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# The Two-Terminal Equivalent Network of a Three-Terminal Electrochemical Cell

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**Abstract**

The two-terminal equivalent network of a three-terminal electrochemical cell is derived. This reveals, in a particularly clear way, how various artefacts arise from the layout of the cell. It is found that the working electrode response appears in series with an inductive artefact, and both appear in parallel with a capacitive artefact. Advice is given on how to diminish the size of these artefacts.

## 1. Introduction

The present work was motivated by a desire to gain a better understanding of the artefacts that arise when measurements are made on three-terminal electrochemical cells.

The principal advantage of three-terminal electrochemical cells is that they permit the use of potentiostats over a wide range of conditions. But a disadvantage is that they introduce some subtle artefacts in recorded data, whose origins are not always understood, and whose removal is problematical. To gain insight into these artefacts, we here develop a *lumped equivalent network* model of a typical three-terminal electrochemical cell.

Before beginning, it must be emphasized that we are concerned only with artefacts that arise inside three-terminal cells, and not at all with artefacts that arise inside associated instrumentation. Our purpose is pure: it is to find the absolute limitations that the cell design places upon any kind of dynamic measurement, even one made by a hypothetically "perfect" (artefact free) instrument.

Of course, the reader will be aware that a vast literature exists on the topic of artefacts arising from instrument design, stretching back to the invention of the potentiostat by Hickling [1]. This literature is, however, beside the point for present purposes, for we seek the equivalent network of a three-terminal cell *valid even when it is disconnected from any measuring instrument.* Instrumental artefacts belong, in fact, to a secondary layer of problems, quite distinct from the primary artefacts under consideration here.

To place the present work in its historical context, our goal is to correct a widespread misconception of long standing, to the effect that dynamic measurements can be carried out on three-terminal electrochemical cells without necessarily introducing artefacts. It turns out that you can't – the best that you can do is minimise them. And, as we shall show, the reason that artefacts are unavoidable is that stray capacitances cannot be decreased to values less than those caused by the dielectric constant of free space.

When we first approached this problem, we feared that the mathematical analysis would be too complex for ready comprehension, because we found that the lumped equivalent network of a three-terminal electrochemical cell had a three-fold axis of symmetry. But then, almost incredibly, we discovered that a two-terminal equivalent network could be derived that had the same impedance response at all frequencies as the original network. This was entirely unexpected, and was pleasing because it contained only series and parallel connections, and hence was very easy to

understand. The structure of this two-terminal equivalent network forms the central result of the present work.

Of course, it is well known that electrochemical cells are systems of spatially distributed impedance, so in the very strictest sense they should not be modelled as lumped equivalent networks at all. But one has to start somewhere, and one thing that can be said in favour of lumped equivalent networks is that they provide powerful insights into the mathematical couplings between individual cell components, and therefore can be used to improve cell design and minimize experimental artefacts. It is also true to say that lumped equivalent networks represent the *simplest possible* couplings between individual cell components, so if you can't solve the lumped equivalent network model, you can't solve the real thing either.

Given that lumped equivalent networks ignore spatially distributed impedances (and hence ignore non-uniform current distributions), we emphasize that the present work has the restricted goal of understanding how the couplings between individual cell components influence the introduction of artefacts. No claim is made that our lumped equivalent network model perfectly represents all possible three-terminal cell designs under all conceivable conditions.

Now, three-terminal electrochemical cells typically have three external nodes that are accessible to the instrumentation – the working electrode, the counter electrode, and the reference electrode. These are connected internally via the electrolyte solution, and externally via the instrumentation. Between them are stray capacitances that consist, largely, of the input capacitances of the measuring instruments, plus the geometrical capacitances arising from the relative placements of the cell components in space. This creates six current paths that complicate the acquisition of experimental data, and these are shown diagrammatically in **Figure 1**.
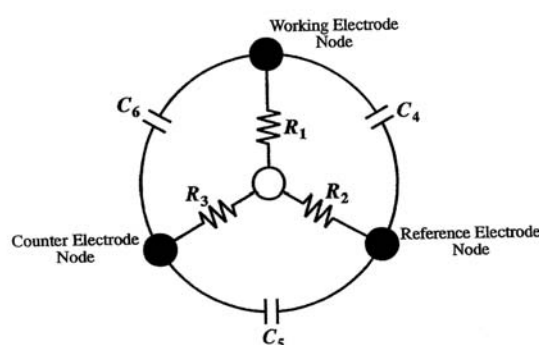


**Fig. 1.** *The three-terminal equivalent network of a three-terminal electrochemical cell. Note the three-fold axis of symmetry, which greatly complicates the network analysis.*

Closed circles indicate the three accessible nodes. The single, central, open circle represents an inaccessible node, which is actually a point in solution just beyond the tip of the Luggin capillary (though henceforth, for brevity, we shall refer to it simply as "the tip of the Luggin capillary"). The other symbols have their conventional significations. $R_1$ is the sum of the resistances between the working electrode node and the tip of the Luggin capillary, $R_2$ is the sum of the resistances in the reference half-cell (including the interior of the Luggin probe itself), and $R_3$ is the sum of all

3

the resistances between the tip of the Luggin capillary and the counter electrode node. The capacitances $C_4$, $C_5$, and $C_6$ are the unavoidable stray capacitances in the system.

To make the mathematical analysis tractable, it is necessary to assume that the interfacial impedances of the working, reference, and counter electrodes are pure resistances. This allows them to be included in $R_1$, $R_2$, and $R_3$, respectively. It turns out that if any of the interfacial impedances is complex, then severe mathematical difficulties arise. Though frustrating, this is not prohibiting for present purposes, because we are more interested in the couplings between electrodes than in their impedances *per se*.

In a typical experiment on a three-terminal electrochemical cell, a time-varying voltage $V_{\text{applied}}$ is applied between the working electrode and the reference electrode, and the resulting current $I_{\text{observed}}$ is observed flowing between the working electrode and the counter electrode. Since what is sought is a measure of the resistance $R_1$, the usual method of proceeding is to form the quotient

$$\frac{V_{\text{applied}}}{I_{\text{observed}}} \quad = \quad R_{\text{observed}} \qquad\qquad ...(1)$$

and then to assume that $R_{\text{observed}} \approx R_1$. But how good is this assumption? We ought to know, because virtually all electrochemists make this assumption tacitly while plotting voltammograms, fast transients, and impedance plane plots, without ever really questioning the validity of the procedure. Yet the procedure must always be at least slightly in error because $I_{\text{observed}}$ and $V_{\text{applied}}$ are measured across different parts of the electrochemical cell. Indeed, on some occasions the procedure must fail completely, such as when $R_2$ and $R_3$ are much larger than $R_1$, and the current is rapidly varying. In the next section we explore this possibility by deriving the two-terminal equivalent network that yields exactly the same impedance as the three-terminal network given in Figure 1, and then investigate how the values of the two-terminal network elements affect the overall response.

Anticipating our central result, we shall find that the main consequence of measuring the current and voltage across different nodes of a three-terminal electrochemical cell is to cause both capacitive and inductive artefacts to appear in experimental data at all frequencies above zero hertz. The inductive artefact would probably be the most easy to recognise, since it would appear as a "loop" in the fourth quadrant of the complex plane of impedance (electrochemical convention). The capacitive artefacts might perhaps be less easy to recognise, since they would principally appear in the first quadrant, and thus might be difficult to distinguish from real data. However, both artefacts would severely affect voltammograms at high scan rates, most obviously by distorting their hysteresis.

## 2. Results

The conventional method of calculating the impedance of complex networks is to treat them as combinations of series and parallel sub-networks. Unfortunately it is not possible to do that for the network shown in Figure 1 because of the three-fold axis of symmetry, and more powerful mathematical methods must be sought. *Kirchhoff's Rules* – which state that the algebraic sum of the currents at any node of a network is zero, and that the algebraic sum of the potential differences around any loop of a network is zero – immediately spring to mind, but in the present case they yield six equations in six unknowns. Although these could actually be solved by the method of determinants, the solution would still require the evaluation of seven sixth-order determinants, which would be an immensely tedious process to carry out. Therefore to speed up the analysis we used *Maxwell's Method*, which required the calculation of only four loop currents. Since it applied both of Kirchhoff's Rules at the same time, this decreased the number of simultaneous equations to four, and thus accelerated the solution.
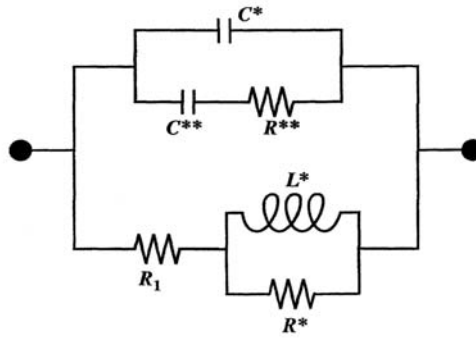


**Fig. 2.** *The two-terminal equivalent network of a three-terminal electrochemical cell. Note the series/parallel arrangement of elements, which greatly simplifies the network analysis. Asterisks (\*) indicate experimental artefacts.*

Omitting details, the result is shown in **Figure 2**. This shows the two-terminal equivalent network that has the same impedance at all frequencies as the three-terminal network shown in Figure 1. Asterisks indicate measurement artefacts. The illustrated network is the canonical one, which is to say, the one that contains the minimum number of circuit elements. Note in particular that the resistance $R_1$ is in series with a shunted inductor, and both are in parallel with a pair of capacitors. These features correspond closely with those commonly seen in *ac* impedance measurements on three-terminal electrochemical cells, particularly those having high electrical resistances due to poorly-conducting electrolyte solutions.

The elements in the two-terminal equivalent network are related to the elements in the three-terminal network by the following transformation formulae:

$$L* \quad = \quad R_2 R_3 C_5 \qquad\qquad\qquad ...(2)$$

$$R* \quad = \quad \frac{R_2 R_3}{R_2 \; + \; R_3} \qquad\qquad\qquad ...(3)$$

$$R** = \left[R_1 R_2 + R_1 R_3 + R_2 R_3\right] \frac{C_5}{R_1 C**} \qquad \text{...(4)}$$

$$C** = \frac{R_2 C_4}{R_1} + \frac{R_3 C_6}{R_1} - \frac{C_4 C_6}{C_5} \qquad \text{...(5)}$$

$$C* = C_4 + C_6 + \frac{C_4 C_6}{C_5} \qquad \text{...(6)}$$

From these equations, the reader may readily write down the full impedance of the two-terminal network by inspection. This is of course identical to the impedance of the three-terminal network. It is particularly striking that the inductance $L*$ appears in the two-terminal network, even though no inductor exists in the three-terminal network. This is interesting philosophically, since it is a rare example of an *epiphenomenon* in the physical sciences. Such an effect is made possible by the multi-node nature of the three-terminal network.

## 3. Discussion

The above analysis indicates that inductive and capacitive artefacts necessarily contaminate all data from three-terminal electrochemical cells, at all frequencies above zero hertz. For cases where the interfacial impedances are simple resistors, the artefacts are described exactly by Equations (2)-(6). For cases where the interfacial impedances are more complex, the artefacts are even more complicated and their analysis remains an unsolved problem. However, we note that the values of $L*$ and $R*$ are independent of $R_1$, so the inductive part of the equivalent circuit remains unchanged even if $R_1$ is replaced by a complex impedance $Z_1$.

From Equations (2)-(6) it is apparent that the inductive artefact can be diminished, but not entirely removed, by decreasing $R_2$ and $R_3$. Metal reference electrodes, large counter electrodes, well-conducting solutions, wide-bore Luggin capillaries, and cells without separators, will all help.

The capacitive artefacts are more problematic, since they depend on the absolute sizes of $C_4$, $C_5$, and $C_6$, and these cannot generally be decreased below about 10pF due to the finite dielectric constant of air. More generally, their values are probably about 1nF. Moreover, the total parallel capacitance is

$$C_{\text{total}}^* = C^* + C^{**}$$

$$= \left(\frac{R_1 + R_2}{R_1}\right) C_4 + \left(\frac{R_1 + R_3}{R_1}\right) C_6 \qquad \text{...(7)}$$

which is much greater than $C_4 + C_6$ if the factors $(R_1 + R_2)/R_1$ and $(R_1 + R_3)/R_1$ are large. In these cases the sizes of the capacitive artefacts could be significantly

diminished by decreasing $R_2$ and $R_3$. On the other hand, if $R_1$ is larger than $R_2$ and $R_3$, then the factors $(R_1 + R_2)/R_1$ and $(R_1 + R_3)/R_1$ would be approximately unity and there would be little to be gained as regards the capacitive artefacts by decreasing $R_2$ and $R_3$. In those cases it would be better to concentrate on decreasing $C_4$ and $C_6$.

Before starting experiments, it would be helpful to have some clear guidelines as to how the inductive and capacitive artefacts might be avoided. These can now be suggested, based on tracing the possible current paths through the two-terminal equivalent network shown in Figure 2. For example, in order to avoid the inductive artefact, it suffices for just one of the following three criteria to be met:

$$R_2 \ll R_1 \qquad \qquad ...(8)$$

$$R_3 \ll R_1 \qquad \qquad ...(9)$$

or

$$\omega R_2 R_3 C_5 \ll R_1 \qquad \qquad ...(10)$$

where $\omega$ is the frequency of the perturbation. Using the same approach it is possible to derive sufficient criteria for avoiding *both artefacts at the same time*. These turn out to be

$$\omega R_2 R_3 C_5 \ll R_1 \ll \frac{1}{\omega C_4\left(1 + \dfrac{R_2}{R_1}\right) + \omega C_6\left(1 + \dfrac{R_3}{R_1}\right)} \qquad \qquad ...(11)$$

This important result can be summed up in one phrase: *to avoid the inductive and capacitive artefacts, make everything small except $R_1$.* (By everything we mean the values of $\omega, R_2, R_3, C_4, C_5$, and $C_6$.) The value of $R_1$, which should henceforth be treated as an experimental variable, and which can be varied by changing the electrode diameter, should be adjusted until it is roughly midway between the inequalities in Equation (11). A satisfying feature of Equation (11) is that the range of values available to $R_1$ increases as $\omega$ decreases, which is what we would have predicted.

Another satisfying feature of Equation (11) is that the minimization of the values of $\omega, R_2, R_3, C_4, C_5$, and $C_6$ is the same recommendation as that usually given to avoid the occurrence of artefacts in instrumentation such as potentiostats. So no compromises are needed in fulfilling these requirements.

Previous work on the theory of artefacts in three-terminal measurements is scant, but we make special mention of the earlier work of Göhr et al. [2], whose theoretical results (in effect) describe certain fractions of the network shown in Figure 1. We also note that the transformation formulae given in ref [3] could be used to derive yet more

forms of the two-terminal equivalent network shown in Figure 2, though none would be so elegant. Moreover, a conductive shunt could be used to decrease the size of the resistance $R_2$, as pointed out in ref [4]. Overall, we emphasize that all the artefacts discussed in the present work arise in the cell and none in the potentiostat, and hence would still appear even if the potentiostat were perfect. In fact, it bears repeating that the potentiostatic principle is strictly valid only at zero frequency (steady current), and that at all other frequencies the three-terminal cell response *necessarily* includes inductive and capacitive artefacts. The onus is therefore on the experimenter to ensure that these artefacts are negligibly small. Equation (11) indicates how this can be achieved.

We also point out the rather obvious fact that the inductive artefact can be removed entirely by (effectively) shorting the reference and counter electrodes, i.e. by reverting to a two-electrode configuration, and using a counter electrode much larger than the working electrode to make sure that the counter electrode's potential remained constant. Although two-electrode cells are undesirable in many instances, it would nevertheless be a useful check that any purported inductive effects were real.

Finally, we remark that Figure 1 is the full equivalent network of a three-terminal electrochemical cell, and can therefore readily be adapted for the study of unknown systems by replacing $R_1$ by $Z_1$, the sought-after impedance of the working electrode. Indeed, for those researchers involved in impedance modelling, we advise that, in future, the textbook "equivalent circuits" of electrochemical systems be embedded in the full equivalent network in Figure 1, to test that cell artefacts are absent, or if they are present, to obtain the most accurate modelling of $Z_1$.

In summary, the moral of the present work is that great dangers lurk in the naive interpretation of time-varying data obtained from three-terminal electrochemical cells, unless special care is taken to minimize the internal resistance of the reference and counter electrode compartments. In fact, the present work suggests that a very large fraction of the literature on the ac impedance of corroding systems in pure water and dilute solutions must certainly be incorrect. Also, many of the inductive loops in the complex plane of impedance, reported widely in the literature, are probably not due to interesting electrochemistry, but are simply artefacts caused by excessive values of $R_2$ and $R_3$. These now need to be re-examined on a case-by-case basis.

## Acknowledgements

## References

[1]  A. Hickling, *Trans. Faraday Soc.*, **38** (1942) 27.

[2]  H. Göhr, M. Mirnik, and C. A. Schiller, *J Electroanal Chem*. **180** (1984) 273.

[3] S. Fletcher, *J Electrochem Soc*, **141** (1994) 1823.

[4] S. Fletcher and M.D. Horne, *J Electroanal Chem*, **297** (1991) 297.
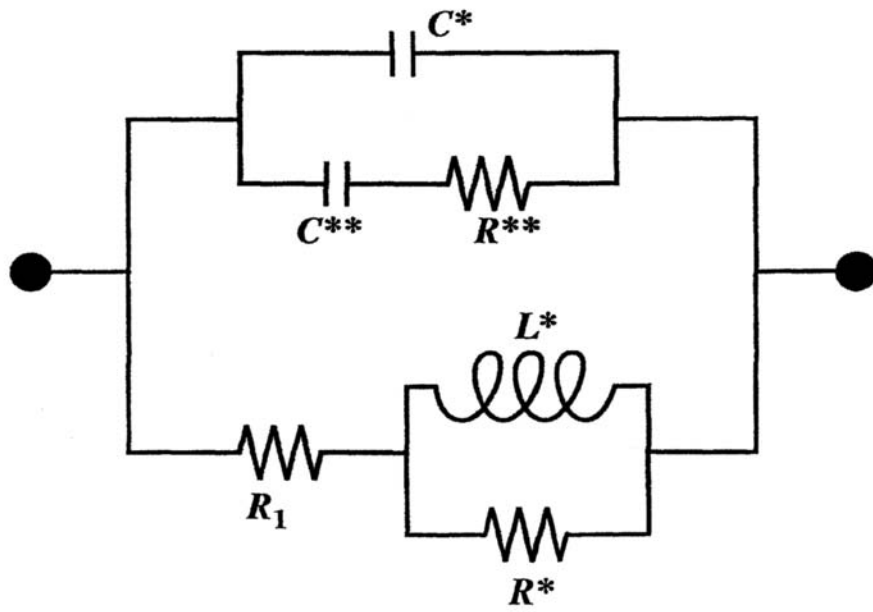
**Figure Captions**

Fig. 1.  The three-terminal equivalent network of a three-terminal electrochemical cell.  Note the three-fold axis of symmetry, which greatly complicates the network analysis.

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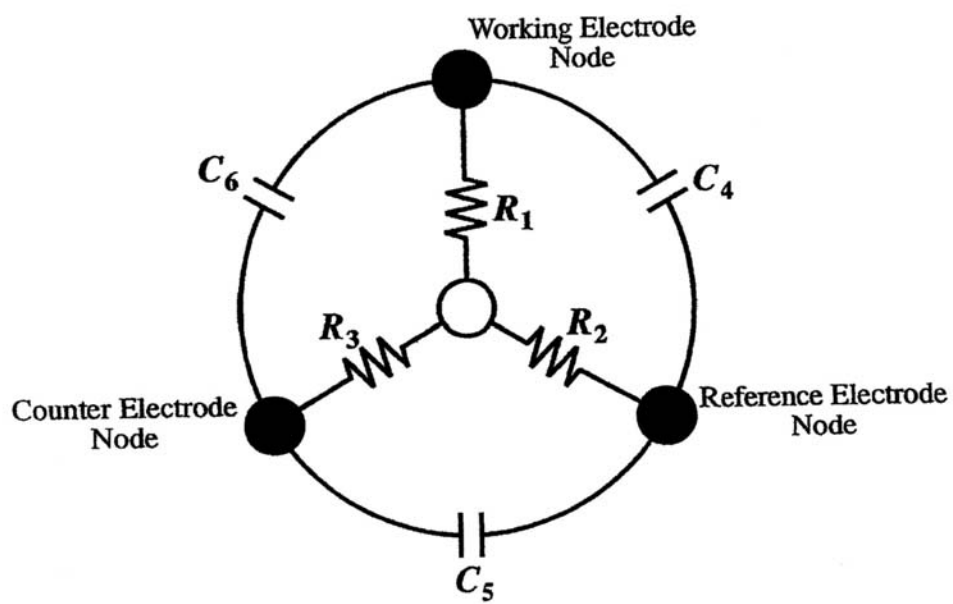
**Figure 1**

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**Figure 2**

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