The Equivalent Circuit Model and Methods for Finding the Initial Guesses

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September 27, 2022

1 The Equivalent Circuit of the Perovskite Device

The equivalent circuit of the perovskite is shown in the plot below. The reasoning behind the equivalent circuit is explained in the paper[ref].

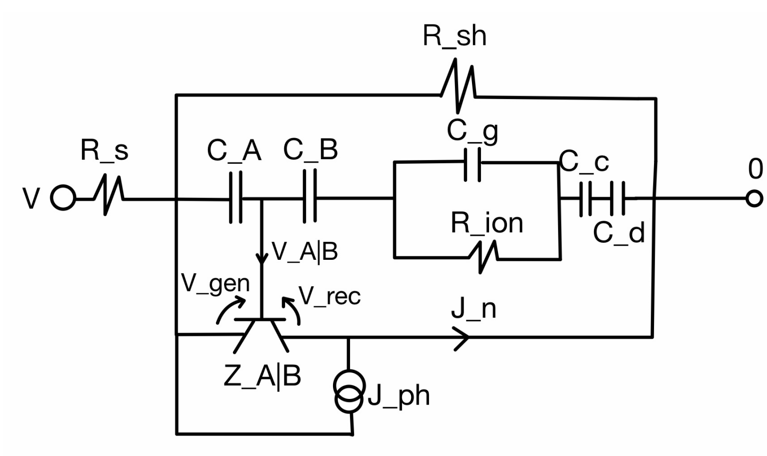

Figure 1: The equivalent circuit of the perovskite device. The meanings of the parameters are listed in the later parts.

By using this circuit, the corresponding function takes in the frequency of the perturbation voltage as the independent variable and returns the impedance

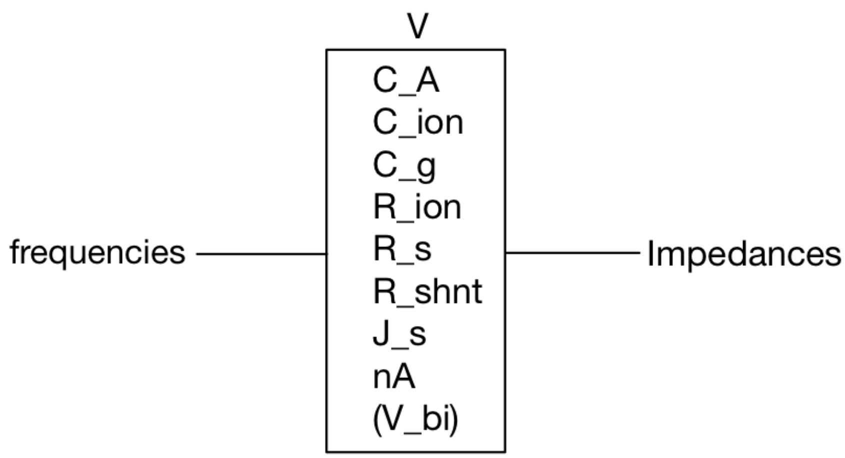

Figure 2: This is the schematic plot of the model. With the given parameters, the model will take in a list of frequencies and output a list of impedances.

of the whole circuit, with given parameters C_A, C_ion, C_g, R_ion, R_s, R_sh, J_s, nA and V_bi (for global fit cases) as shown in Fig. 2.
C_A, C_g, R_ion, R_s, and R_sh are elements shown in the circuit, while C_ion is the capacitance of the ionic branch(not including C_g), J_s is the saturation current density, and nA is the ideality factor of the transistor. The calculation of the total impedance includes using basic electronics laws and the property of the transistor. The detailed derivation is shown in the paper[refff].

2 The Initial Guess Finding Function

2.1 Individual Fit for Non-0 Bias Voltage

A set of initial guesses can be obtained from the data directly by extracting some important information using different plot representations.
In order to find the initial guess, the important points in the plots are extracted, including $R_{n\infty}$, R_{n0}, ω_n and C_G. By using these points, relations illustrated in the paper[refff], and a guess of R_{ion} by the user, the initial

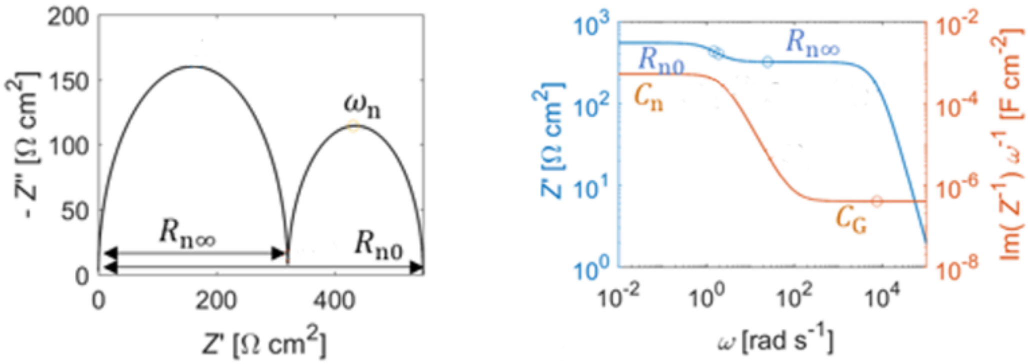

Figure 3: On the left is the Nyquist plot(the real part of total impedance vs. the imaginary part) of the Impedance. On the right is the real part of the impedance and effective capacitance vs. frequency. The important points are circled out in the plots with further explanation in the main text.

guesses can be obtained in the following way.

1. According to the paper,

$$\frac{n_A}{J_n} = R_{n\infty}\frac{q}{k_B T} \tag{1}$$

   Therefore,

$$n_A = \frac{J_n R_{n\infty} q}{k_B T} \tag{2}$$

   where J_n can be deduced from the experiment data of J and light intensity, $R_{n\infty}$ is read from the plot, k_B is the Boltzmann constant, q is the electric constant, and T is the room temperature (300K by default). In this way, the initial guess of n_A is obtained.

2. According to the paper,

$$1 - \frac{C_{ion}}{C_A} = k, \tag{3}$$

   and

$$C_{ion} = \frac{1}{\omega_n k R_{ion}}, \tag{4}$$

where

$$k = \frac{R_{n\infty}}{R_{n0}}. \tag{5}$$

In equations (3) and (4), $R_{n\infty}$, R_{n0}, and ω_n is read from the plot, and R_{ion} has to be guessed by the user without a way to be determined directly from the data (the shape of the plot is not very sensitive to the value of R_{ion} as well). With this information, the initial guesses of C_{ion} and C_A can be obtained.

3. According to the paper,

$$J_n = J_s exp\left(\frac{(V_{A|B} - V_n)q}{n_A k_B T}\right), \tag{6}$$

where $V_{A|B}$ is the voltage connected to the transistor at the first interface as shown in Fig. 1, and V_n is the voltage at the right-hand side of the transistor, equal to 0 in this case.

Also, it can be obtained using basic electronics that

$$V_{A|B} = kV \tag{7}$$

at steady state. Therefore,

$$J_s = J_n/exp\left(\frac{kVq}{n_A k_B T}\right), \tag{8}$$

4. The value of C_G can be directly used as the initial guess of C_g. Because at higher frequency, the ionic branch contributes to most of the effective capacitance, so $C_G = (1/C_g + 1/C_{ion})^{-1}$. However, the C_{ion} is much larger than C_g, so C_g will contribute mostly to the value of C_G. Therefore,

$$C_g \approx C_G \tag{9}$$

5. The R_s will cause a shift of the starting position of the Nyquist plot, so the initial guess of R_s is taken to be the minimum value of the real part of the impedance. And the initial guess of R_{sh} is just taken to be a very large value(10^5 by default).

By using the routine illustrated above, a set of initial guesses for parameters C_A, C_{ion}, R_{ion}, C_g, J_s, n_A, R_s,and R_{sh} can be obtained.

2.2 Individual Fit for 0 Bias Voltage Case

In this scenario, the obtainable initial guesses are different. Specifically, it is impossible to separate C_A from C_{ion} and J_s/n_A can only be obtained together.

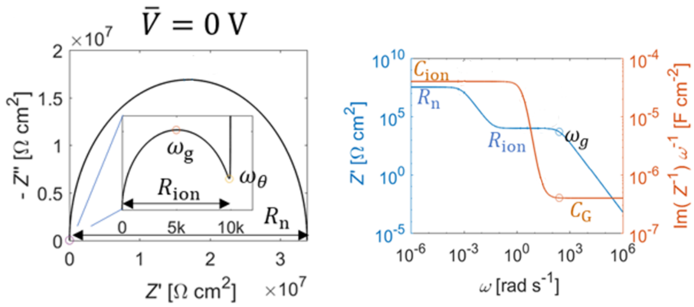

Figure 4: These are the plots for 0 bias voltage. On the left is the Nyquist plot(the real part of total impedance vs. the imaginary part) of the Impedance. On the right is the real part of the impedance and effective capacitance vs. frequency. The important points are circled out in the plots with further explanation in the main text.

Similar to the previous section, the steps for finding the initial guess are:

1. R_{ion} and C_{ion} can be directly obtained as shown in the left and right plot respectively.

2. According to the paper,

$$C_g = 1/(R_{ion}\omega_g). \tag{10}$$

   where ω_g can be obtained from the plot directly.

3. According to the paper,

$$R_n = \frac{k_B T n_A}{q J_s}. \tag{11}$$

   Therefore,

$$J_s/n = \frac{k_B T}{R_n q}. \tag{12}$$

   where R_n can be obtained from the plot directly.

4. Also, R_n is taken as the initial guess for $R_s h$ and the initial guess of R_s is obtained in the same way as in the previous section.

By using the routine above, a set of initial guesses for parameters C_{ion}, C_g, R_{ion}, J/n_A, R_s and R_{sh} can be obtained.

2.3 Global Fit Without 0 Bias Voltage

For this case, the tool will use the set of data with the largest bias voltage and find a set of initial guesses using the method of individual non-0 bias voltage cases. However, we assumed in the model that the value of C_A and C_{ion} will change with the bias voltage,

$$C(V) = C(0)\sqrt{V_{bi}/(V_{bi} - V_b)}, \tag{13}$$

where C could be C_A and C_{ion}, V_b is the bias voltage, and V_{bi} is the built-in potential of the interface. For the initial guess of the V_{bi}, it is taken to be 0.2 + maximum bias voltage by rule of thumb, since V_{bi} has to be bigger than all of the V_bs according to eq(13).

In reality the built-in potential could be smaller than the bias voltage and should also be different for each interface. Therefore, this model can only give an approximate estimation of the built-in function with considerable bias.

2.4 Global Fit With 0 Bias Voltage

The initial guess finding routine should be nearly the same as global fit without 0 bias voltage. The only difference is, the initial guesses of R_{ion} and R_{sh} can be obtained using the same method as in the individual 0 bias voltage case.

2.5 Another Method for Finding the initial guesses of n_A and J_s for Global Fit

Starting from eq(8), by taking logarithms on both sides and doing some manipulation,

$$V = n_A k \frac{q}{k_B T}(log J_n - log J_s) \tag{14}$$

Therefore, if V is plotted against $log J_n$, the gradient and the intersect with the x-axis will respectively be,

$$grad = n_A k \frac{q}{k_B T}, \tag{15}$$

and

$$x_0 = -grad \cdot log(J_s). \tag{16}$$

In this way, for global fitting cases, by plotting the known V(bias voltage) against known J_n and doing a linear fit to fine the gradient and x intersect, initial guesses of n_A and J_s can be obtained correspondingly.

3 The Fitting Function

From section 1 a model is constructed, and from section 2 the initial guesses for the parameters in the model are obtained. Then the package "lmfit" in Python is used to carry out the fit. In principle, for a list of given experimental frequencies, the function will find the set of parameters, using which the output of the model will have the least square difference of impedance from the experimental impedance. Meanwhile, a weight of 1/(values of impedance) is applied. Because for different bias voltages, the magnitudes of the impedance differ by orders of magnitude. This weight will help balance the influence on the least square difference of the impedance from different bias voltages.

Additionally, because the original package does not support complex-valued fitting, each value of impedance is separated to a pair of a real part and an imaginary part and then passed into the fitting function. Further explanation of the minimising algorithm should refer to the "least-square" section of the document of the "lmfit" package.