How to Choose an Equivalent Circuit

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I address here some common questions about equivalent circuits and how to choose them. These will be in the context of using impedance measurements to learn about reaction mechanisms, and for simplicity we assume that mass transport is not a complicating factor. The first issue is of course why use equivalent circuits at all? There is a school of thought that says that they should be avoided and a physico-chemical kinetic model used to predict the impedance function that is then fitted to the data. By the simple analogy with fitting data to a straight line, I show that equivalent circuits have an important role as a measurement model, and can help to narrow down the choices of possible physico-chemical models.

The issue of the non-uniqueness of equivalent circuits is addressed, and it is shown that although different equivalent circuits may describe the same impedance data, the key kinetic information that is deduced from these circuits is the same, and is the same as that which can be deduced from a purely kinetic model. Given this, it might be though that any equivalent circuit is as good as any other, but there are some simple reasons to choose one form over another, though the choice may depend on the goals of the researcher. These issues are reviewed, and include such factors as: the ease of estimating starting values for data fitting; avoidance of parameter ambiguity; the accuracy of extracting kinetic parameters; the ease of estimating stability of the mechanism; and the automated testing of Kramers-Kronig (KK) conditions (conditions required for verifying data validity).

The distinction between active and passive systems is discussed, and the need to use a negative resistor in some active circuits is introduced. All passive circuits, which include all those with positive capacitors, resistors and inductors, automatically satisfy the KK conditions. Electrochemical systems generate power, and therefore sometimes need to be modeled with active circuits. Negative resistances must be use with care, but some circuits satisfy KK and are therefore preferred. Guidelines for how to choose circuits in these cases are given.

There are some simple ideas that guide the choice of circuit if some minimal information is known about the reaction mechanism. For example, mechanisms that do not admit a nonzero steady state current will not have a dc current path through them.

All the ideas presented are illustrated by simple examples, in which the logic of building up to a valid circuit is presented.

1. D.A. Harrington and P. van den Driessche, Mechanism and Equivalent Circuits in EIS, *Electrochim. Acta*, **56** 8005 (2011).