Electrolysis power calculation

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1 Introduction

There have recently been some claims, notably by Barry Kort in the Comments section of the Wikipedia item on cold fusion [1] that excess heat apparently observed during electrolysis of heavy water is an artifact of the calculation of the power dissipated in the cell, because the cell resistance, and therefore cell voltage, fluctuate, due to the formation of bubbles partly covering the electrodes for some time. These claims are informal, in such vehicles as Wikipedia and google groups as well as private emails.

We have, some years ago, investigated the effect on power calculation of cell current and voltage fluctuations in galvanostat configurations that were close to instability [2], as in fact used in published work [3, 4] and concluded that there was no significant effect, even if there were current fluctuations, as long as these are uncorrelated with the cell voltage fluctuations - as they were found to be. However, the recent claims invoke a factor not taken into account in the earlier work, that is, the finite reaction time of the current control circuit, or its finite slewing rate. It is true that this means that whenever the cell resistance changes, there is a current transient away from its controlled value, and it takes a finite time for this to relax back to the nominal value. This might in principle lead to a computed mean power different from that obtained from the mean cell voltage multiplied by the (assumed) constant current, or even multiplied by a fluctuating current's mean. This will be examined in this report.

1.1 Note

The proposed mechanism is in fact unlikely; bubbles will not normally significantly change the electrolyte resistance, except in cells in which the electrodes are close together. Bubbles will normally mainly change the free area of the electrodes, and thus, at controlled constant current, the current densities at the cathode and anode. Current density (cd) and electrode potential are related (at the high current densities applied to cold fusion cells) by the Tafel relation, and a change in cd means a change in electrode potential and thereby total cell voltage. The change needs some time, because the electrodes' electric double layer must be charged to the new potential and this takes time. This case will be briefly trated in the last part of this report but, for the moment, a type of cell is assumed, in which total electrolyte resistance is changed by bubbles.

2 Simple model

Fig.1 shows a model of a fluctuating cell resistance, which is R_a on average, jumps to $R_a + \delta R$ at time zero, back to R_a at t_1, etc. All three time intervals are assumed equal. The two changes cancel each other, so the average resistance is R_a. The current is controlled to be I_a and the average cell voltage is E_a. We identify the four time regions $1 \ldots 4$, which must be treated separately and consecutively.

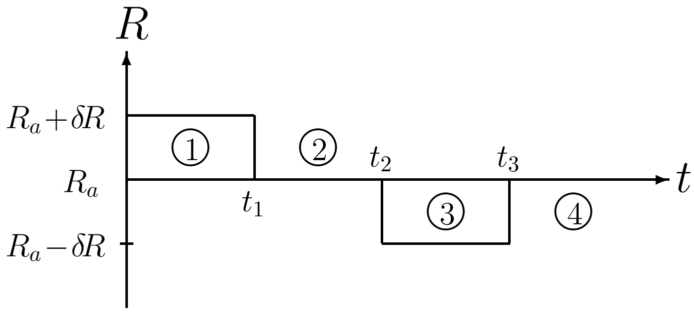

Figure 1: Cell resistance model

We assume a constant current generator, which however responds with a certain time constant τ to a step change in load resistance.

What we want is the power $P(t)$ at any time t, especially how it deviates from what should be the mean, $I_a E_a = I_a^2 R_a$.

A given step change in resistance will result initially in an opposite current transient, assuming that the current generator's output voltage E at the instant of the step change does not change but takes time to change to the required new value. The step change in current, δI will then decay by an exponential function with time constant τ so that the current will tend to revert to I_a. Depending on the value of τ, the decay might be complete well within the duration of the change (e.g. $0 \ldots t_1$), or it may not have relaxed to I_a within that time. This is the general case. The mathematics of this is that for a given cell voltage E and cell conductance $A = R^{-1}$, and differentiating Ohm's law

$$I = E\,A\,, \tag{1}$$

with respect to time, we get a change in current

$$\frac{\mathrm{d}I}{\mathrm{d}t} = E\frac{\mathrm{d}A}{\mathrm{d}t} \tag{2}$$

or

$$\delta I = E\delta A \tag{3}$$

which we discretise below in a two-point approximation.

Initial condition

At $t < 0$, we have the following:

- $I = I_a$
- $R = R_a$
- $E = I_a R_a$.

At $t = 0$ there is step change $+\delta R$ in resistance, and we have then

- $R = R_a + \delta R$
- $E = I_a R_a$.

Interval 1

At $t = 0$ the current changes by δI_0 from E/R_a to $E/(R_a + \delta R)$,

$$\delta I_0 = E\Big(\frac{1}{R_a + \delta R} - \frac{1}{R_a}\Big) \tag{4}$$

that is, we start region 1 with $I_a + \delta I_0$, which then approaches the nominal current I_a exponentially as

$$I = I_a + \delta I_0 \exp(-t/\tau) \tag{5}$$

so that at $t = t_1$ we have current I_1,

$$I_1 = I_a + \delta I_0 \exp(-t_1/\tau) \tag{6}$$

(which may or may not be practically equal to I_a) and cell voltage

$$E_1 = I_1 \, (R_a + \delta R) \; . \tag{7}$$

The power varies during this interval as

$$P(t) = I^2 (R_a + \delta R) = \Big(I_a + \delta I_0 \exp(-t/\tau)\Big)^2 (R_a + \delta R) \tag{8}$$

Interval 2

At t_1 the resistance jumps back to R_a, resulting in another current transient

$$\delta I_1 = E_1\Big(\frac{1}{R_a} - \frac{1}{R_a + \delta R}\Big) \tag{9}$$

and so during interval 2 the current is

$$I = I_1 + \delta I_1 \exp(-(t - t_1)/\tau) \tag{10}$$

and at $t = t_2$

$$I_2 = I_1 + \delta I_1 \exp(-(t_2 - t_1)/\tau) \; , \tag{11}$$

cell voltage

$$E_2 = I_2 \, R_a \tag{12}$$

and power during the interval

$$P(t) = I^2 R_a = \Big(I_1 + \delta I_1 \exp(-(t - t_1)/\tau)\Big)^2 R_a \; . \tag{13}$$

Interval 3

The resistance now jumps to $R - \delta R$ and we again have a (positive) current transient. The quantities are

$$\delta I_2 = E_2\Big(\frac{1}{R_a - \delta R} - \frac{1}{R_a}\Big) \; , \tag{14}$$

$$I = I_2 + \delta I_2 \exp(-(t - t_2)/\tau) \; : \tag{15}$$

at $t = t_3$ we have current I_3,

$$I_3 = I_2 + \delta I_2 \, \exp(-(t - t_2)/\tau) \; , \tag{16}$$

cell voltage

$$E_3 = I_3 \, (R_a - \delta R) \tag{17}$$

and

$$P(t) = I^2 (R_a - \delta R) = \Big(I_2 + \delta I_2 \, \exp(-(t - t2)/\tau) \Big)^2 (R_a - \delta R) \; . \tag{18}$$

Interval 4

Now the resistance goes back to R_a and we have

$$\delta I_3 = E_3 \Big(\frac{1}{R_a} - \frac{1}{R_a - \delta R} \Big) \; , \tag{19}$$

$$I = I_3 + \delta I_3 \, \exp(-(t - t_3)/\tau) \; , \tag{20}$$

$$E = I \, R_a \tag{21}$$

and

$$P(t) = I^2 R_a = \Big(I_3 + \delta I_3 \, \exp(-(t - t3)/\tau) \Big)^2 R_a \; . \tag{22}$$

We do not specify an end to this time region and can carry the power calculation to any $t > t_3$ value we choose.

Power calculation

We want the mean power at a time in region 4 at some t for which both current and voltage have relaxed to their steady values I_a and E_a. This will be at some multiples of τ after t_3. At such time t, this is given by

$$< P(t) > = \frac{1}{t} \int_{x=0}^{t} P(x) \, \mathrm{d}x \; . \tag{23}$$

The functions $P(t)$ are as described above. The expressions can be integrated analytically but since we want to plot the current functions anyway, it was chosen here to use the sequence of current points generated and integrate the $I^2 R$ function numerically from that.

We normalise time by the pulse length, so that $t_1 = 1$, etc, and also the time constant τ, which will now be realtive to t_1. Three runs of the program were done and the results presented in the Tables.

Figs. 2, 3 and 4 show the various time functions. Clearly there are perturbations to all quantities, but these relax again to close to what is expected at the end of the resistance changes. Some very small errors in the mean power remain after the resistance changes, however, but only for rather unrealistically large τ.

Table 1: Responses to resistance steps for $\tau = 0.03$. Mean $R = 10\Omega$, nominal current 1A, mean cell voltage 10V, nominal power $P = 10$W which is also the nominal mean, $<P>$. Resistance jumps by $\pm 1\Omega$.

t	P	$<P>$	%error
1	11.000	10.977	9.77
2	10.000	10.500	5.00
3	9.000	10.008	0.08
3	9.626	10.002	0.02
4	10.000	10.000	0.00
5	10.000	10.000	0.00

Table 2: Responses to resistance steps for $\tau = 0.1$. Other parameters as in Table 1.

t	P	$<P>$	%error
1	11.000	10.849	8.49
2	10.000	10.503	5.03
3	9.000	10.054	0.54
3	8.824	10.034	0.34
4	10.000	10.003	0.03
5	10.000	10.002	0.02
6	10.000	10.002	0.02
7	10.000	10.002	0.02

Table 3: Responses to resistance steps for $\tau = 0.3$. Other parameters as in Table 1.

t	P	$<P>$	%error
1	10.929	10.480	4.80
2	10.071	10.511	5.11
3	9.072	10.190	1.90
3	8.373	10.160	1.60
4	9.939	10.011	0.11
5	9.998	10.006	0.06
6	10.000	10.005	0.05
7	10.000	10.004	0.04
8	10.000	10.004	0.04
9	10.000	10.003	0.03
10	10.000	10.003	0.03

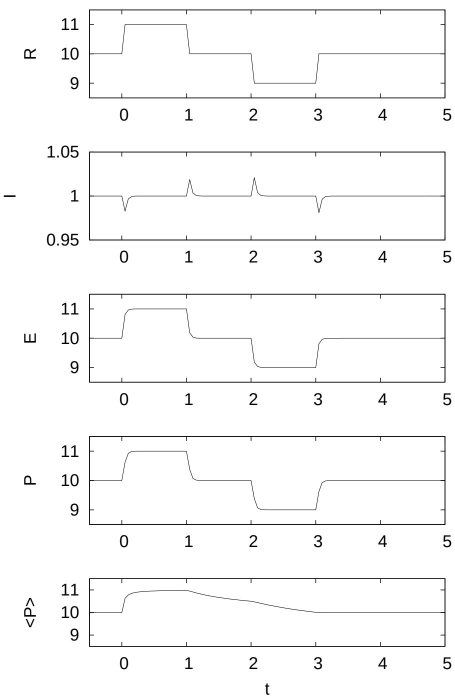

Figure 2: Time functions as marked for $\tau = 0.03$

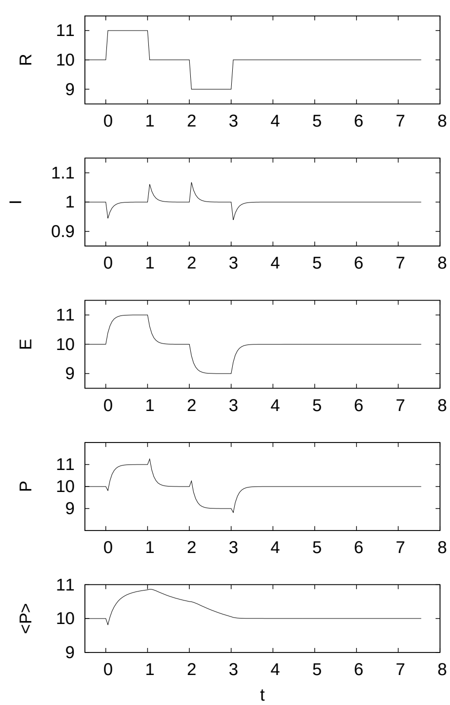

Figure 3: Time functions as marked for $\tau = 0.1$

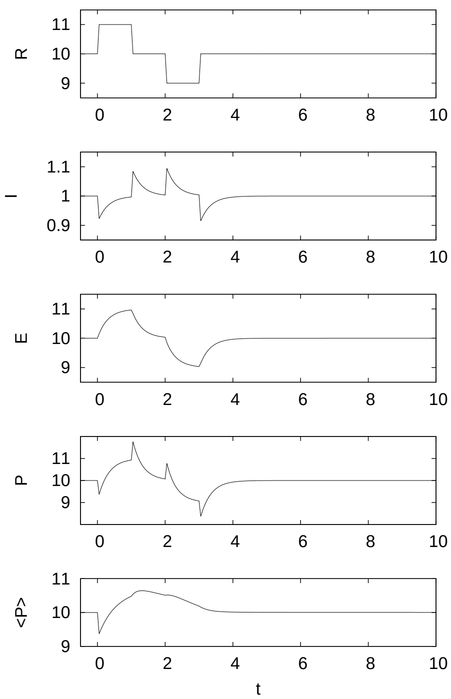

Figure 4: Time functions as marked for $\tau = 0.3$

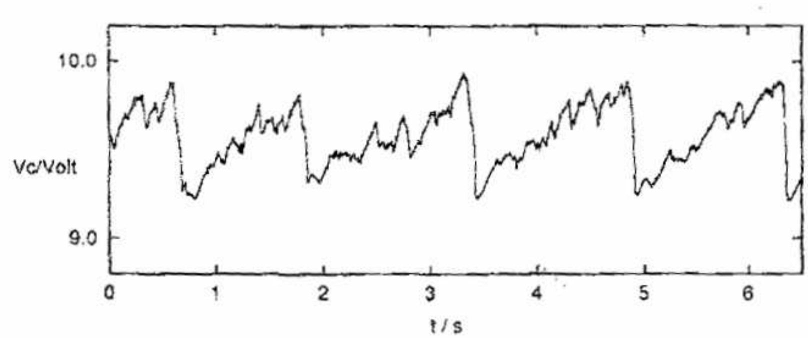

Figure 5: Real experimental cell voltage against time.

3 A realistic model

Although the above already seems to lay the charge of wrong power calculation to rest, it might be of some interest to look at a better model of cell resistance. In a previous paper [2], we recorded cell voltage against time at constant current over 6.5 s, and got the trace seen in Fig. 5. Sampling was at 10 kHz, and the paper shows a power spectrum of the signal, from which we note that it flattens out at about 3 kHz, so there are no significant components above that frequency.

Fig. 6 shows the circuit commonly used for constant current electrolysis; it is a potentiostat wired for constant current, operating such that the current going through the load R is kept at e_i/R_i. The operational amplifier normally has a roughly first-order response, a dc gain of

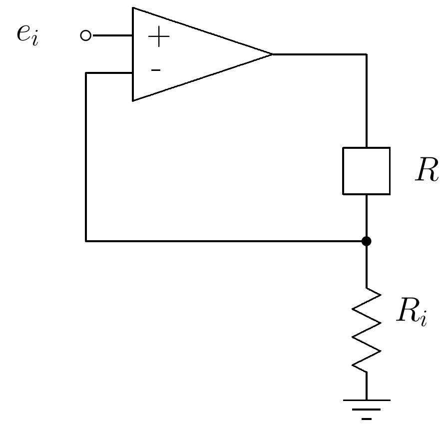

Figure 6: Potentiostat in galvanostatic mode.

somewhere in the region of 10^6 or more, and thus a bandwidth of 1 MHz or more. An analysis along the lines given in [5, pp.330-333] gives the result that, in the frequency domain,

$$I(\omega) = \frac{e_i}{R_i} \frac{1}{1 + j\omega\tau} \tag{24}$$

where

$$\tau = \frac{A}{K} \tau_a \ , \tag{25}$$

A being the transfer function, here simply equal to $R_i/(R + R_i)$, R_i being the current control resistor; K the op-amp's dc gain and τ_a its first-order time constant. This is typically about 0.1s, so τ comes out rather small, of the order of 10^{-4} give or take an order of magnitude. For this reason, and considering Fig. 2, it is unlikely that the slewing rate of the current supply leads to a false power calculation; that is, a value appreciably different from $I_a^2 < E >$, normally used to calculate the power.

Unfortunately the real data no longer exists, so an artificial model was constructed. If we again assume that the cell is such that bubbles cause fluctuations in cell resistance, then the cell resistance (at constant current) is proportional to the cell voltage, so R will vary as seen in Fig. 5. We note ramps, probably due to a slow build-up of bubbles, with a sharp decrease when a bubble detaches, on average with a duration of roughly 1.5 s, and superimposed on these, smaller ramps of shorter duration; and noise on top of these. The model used here is then, ramps of 1 ± 0.2 s period with shorter ramps of 0.2 ± 0.05 s period, all overlaid with gaussian noise and digitally low-pass filtered. Fig. 7 shows the result, the top plot showing resistance R. This consists of 10000 points representing a 10s duration, and larger bubble lives of about 1s. We now want to calculate the power P against time and its time average $< P >$, from the synthetic signal, for which, using (2), we need to compute the current I. This can be done by applying a discrete form of the first-order filter function (24). An FIR low-pass discrete filter that does this is

$$U_i = \alpha \, u_{i-1} + (1 - \alpha) S_i \tag{26}$$

where S is the sequence to be filtered, U is the new, filtered sequence and α the filter parameter. There is a known relation between α and our τ. Given the sequence of points with unit sampling interval, but that the large bubbles have an average duration of 1000 intervals, we can relate the time constant to both absolute time and sequence numbering, and get the following α values in Table 4.

Table 4: α values for some τ

τ/s	τ units	α
0.01	10	0.9
0.02	20	0.95
0.05	50	0.98
0.10	100	0.99

In what is to follow, we chose a time constant of 0.05s, which is rather large for the control circuit, so this is a pessimistic value.

What needs to be differentiated is not the resistance but its inverse A, as given from (2). Taking the running index as n, we have for the cell voltage

$$E_n = I_n/A_n \tag{27}$$

and I_n given from (2). Differentiation is done using the 3-point BDF expression [6], see also tables in Britz [7, p.281],

$$\frac{\mathrm{d}A_n}{\mathrm{d}t} \approx \frac{1}{2\delta t}\big(A_{n-2} - 4A_{n-1} + 3A_n\big) \tag{28}$$

and similarly for I,

$$\frac{\mathrm{d}I_n}{\mathrm{d}t} \approx \frac{1}{2\delta t}\big(I_{n-2} - 4I_{n-1} + 3I_n\big)\ . \tag{29}$$

This is a better formula than simple differences between neighbouring points. It requires knowledge of two prior points, but this can be handled by starting the computation at the 3rd point in the sequence. Likewise, the current is differentiated as a three-point formula.

In terms of our sequence, we have discretely, at step n, using (28) and (29) substituted in (2), for the next I_n,

$$I_n = \frac{1}{3}\big(E_n(A_{n-2} - 4A_{n-1} + 3A_n) + 4I_{n-1} - I_{n-2}\big)\ . \tag{30}$$

The new I_n is then low-pass filtered using the above digital filter (26). Each new I_n gives rise to a new E_n, and a new power P_n, from which the running mean $<P>_n$ is computed. Fig 7 shows the results. We note small changes in the current, and larger changes in cell voltage and power but also that the mean power approaches the nominal power, in this case 10W, as time progresses. The main errors in power arise at startup, and this is gradually corrected in time.

4 Sinusoidal resistance

A sinusoidally changing resistance was also tried, and was processed as the above ramp-like signal. The result is shown in Fig. 8, As for Fig. 7, the period of the sine wave was 1s and the amplitude 1V. The current response was lowpass filtered with time constant 0.02s, using $\alpha = 0.95$. It is seen that the running mean power initially deviates from the nominal value but recovers during the 10s stretch, approaching the expected value of 10W.

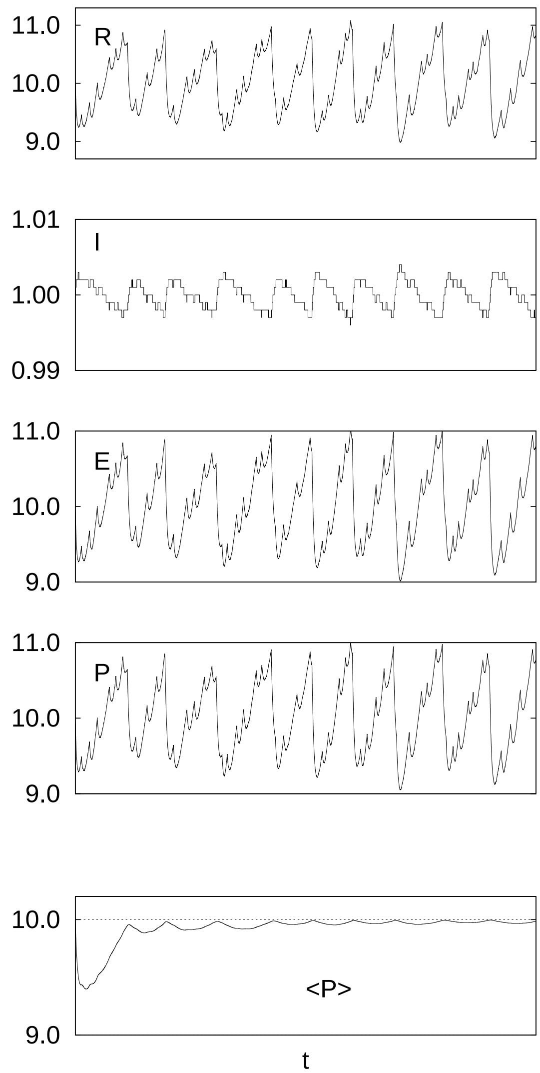

Figure 7: Power calculation using the data mimicing that in Fig. 5, filter constant $\tau = 0.95$, corresponding to a time constant of 0.02s

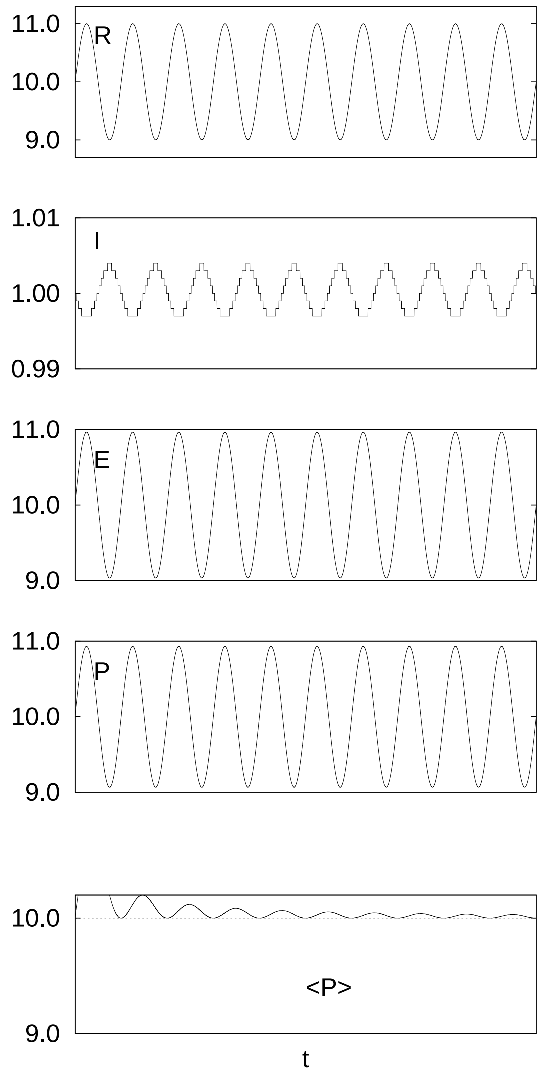

Figure 8: Power calculation using a sinusoidally changing resistance, filter constant $\tau = 0.95$, corresponding to a time constant of 0.02s

5 A more realistic model of the cell behaviour

As mentioned in the Introduction, the electrolyte resistance is not likely to change greatly by the appearance of bubbles, since these will have their greatest effect near the electrodes, and will affect the available electrode area more than electrolyte resistance, thus changing the current density at constant applied current. Fig. 9 shows the more realistic model of a cell in which a largish current flows. We have, as above, an electrolyte resistance R, a double layer capacitance C, and the faradaic element, bypassing the capacitance, can be regarded as roughly resistive, at least at lower frequencies, and is denoted as R_f. This R_f is inversely proportional to the current density J and that will vary with electrode area according to the Tafel equation

$$E = a + b \ln J \tag{31}$$

where a and b are Tafel constants. For small changes of the current density, there is a roughly linear relation for both J and R_f with respect to electrode potential and therefore total cell voltage, as for the simpler model used above.

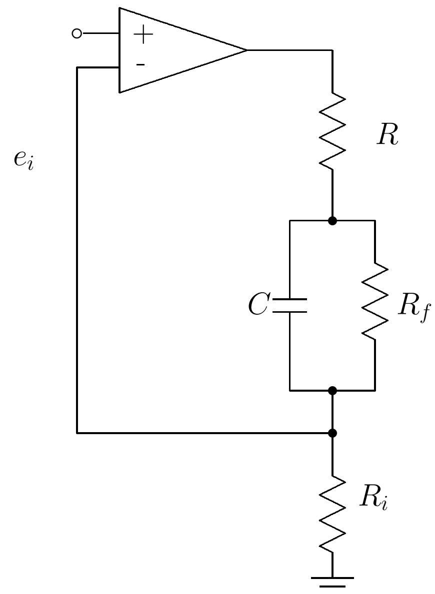

Figure 9: Galvanostat with more realistic cell model

Total current is, as before, controlled by resistor R_i. The transfer function is now a little more complicated. It is the ratio, at angular frequency ω, of the voltage at the top of R_i (and thus at the inverting op-amp input) to the output of the op-amp. The faradaic element has an impedance Z_c given by

$$Z_c = \left(j\omega C + 1/R_f\right)^{-1} \tag{32}$$

so that the total load Z on the op-amp, apart from R_i, is

$$Z = R + Z_c = R + \left(j\omega C + 1/R_f\right)^{-1} \tag{33}$$

and the transfer function A is

$$\begin{aligned} A(\omega) &= \frac{R_i}{R_i + R + Z_c} \\ &= \frac{R_i\big(1 + j\omega\tau_f\big)}{R_f + \big(R_i + R\big)(1 + j\omega\tau_f)} \end{aligned} \tag{34}$$

in which $\tau_f = R_f C$. This corresponds to a kind of high-pass filter function with time constant τ_f or angular break frequency τ_f^{-1}. It is easy to see that A has a lower limit at low frequencies of $R_i/(R + R_i + R_f)$ and an upper limit at high frequencies of $R_i/(R + R_i)$. The current will therefore now be filtered by a function equal to that given in (34) multiplied by the filter term given in (24). I have not tried to devise a digital filter for this compound filter function. However, given that we already know that (24) has no significant effect and that τ_f normally will be rather small, we cannot expect this model to predict false power calculations either. For example, a double layer capacity of about 1 μF, and a mean R_f value of about 1 Ω (not unrealistic values), τ_f becomes about 10^{-6}s, too small to have the suspected effect.

6 Conclusion

For realistic cell resistance fluctuations and current control circuits, the long-term running mean power calculation is correct within small error bounds. The time constant of the control circuit (or its slewing rate) will not, in practice, lead to false power calculations, and therefore not to significant excess power artifacts.

References

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