11 Effects Due to Uncompensated Resistance and Capacitance

Electrochemists are aware of the annoying residual uncompensated solution resistance $R_u$ between the Luggin probe and the working electrode, see for example [74]. Although it is possible in principle to compensate fully for the $iR$ error thus introduced [131,132], this is rarely done, as it introduces, in practice, undesirable instrumental oscillations or, in the case of damped feedback [132], sluggish potentiostat response.

The other often annoying fact electrochemists must live with is the double layer capacitance $C_{dl}$. This produces capacitive currents whenever the applied potential changes (see again [74]). The two effects work together, as capacitive currents also give rise to further $iR$ errors.

With potential step methods, the capacitive current is a transient, decaying with a time constant equal to $R_uC_{dl}$. The usual procedure is to wait several of these time constants before making the current measurement, by which time the capacitive current has declined to a negligible value. It is therefore not a serious problem with potential step experiments.

Where both capacitive current and $iR$ do interfere is with a.c. voltammetry (not gone into here) and LSV experiments. An early classic study is that of Nicholson [415], who investigated the effects of $iR$ alone, pointing out that a simple correction, from measured currents and known $R_u$, for the potentials, does not work. The LSV curve becomes distorted and such a correction does not retrieve the shape of the curve as it would otherwise be in the absence of an $iR$ effect. The reason is that the varying current during the sweep changes the electrode potential by a varying amount $iR_u$, and thus the potential program, that was intended to be linear with time, is no longer so. Bowyer et al. [128] and Strutwolf [529] show examples of such distorted potential-time relations and also distorted LSV curves, see also below.

The simulation literature deals with this problem sporadically, although it is often simply ignored. The $iR$ effect introduces nonlinear boundary conditions (see below), and these have been dealt with in various ways. Gosser [274] advocates simple subtraction, using known measured currents of the experiment one is simulating in order to fit some parameter. Deng et al. [206] use a stepwise procedure that successively solves for each of the several unknowns without iteration. Iteration using binary searches have been used [162,270,529], as well as a Gauss-Seidel method [574]. Safford et al. [489]
rejected binary searching as too slow and Newton-Raphson iteration as unreliable, and used the van Wijngaarden-Dekker-Brent root-finding method, as described in Press et al. [452]. This is as reliable as a binary search (bisection) but faster, using a parabolic fit at each step. Despite the misgivings of some investigators, the best method is probably Newton-Raphson iteration, as used by Rudolph [477].

Simulations must thus handle the nonlinear boundary conditions. Some have taken the easy way out and used explicit methods [123, 429]. Bieniasz [105] used the Rosenbrock method (see Chap. 9), which makes sense because it effectively deals with nonlinearities without iterations at a given time step.

The classic work in this connection is that by Imbeaux and Savéant [313], who took the integral equation approach (see Chap. 9), incorporating the \(iR\) effects. They also established the formulation of the problem and the way to normalise both the uncompensated resistance \(R_u\) and double layer capacitance \(C_{dl}\), adopted by most workers since then. Their normalisation of \(R_u\) followed that of Nicholson [415].

In the next discussion, only the LSV problem will be considered, since it is here that the major problems lie. The capacitive current component is, at any given time, given by

\[
i_c = -C_{dl} \frac{dE}{dt} \tag{11.1}
\]

where the negative sign is intended to produce a (positive) cathodic current from a cathodic-going sweep. This current will give rise to an \(iR\) error in the applied potential, equal to \(+i_c R_u\) (that is, the applied potential will be a little more positive than intended). The Faradaic current will contribute a similar \(iR\) error.

First we must normalise some quantities, to make them compatible with the other dimensionless parameters already used. We refer to the normalisation formulae on p.26. Recall that we have normalised voltage by the factor \(\frac{nF}{RT}\) and that the time unit \(\tau\) for LSV is equal to \(\frac{RT}{nFv}\) (\(v\) being the sweep rate), or the time the sweep takes to traverse one normalised potential unit \(p\).

Resistance has units of volts per amperes, and thus must be converted to \(p\) units per \(G\) units. Using the normalisations in Chap. 2, this comes to

\[
\rho = R_u \frac{nF}{RT} nFD^\frac{1}{2} c^* \sqrt{\frac{nFv}{RT}}. \tag{11.2}
\]

This is as presented in [313], and is not normally simplified further. For capacity, which has units of current \(\times\) time per volts, these become \(GT\) units per \(p\) units here and conversion leads to

\[
\gamma_c = C_{dl} \frac{1}{nFD^\frac{1}{2} c^*} \sqrt{\frac{RTv}{nF}}, \tag{11.3}
\]

also normally written in this unsimplified form.