Equivalent Circuits for Electrochemical Surface Reactions

D. A. Harrington,
Department of Chemistry,
University of Victoria,
Victoria, B.C., V8W 3V6,
Canada.
Email: dharr@uvic.ca

and

P. van den Driessche,
Department of Mathematics and Statistics,
University of Victoria,
Victoria, B.C., V8W 3P4,
Canada.
Email: pvdd@math.uvic.ca

The methods for deriving the electrochemical impedance from kinetic parameters are well known, and it is possible to fit data to kinetic models without invoking the concept of an equivalent circuit. However, fitting electrochemical impedance spectroscopy (EIS) data to equivalent circuits is the usual first step in data analysis. Therefore, it is useful to know which types of equivalent circuits arise from which types of mechanisms. Here we give partial answers to three general questions:

1. Is there a simple way to deduce the number of circuit elements in an equivalent circuit from inspection of the reaction mechanism?

2. Can we find classes of mechanisms that may give rise to inductors in their equivalent circuits, or that cannot give rise to inductors?

3. Can we find equivalent circuits in which the circuit element values are simply related to the kinetic parameters of individual reaction steps or the coverages of surface species?

Our answers are given for mechanisms involving surface adsorbed species, in which mass transport of solution species to and from the electrode surface is fast. Langmuir (mass-action) kinetics are assumed for convenience, although many of the conclusions are valid under less restrictive conditions. Autocatalytic reactions are excluded from the mechanisms considered.

The number of circuit elements is related to two parameters easily deduced from steps of the reaction mechanism: (1) I, the number of independent reactions steps. Reactions are independent if none can be written in terms of the others, in the sense of Hess's law. (2) X, a parameter that depends on whether the overall reaction is catalytic or is a "dead-end" reaction whose final products are surface-adsorbed species. More specifically, $X = 2$ if a balanced reaction can be constructed from electrons and the soluble species involved in the mechanism, and $X = 0$ otherwise. D.c. current can flow through an equivalent circuit for the $X = 2$ case, but the $X = 0$ case is blocking (capacitive) at low frequencies. Typically an equivalent circuit has I resistors and $I - X/2 + 1$ capacitors or inductors (including the double-layer capacitance and excluding the solution resistance).

The following statements about the presence of inductors in equivalent circuits may be derived:

(a) Inductors cannot arise in a single-step mechanism.
(b) Inductors cannot arise at equilibrium [1].
(c) Inductors cannot arise in a mechanism with a single electron-transfer step whose electronless reaction graph is a tree (has no cycles, e.g., the mechanism in the figure).
(d) For mechanisms with a single adsorbed species, inductors signal the presence of two electron-transfer steps, one that is oxidative in the direction of adsorption and one that is reductive in the direction of adsorption [2].

In the conventional equivalent circuit, the circuit elements have positive values of capacitance, resistance, or inductance. Usually a canonical form is chosen, i.e., one with the minimum number of circuit elements, and the numbers of elements are then as given above. There are typically still several choices of circuit that satisfy these requirements. For RC circuits, a ladder form can be shown to have the simplest relationship between circuit element values and kinetic parameters, but the value of an element is still typically a function of rate constants from multiple reaction steps.

There may sometimes be advantages to choosing non-conventional circuits with more than the minimum number of elements or with negative element values. Advantages include the ability to write the circuit down by inspection of the reaction mechanism and the ability to relate element values to the rates of individual reaction steps or to coverages of individual species. For the mechanisms in (c) above, it is possible to find a "topological" equivalent circuit that is closely related to the graph of the mechanism (see figure). The capacitance values are proportional to the surface coverages of the species and the resistors are related to the rates of the individual steps.

[1] D.A. Harrington and P. van den Driessche, Electrochim. Acta, 44 (1999) 4321.
[2] D.A. Harrington and P. van den Driessche, J. Electroanal. Chem., 501 (2001) 222.