reactions are competitive, depending on the partial pressure of oxygen in the system

\[
\text{Si}(s) + O_2(g) = \text{SiO}_2(s)
\]

\[
\text{Si}(s) + \frac{1}{2} O_2(g) = \text{SiO}(g)
\]

The oxidation of silicon to silica is the only reaction occurring at high oxygen pressures, but it is insignificant at low pressures below 10⁻² atm at 1400°C or 10⁻⁵ atm at 1200°C, as shown in Fig. 1.14 Gaseous SiO₂ is a dominant product of the oxidation at low oxygen pressures. Although oxygen is a stronger oxidant than chlorine, under reduced oxygen atmospheres, the two are comparable. Thus the formation of Si-O-Cl phases could be considered from the direct oxychlorination of Si and the gas phase interactions

\[
\begin{align*}
\text{Si}(s) + O_2(g) + 2\text{HCl}(g) &= \text{SiOCl}_2(g) + \text{H}_2\text{O}(g) \\
\text{SiO}(g) + O(g) + \text{SiCl}_4(g) &= 2\text{SiOCl}_2(g) \\
\text{SiOCl}_2(g) + \text{SiCl}_4(g) &= \text{Si}_2\text{OCl}_6(g) \\
\text{Si}(s) + O_2(g) + \text{Si}_2\text{OCl}_6(g) &= \text{Si}_4\text{O}_2\text{Cl}_6(s)
\end{align*}
\]

The oxygen-rich chlorosiloxane phase, not necessarily have occurred in the Si-SiO₂ interface due to the pressure gradient, as suggested by Monkowski et al., and to trapping of gaseous chlorine molecules.

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**Table I. The Si-O-Cl ion species present in the CVD process**

<table>
<thead>
<tr>
<th>Observed ion species*</th>
<th>Probable neutral precursor**</th>
</tr>
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<tbody>
<tr>
<td>SiOCl₂</td>
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<td>SiOCl</td>
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<tr>
<td>SiOCl₂Cl</td>
<td>SiOCl₂Cl</td>
</tr>
</tbody>
</table>

*Observed only above 800°C. They probably come from the interaction between SiCl₄ and H₂O.

**The majority of ions seems to derive from a neutral precursor SiO₂Cl₄-SiO₂Cl₆, where n = 2-11, except those with = symbol.

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A Method for Estimating Impedance Parameters for Electrochemical Systems That Exhibit Pseudoinductance

Digby D. Macdonald (pp. 2062-2064, Vol. 125, No. 12)

J. Ross Macdonald and D. R. Franceschetti: In his paper, Macdonald proposed a simple electrical equivalent circuit, including an inductive element, for systems with pseudoinductance behavior and presents an approximate method for deriving estimates of circuit element values from experimental data. In earlier work we have shown that many different, but electrically equivalent, circuits may be employed to represent situations where electrode or interfacial adsorption effects lead to a pseudoinductance, or equivalently a pseudocapacitance which may be either positive or negative. Macdonald’s equivalent circuit is the same as that of our Fig. 4c, except that he does not include bulk (or solution) resistive and capacitative elements in his circuit. In analyzing experimental data he has substracted out the nonnegligible bulk resistance of the system without explicitly mentioning doing so. We have previously presented and discussed in detail an equivalent circuit for homogeneous materials which includes bulk, reaction, and adsorption effects and provides a superior representation of small-signal a-c response for a wide range of systems (see especially Fig. 4b of Fini).

Macdonald illustrates his approach with an analysis of the data of Armstrong and Henderson on transpassive chromium in 0.5M H₂SO₄, actually subject to a steady bias of 1390 mV. The numbers which label each point in Fig. 3 of his paper are, in fact, radial frequencies (1/sec) rather than Hz, as stated in the caption. Macdonald demonstrates that his simplified approach to data analysis works quite well in this case. Since the actual numerical data for this particular case no longer exist, we assume that Macdonald obtained his representation of the Armstrong-Henderson data by scaling from their Fig. 4c, although this is not stated in his work.

While noting that the charge transfer resistance for a pseudoinductance system might be obtained through the use of the (complex) nonlinear least squares fitting procedure of (J.R.) Macdonald and Garber, Macdonald characterizes this method as cumbersome and not well suited to routine application in corrosion research. As far as we know, he has made this judgment without ever actually using the method. After many hundreds of fits to many varieties of impedance/admittance-frequency data, we are convinced that the method is easy to apply, is suitable for routine use, and will always yield better parameter estimates than can be obtained from the few data points employed in Macdonald’s approximate approach. In most cases, using his estimates (or the appropriate transforms of them) as input values will result in rapid convergence of the least squares fit. Unlike estimates obtained from Macdonald’s method, the parameters estimated by the least squares procedure will reflect all the data, with estimated standard deviations of the parameters and of the over-all fit being determined as well, allowing meaningful comparison to be made of fits and parameter estimates for different equivalent circuits.

We requested that Macdonald send us his scaled data so that we could carry out a complex least squares fit of it to compare with his results. Unfortunately, it had not arrived by the deadline for the present note.

D. D. Macdonald: In the discussion given above, Macdonald and Franceschetti have raised a number of points that deserve clarification.

First, the series resistance can be compensated for electronically using positive feedback techniques, so that, in principle, inclusion of the series resistance in the equivalent circuit is not necessary. Of greater significance, however, is the fact that the series resistance has no effect on the analysis as formulated, since its value is determined as the infinite frequency intercept on the real axis. Accordingly, inclusion of a series resistance in the equivalent circuit would merely shift the origin of the complex plane along the real axis.

Second, the discussors stress the fact that their nonlinear least squares method for estimating the impedance parameters uses all of the experimental impedance vs. frequency data, and not just four characteristic points as employed by the approximate method

18 R. D. Armstrong, Private communication.
20 Materials Research Center, SRI International, Menlo Park, California 94025.
outlined by the author. They rightly point out that the impedance parameters calculated from the least squares fit will be more accurate than those obtained using the approximate method. The author does not dispute this claim. Indeed, it is stated in the paper that the approximate method could be used for estimating the input parameters for the more sophisticated non-linear least squares technique. However, the author did claim, and he reiterates that claim here, that for the majority of cases that are likely to be encountered in corrosion research, the approximate method yields data that are sufficiently precise for most purposes, provided that the first and fourth quadrant subspectra are essentially independent of one another in the neighborhood of the maxima in the reactance. Of course, this conclusion may not apply to those systems that indicate a more complicated equivalent circuit; this point can be settled only by further analysis.