqrt{\sqrt{1 + g^2} - g} \right) \tag{17}$$

with $g = K_a/\omega$. For the impedance representation one obtains:

$$Z(\omega) = \frac{Z_0}{\sqrt{2}} \left(\sqrt{\frac{\sqrt{\omega^2 + K_a^2} + K_a}{\omega^2 + K_a^2}} - j \sqrt{\frac{\sqrt{\omega^2 + K_a^2} - K_a}{\omega^2 + K_a^2}} \right) \tag{18}$$

with $Z_0 = (Y_0)^{-1}$. As for eq. (16) an alternative expression for eq. (18) can be given:

$$Z(\omega) = \frac{Z_0}{\sqrt{2\omega}} \left(\sqrt{\frac{\sqrt{1 + g^2} + g}{1 + g^2}} - j \sqrt{\frac{\sqrt{1 + g^2} - g}{1 + g^2}} \right) \tag{19}$$

From eqs (17) and (19) it is obvious that for $g<1$ (high frequencies) these equations change to the Warburg or semi-infinite diffusion dispersion:

$$Y(\omega) = Y_0 \sqrt{j\omega} = Y_0 \left(\sqrt{\omega / 2} + j \sqrt{\omega / 2} \right) \tag{20}$$

For low frequencies the imaginary part disappears (=0) resulting in a dc-resistance with $R_{dc} = Z_0\, K_a^{-0.5}$. It is important to notice that the diffusion process is semi-infinite, yet because of the side reaction, the impedance reaches a finite dc value for $\omega \rightarrow 0$.

For the representation of the Gerischer dispersion eq. (1) is used in the NLLSF-program. The CDC-symbol is 'G'. The parameters needed (or fitted) by the program are Y_0 (in ohm^{-1}s$^{0.5}$) and K_a (in s^{-1}). An example of the Gerischer impedance is presented in fig. 7. For display purposes the Gerischer impedance has been offset by a series resistance (CDC: *RG*). Parameter values are: R=20 Ω, Y_0=0.01 S^{-1}s$^{0.5}$ and K_a=2 s^{-1}. Estimates for Y_0 can easily be found by using the 'Find Line' option in 'Data Cruncher' for the high frequency (Warburg like) part. The estimate for K_a can be obtained from the resistance value measured between the high frequency and the low frequency intercept, R_{dc}, with the real axis:

$$K_a = (Y_0 \cdot R_{dc})^{-2} \tag{21}$$

For further reading on the Gerischer impedance see [16,17].

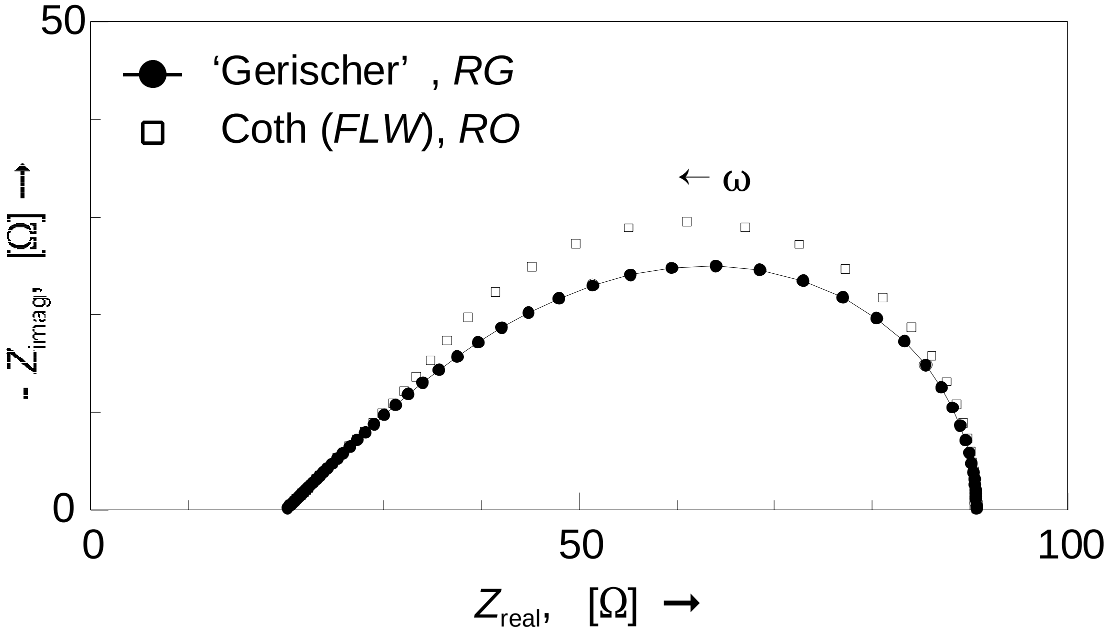

Figure 7: Example of the dispersion of a 'Gerischer' element. For clarity a series resistance of 20 Ω is added. Parameters: Y_0= 0.01 S·s$^{0.5}$, K_a = 2 s^{-1}. For comparison the dispersion of a *FLW* is added (Coth-function , open squares). Parameters: Y_0= 0.01 S·s$^{0.5}$, B = 0.7071 s$^{0.5}$. At high frequencies the dispersion of both elements simplifies to a (identical) semi-infinite Warburg response. Frequency range is 1 mHz to 100 kHz, 11 points/decade.

4. Examples of CDC's

In figure 8 the well-known Randles circuit is shown. The CDC for this circuit is given by:

$$\boldsymbol{R_{\mathrm{i}}\ (\ C_{\mathrm{dl}}\ [\ R_{\mathrm{ct}}\ W\ ]\ )} \qquad (22)$$

Where $\mathbf{R}_i$ is the ionic resistance of the electrolyte, $\mathbf{C}_{dl}$ is the double layer capacitance and $\mathbf{R}_{ct}$ is the charge transfer resistance. The semi-infinite diffusion is represented by the Warburg (**W**).

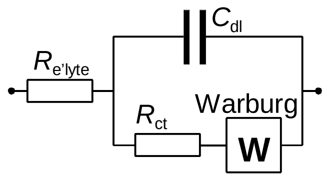

Figure 8: Simplest form of a Randles type equivalent circuit. *CDC*: R(C[RW]). $R_{\mathrm{e'lyte}}$ is the ionic resistance, R_i, of the electrolyte.

Figure 9 shows the equivalent circuit of a mixed, oxygen ion conducting ceramic with electrode dispersion. The electronic resistance, R_{el}, is placed directly between the electrodes. The ionic conduction path includes the ionic (bulk) resistance and the grain boundary resistance. Frequency dispersion is introduced by the dielectric capacitance (bulk- or geometric capacitance) and the capacitance related to the grain boundary interface. The electrode dispersion depicts the reaction between the oxygen ions and the oxygen in the ambient at the electrode surface. This sub-circuit is quite a simplification of what generally is encountered. C_{dl} and R_{ct} represent the double layer capacitance and the charge transfer resistance. $Z_{\mathrm{diff.}}$ represents the adsorption-diffusion related processes, here given as a Warburg impedance. The CDC for the circuit of fig. 9 is given by:

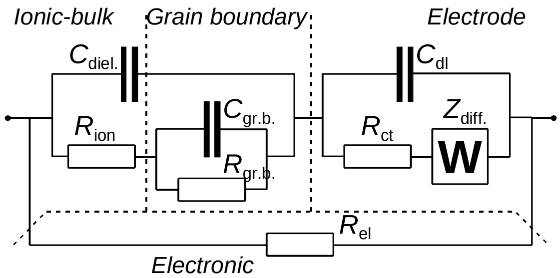

Figure 9: Complex equivalent circuit for a mixed conducting oxide ceramic with reversible electrodes. The CDC is: (R[(C[R(RC)])(C[RW])]).

$$\boldsymbol{(\ R_{\mathrm{el}}\ [\ (\ C_{\mathrm{diel}}\ [\ R_{\mathrm{ion}}\ (\ R_{\mathrm{gr.b.}}\ C_{\mathrm{gr.b.}}\ )\ ]\ )\ (\ C_{\mathrm{dl}}\ [\ R_{\mathrm{ct}}\ W_{\mathrm{diff.}}\ ]\ )\ ]\ )} \qquad (23)$$

The development of this CDC is presented in the graphical cartoon below (figure 10).

The best route for developing the CDC is to start from the 'terminals' of the equivalent circuit. Next define the complex elements, starting with an internal parallel circuit (odd level). The next level of complex elements must have an internal series circuit (even level).

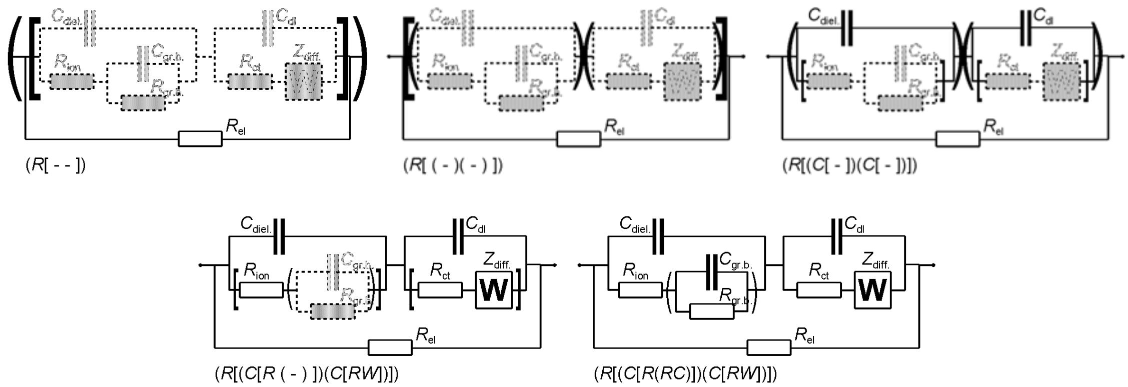

Figure 10: Schematic development of the CDC from figure 8. The CDC starts with a complex element **'(--)'**, which is a combination of R_{el} in parallel with a series complex element **'(*R*[- -]'**. The series complex element consists of two parallel type complex elements: **(*R*[(-) (-)])**. These complex elements are further developed. For the bulk response it consists of $C_{\mathrm{diel.}}$ parallel to a series complex element, **(*R*[(*C*[-]) (-)])**, which can be resolved further into R_{ion} in series with the parallel combination of $C_{\mathrm{gr.b.}}$ and $R_{\mathrm{gr.b.}}$: **(*R*[(*C*[*R*(*RC*)]) (-)])**. Finally the electrode response can be filled in, *C*dl in parallel to a series complex element consisting of R_{ct} and *W*: **(*R* [(*C* [*R* (*R C*)]) (*C* [*R W*])])**.

Table 1. List of elements, corresponding symbols and dispersion relations.

Element description	Symbol for CDC	Dispersion relation Admittance	Impedance	Parameters
Resistance	**R**	$1 / R$	R	R
Capacitance	**C**	$j\omega C$	$-j / \omega C$	C
Inductance	**L**	$-j / \omega L$	$j\omega L$	L
Warburg	**W**	$Y_0\sqrt{(j\omega)}$	$1 / Y_0\sqrt{(j\omega)}$	Y_0
CPE	**Q**	$Y_0(j\omega)^n$	$(j\omega)^{-n} / Y_0$	Y_0, n
FSW*	**T**	$Y_0\sqrt{(j\omega)}$ Tanh$[B\sqrt{(j\omega)}]$	Coth$[B\sqrt{(j\omega)}]/Y_0\sqrt{(j\omega)}$	Y_0, B
FLW†	**O**	$Y_0\sqrt{(j\omega)}$ Coth$[B\sqrt{(j\omega)}]$	Tanh$[B\sqrt{(j\omega)}]/Y_0\sqrt{(j\omega)}$	Y_0, B
Gerischer	**G**	$Y_0\sqrt{(k+j\omega)}$	$(k+j\omega)^{-½}/Y_0$	Y_0, k
Fractal Gerischer‡	**F**	$Y_0\,(k+j\omega)^{\alpha}$	$(k+j\omega)^{-\alpha}/Y_0$	Y_0, k, α

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* The FSW (Finite Space Warburg) element is the Tanh function in the admittance representation.
† The FLW (Finite Length Warburg) element is the Coth function in the admittance representation.
‡ The Fractal Gerischer is to be included in a future release.